OUTLINES OF INDUSTRIAL CHEMISTRY

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OUTLINES

OF

INDUSTRIAL CHEMISTRY

A TEXT-BOOK FOR STUDENTS

BY

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WITH ASSISTANCE IN REVISION FROM

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To the Memory of

LEWIS MILLS NORTON

DURING NINE YEARS PROFESSOR OF INDUSTRIAL CHEMISTRY
IN THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

This Book is Dedicated

IN TOKEN OF WARM PERSONAL REGARD FOR THE KINDLY MAN
AND GRATEFUL APPRECIATION OF
THE HELPFULNESS AND INSPIRATION OF HIS TEACHING

THE AUTHOR

PREFACE TO THE FIRST EDITION

The object of this book is to furnish an elementary course in Industrial Chemistry, which may serve as the ground work for a more extended course of lectures, if desired. The writer has endeavored to describe briefly, within the limits of one moderate-sized volume, the more important industrial chemical processes, but omitting matters of detail which properly belong in the larger handbooks. Numerous references are made in the text to periodicals and journals, and to the standard handbooks and encyclopædias and many special works, where details, lacking in this book, may be found. The bibliographical lists following each section are not complete, but only include those works which will usually be found in most chemical libraries; the references to the journal literature are merely those articles to which the author's attention has been drawn in the preparation of class-room exercises. The diagrams illustrating the text have, in most cases, been drawn as simply as possible, purposely showing only the essential features.

In the selection and order of arrangement of the several subjects, the author has necessarily been influenced by his work in this Institute and the requirements of his own class, but it is believed that the book as a whole will be found applicable to the work in most institutions of learning where industrial chemistry is taught. The subject of Metallurgy has been entirely omitted, since there are already several excellent brief text-books dealing with it alone, and instruction in it is generally given independently of that relating to technical chemistry. Likewise the important subject of the coal-tar colors has been condensed into the briefest possible outline, because this is nearly always included in courses in organic chemistry, and there are several small manuals treating of it. Analytical processes have also been omitted as foreign to the intended scope and purpose of the book.

It is assumed that students taking this course are familiar with the elements of general chemistry, both inorganic and organic, and with the elements of physics.

In the compilation of this work, free use has been made of many of the standard English, German, and French hand-books and encyclopædias, particularly of Professor T. E. Thorpe's Dictionary of Applied Chemistry, the works of Professor Lunge on Sulphuric Acid and Alkali, and Coal-tar and Ammonia, Ost's Technischen Chemie, and Dammer's Handbuch der chemischen Technologie.

The following business firms have courteously loaned cuts and drawings for the illustrations: Curtis Davis & Co., Cambridgeport, Mass., slabbing machine and soap kettle; William Campbell & Sons, Cambridgeport, Mass., rendering tank; The De La Vergne Refrigerating Machine Co., New York, refrigerating machine; H. L. Dixon, Pittsburg, Pa., tank furnace for glass; United Gas Improvement Co., Philadelphia, water gas plant; John Johnson & Co., New York, filter press; Semet-Solvay Company, Syracuse, N.Y., coke oven; R. D. Wood & Co., Philadelphia, Pa., Taylor gas producer.

The writer wishes to acknowledge his indebtedness to the following friends for assistance and advice in the revision of those portions of the work treating of their specialties: C. D. Jenkins, State Gas Inspector of Massachusetts, Illuminating Gas; A. D. Little, Consulting Chemist, Wood Pulp and Paper; J. W. Loveland, Superintendent Curtis Davis & Co., Soap Manufacturers, Soap, Candles, and Glycerine; F. G. Stantial, Superintendent Cochrane Chemical Co., Sulphuric, Hydrochloric, and Nitric Acids; the following members of the instructing staff of the Massachusetts Institute of Technology: Professor A. H. Gill, Fuels and Oils; G. W. Rolfe, Starch, Glucose, and Sugar; S. C. Prescott, Fermentation Industries; J. W. Smith, Textile Industries.

Special thanks are due to Dr. W. R. Whitney, of the Institute of Technology, for much assistance in the proof-reading, and also to Dr. B. L. Robinson, Curator of the Gray Herbarium, Harvard University, for his painstaking revision of the botanical nomenclature.

In the labor of preparation of the book, the author has also had much help from his wife, who copied the entire manuscript and has assisted in the reading of all of the proof.

FRANK H. THORP.

BOSTON, MASS., October, 1898.

In this new edition, such errors as have been brought to the writer's notice have been corrected, but material changes have not been generally attempted, owing to press of other work. The author wishes to express his indebtedness to those who have called attention to weak parts in the book, and heartily invites further criticism.

F. H. T.

BOSTON, MASS., October, 1899.

PREFACE TO THE SECOND EDITION

The important advances made in the chemical industries since the appearance of the first edition, and the establishment of several successful manufactures which at that time were not beyond the experimental stage, have necessitated giving the text considerable revision, with material additions and corrections. Such errors of statement or of proof-reading as have been noted have been corrected, and further criticism by instructors and others interested in the subject is invited.

It appeared desirable that a short outline of elementary metallurgy should be included, in order that the book might better meet the requirements of the courses of study of certain colleges and technical schools. With the exception of the paragraphs upon bismuth, cadmium, and magnesium, this has been prepared by Mr. Chas. D. Demond, and is now included as Part III of the new edition.

In connection with the material introduced, the writer wishes to express here his obligations to the following firms for permission to make abstracts and copy illustrations from their publications and catalogues: The Allis-Chalmers Co., Chicago; The Engineering and Mining Journal, New York; The Sugar Apparatus Manufacturing Co., Philadelphia.

F. H. T.

Boston, April, 1905.

PREFACE TO THE THIRD EDITION

THE great progress which has been made in Chemical Industry since the publication of the second edition of this work in 1905 has necessitated entire rewriting of many sections of the book, with elimination of much obsolete matter and the introduction of much new material. While the general plan of the former editions has been retained, in treating the various subjects use has been made of the modern concepts and theories of chemistry wherever these promised to make clearer the phenomena involved. Extended mathematical or theoretical discussion of the processes has been avoided as beyond the scope of the book. It is not supposed that the expert will find this book a guide in his own particular field, for its purpose is to impart to students and others not already familiar with the processes of chemical industry, some knowledge of the plant and methods employed in the more important manufacturing operations based upon chemical changes.

F. H. T.
W. K. L.

BOSTON, March, 1916.

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GENERAL REFERENCES ON INDUSTRIAL CHEMISTRY

Chimie Industrielle. A. Payen. Paris, 1867.

Grundriss der chemischen Technologie. H. Post.

Abriss der chemischen Technologie. C. Heinzerling. Berlin, 1888. (T. Fischer.)

Traité de Chimie appliquée à l'Industrie. Adolphe Renard. Paris, 1890.

Handbuch der chemischen Technologie. Dr. O. Dammer. 5 Vols. Vol. I, 1895. Vol. II, 1895. Vol. III, 1896. Stuttgart. (F. Enke.)

Chemical Technology. R. Wagner. Translated by Wm. Crookes. New York, 1897. (D. Appleton and Co.)

Encyclopaedisches Handbuch der technischen Chemie. F. Stohmann und Bruno Kerl. Vol. I, 1888. Vol. II, 1889. Vol. III, 1891. Vol. IV, 1893. Vol. V, 1896. Vol. VI, 1898. Vol. VII, 1900. Braunschweig. (F. Vieweg.)

Chemical Technology. Edited by C. E. Groves and William Thorp. Vol. I, Fuel, 1889. Vol. II, Lighting, 1895. Vol. III, Gas Lighting, 1900. Vol. IV, Electric Lighting, 1903.

Handbuch der chemischen Technologie. Dr. Ferdinand Fischer. 2 Vols. Vol. I, 1900. Vol. II, 1902. Leipzig. (O. Wigand.)

Lehrbuch der chemischen Technologie. Dr. Ferdinand Fischer. Leipzig, 1903.

Handbook of Chemical Engineering. G. E. Davis. 2d ed. 2 Vols. Manchester, 1905.

Traité Chimie Appliquée. C. Chabrie. 2 Vols. Paris, 1905. (Masson et Cie.)

Chemische Technologie der Neuzeit. Edited by O. Dammer. 3 Vols. Stuttgart, 1910. (Enke.)

Chemistry for Engineers and Manufacturers. Bertram Blount and A. G. Bloxam. 2 Vols. London, 1905. (Griffin and Co.)

Modern Industrial Chemistry. H. Bluecher. Translated by J. P. Millington. New York, 1911. (Stechert & Co.)

Handbook of Industrial Organic Chemistry. S. P. Sadtler. Philadelphia. 4th ed. 1912. (J. B. Lippincott.)

A Dictionary of Applied Chemistry. T. E. Thorpe. 2d ed. 5 Vols. London, 1912–13. (Longmans, Green and Co.)

Vorlesungen über Chemische Technologie. Dr. H. Wichelhaus. 3te Auf. Dresden, 1912. (Steinkopff.)

Lehrbuch der Chemischen Technologie und Metallurgie. Edit. by B. Neumann. Leipzig, 1912. (S. Hirzel.)

General and Industrial Chemistry. E. Molinari. 2 Vols. Translated by E. Feilmann. Philadelphia, 1912. (Blakiston's Sons Co.)

Lehrbuch der technischen Chemie. H. Ost. 8th ed. Leipzig, 1914. (Jänecke.)

Industrial Chemistry. Chapters by Specialists. Edited by A. Rogers and A. B. Aubert. New York. 2d ed. 1915. (Van Nostrand Co.)

ABBREVIATIONS OF THE NAMES OF JOURNALS

FREQUENTLY OCCURRING IN THE LITERATURE OF INDUSTRIAL CHEMISTRY

A. or Ann. = Annalen der Chemie und Pharmacie, by Liebig and others, 1832 +.
Ann. chim. phys. = Annales de Chimie et de Physique. Paris, 7 series, 1789 +.
Ber. = Berichte der deutschen chemischen Gesellschaft. Berlin, 1868 +.
Bull. Soc. Chim. = Bulletin des Seances de la Société chimique de Paris, 2 series, 1864 +.
Chem. Centralb. = Chemisches Centralblatt. 4 series, 1829 +.
Chem. Ind. = Zeitschrift für die chemische Industrie. 1878 +.
C. N. or Chem. N. = Chemical News. 1860 +.
C. R. or Compt. rend. = Comptes-rendus hebdomadaires des Seances de l'Academie des Sciences. Paris, 1835 +.
Chem. Zeit. = Chemiker-Zeitung. 1877 +.
Dingl. J. = Dingler's polytechnisches Journal. 1820 +.
Electrochem. Ind. = Electrochemical Industry. 1902 + 1909.
Eng. Min. Jour. = Engineering and Mining Journal. 1866 +.
Jahresb. = Jahresbericht über die Fortschritt der Chemie, u. s. w.
J. Am. Chem. Soc. = Journal of the American Chemical Society. New York, 1879 +.
J. Chem. Soc. = Journal of the Chemical Society of London. 1849 +.
J. Ind. Eng. Chem. = Journal of Industrial and Engineering Chemistry. 1909 +.
J. Soc. Chem. Ind. = Journal of the Society of Chemical Industry. London, 1882 +.
Met. Chem. Eng. = Metallurgical and Chemical Engineering. 1909 +.
Trans. Am. Inst. Chem. Eng. = Transactions of the American Institute of Chemical Engineers. 1908 +.
Trans. Am. Inst. Elect. Eng. = Transactions of the American Institute of Electrical Engineers. 1884 +.
Trans. Am. Inst. Min. Eng. = Transactions of the American Institute of Mining Engineers. 1871 +.
Trans. Am. Electrochem. Soc. = Transactions of the American Electrochemical Society. 1902 +.
W. J. = Wagner's Jahresbericht der chemischen Technologie. 1855 +.
Zeitschr. angew. Chem. = Zeitschrift für angewandte Chemie. Berlin, 1887 +.
Zeitschr. anorg. Chem. = Zeitschrift für anorganische Chemie. 1892 +.
Zeitschr. Chem. Ind. = Zeitschrift für die chemische Industrie. 1887 +.
Zeitschr. Elektrochem. = Zeitschrift für Elektrochemie. 1894 +.
Zeit. physikal. Chem. =Zeitschrift für physikalische Chemie. 1887 +.

RELATION BETWEEN WEIGHTS AND MEASURES

FREQUENTLY OCCURRING IN THE LITERATURE OF INDUSTRIAL CHEMISTRY

1 linear inch = 2.54 centimeters.
1 linear foot = .3048 meter = 30.48 centimeters.
1 linear yard = .914 meter = 91.44 centimeters.
1 linear mile = 1609. meters = 1.609 kilometers.

1 cubic inch = 16.387 cubic centimeters.
1 cubic foot = 7.48 gallons = 28.315.
1 cubic foot of water at 16.5° C. weighs 62.355 pounds.

1 fluid ounce = 29.574 cubic centimeters.
1 quart = 946.6 cubic centimeters.
1 gallon U.S. = 231. cubic inches = 3.7854 liters.
1 gallon, U.S., of water at 16.5° C., weighs 8.3356 pounds.

1 grain = .064799 gram.
1 ounce Avd. = 28.3495 grams.
1 pound Avd. = 7000. grains = 453.593 grams.
1 ounce Apoth. = 31.103 grams.

1 centimeter = .39370 inch.
1 meter = 39.37 inches.
1 kilometer = .621 mile.

1 liter = 1.057 quarts = 61.023 cubic inches.
1 hektoliter = 26.425 gallons.

1 gram = 15.432 grains.
1 kilogram = 2.2046 pounds Avd. = 35.274 ounces.

1 cubic centimeter = .034 fluid ounce = .272 dram.

In solutions,
1 grain per gallon = .017118 gram per liter.
1 grain per gallon × 17.1 = parts per million.
1 gram per liter = .008345 pound per gallon = 58.42 grains per gallon.
1 gram per liter = .06242 pound per cubic foot.

OUTLINES OF INDUSTRIAL CHEMISTRY

PART I

INORGANIC INDUSTRIES

INTRODUCTION

Industrial chemistry deals with the preparation of products from raw materials, through the agency of chemical change. But there is an occasional exception to this definition; for a few industries, depending on strictly *mechanical* changes, are classed among the chemical industries. Since a sharp line cannot be drawn between chemical and mechanical technology, a study of the former necessarily involves some consideration of the mechanical appliances and apparatus, by means of which the chemical reactions are carried out.

The products of chemical industry are exceedingly numerous and varied in character, but comparatively few come into the hands of the mass of the people for direct consumption. Many of them are used only in making other substances, for it is often the case that the finished product, by-product, or waste from one industry becomes the raw material for another, and it rarely happens that one manufacturer, starting with the raw materials found in nature, produces from them articles for popular use. Thus the chemical industries become a network of interlacing processes, and in considering one it is often difficult to separate it from others which have a more or less direct bearing upon it. Furthermore, as competition has become very close in many lines, the use which may be made of by-products and waste is so important, that processes are often carried out with the view of obtaining larger yields or better quality of the by-products, which may have become a source of considerable profit. In a few instances, it might be said that what were originally the by-products are now the chief products and main support of these particular industries. This is especially true in the case of the Leblanc Soda Industry, which would long since have been abandoned were it not for its production of hydrochloric acid. The utilization of waste materials furnishes an almost inexhaustible subject for investigation by the industrial chemist.

The manipulations of most frequent occurrence in the various processes are here defined and explained for the sake of brevity in the text.

LIXIVIATION

Lixiviation is the process of separating *soluble* from insoluble substances by dissolving the former in water or some other solvent. The mixture of substances is put into a suitable vessel, the solvent poured over it, and the whole allowed to stand until a strong solution is obtained, which is then drawn off from the residue. This process is repeated as often as necessary, until the desired amount of soluble matter has been removed. Sometimes the mixture is put into baskets, or on gratings, which are suspended in tanks of water. The solution being denser than the solvent sinks to the bottom as it forms, and water comparatively free from dissolved material is thus constantly brought into contact with the substance to be lixiviated. The insoluble substance remains on the grating or in the baskets. When desired, the soluble material may be recovered from the solution by evaporation or precipitation. **Extraction** is the term usually employed when some solvent other than water is used in lixiviating. Thus we speak of extraction by steam, alcohol, carbon disulphide, etc.

LEVIGATION

Levigation is the process of grinding an *insoluble* substance to a fine powder, while wet. The material is introduced into the mill together with water, in which the powdered substance remains suspended, and flows from the mill as a turbid liquid or thin paste, according to the amount of water employed. There is no loss of material as dust, nor injury or annoyance to the workmen. Further, any soluble impurities in the substance are dissolved, and the product thereby purified. The greatest advantage of this process is the facility it affords for the subsequent separation of the product into various grades of fineness, because of the *slower* subsidence of the *finer* particles from suspension. The turbid liquid flows into the first of a series of tanks, and is allowed to stand for a certain time. The coarsest and heaviest particles quickly subside, leaving the finer material suspended in the water, which is drawn from above the sediment into the next tank. The liquid is passed from tank to tank, remaining in each longer than it remained in the preceding, since the finer and lighter the particles, the more time is necessary for their deposition. In some cases a dozen or more tanks may be used, and the process then becomes exceedingly slow, as very fine slimes or muds may require several weeks for the final settling. But as a rule, from three to five days is sufficient.

The term "levigation" is now often applied to mere sedimentation, a substance being simply stirred up in water, without previous wet-grinding, in order to separate the finer from the coarser particles, as above.

EVAPORATION

Evaporation, in a technical sense, denotes the conversion of a liquid into a vapor for the purpose of separating it from another liquid of higher boiling point, or from a solid which is dissolved in it. In the great majority of cases, the liquid evaporated is water. If the liquid evaporated is to be recovered, the vapors are condensed, and the process then becomes one of Distillation (see p. 9).

There are four general methods of evaporation: —

1. Spontaneous evaporation in the open air.
2. Evaporation by application of heat directly from a fire to the vessel containing the liquid.
3. Evaporation by indirect application of heat from the fire, as by means of steam, with or without pressure.
4. Evaporation under reduced pressure.

The first method, by spontaneous evaporation in the open air, is comparatively slow, and requires exposure of very large surfaces of liquid. The time necessary depends upon the temperature and humidity of the air, and the completeness with which the vapors are removed from the surface of the liquid; hot, dry weather, especially if a brisk wind is blowing, evaporates water quite rapidly. This process is only used for the manufacture of salt from sea water, or from natural brines. In certain warm countries considerable quantities of salt are thus prepared, and in this country some is made from a brine found near Syracuse, N.Y. Sometimes weak brines are allowed to trickle in fine streams over tall piles or "ricks" of brushwood in the open air. The liquid being so exposed in thin layers, to the air and wind, is concentrated to such a degree that it will pay to complete the evaporation by artificial heat.

The second method,* by direct application of heat from a fire, is very largely used in the arts. This may be done in two general ways: —

(*a*) The flames, or hot gases from the fire, are generally allowed to play directly on the bottom of the vessel containing the liquid; or they may pass through flues or pipes, set into the vessel, so that the liquid surrounds them on all sides (Fig. 1). Such pans are often several yards in length, and may contain one large flue, or several small ones, according to the work desired; but this form of apparatus is expensive to build, and difficult to keep in repair.

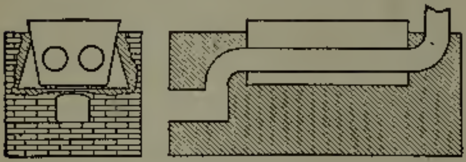

FIG. 1.

(*b*) The flames and hot gases may be conducted over the surface of the liquid to be evaporated. This mode is only used for coarse and common products, or in the concentration or recovery of waste materials. But it has the advantage that the bottom of the pan is less liable to be injured by the crusting of a precipitate upon it. Another point often in favor of surface heating is that the liquid is evaporated in a reducing atmosphere. But as flue dust and ashes are liable to fall into the pans, the product is usually impure. Large shallow pans are used, which are generally arched over with brick, in order that the heat may be better utilized, through radiation from the brick walls. There are various ways of setting the pans for this process; a simple method is shown in Fig. 2. A modification of this method is the use of a long cylinder, set at a slight incline, and revolving about its longitudinal axis (Fig. 3). The lower end is open for the entrance of the flames and gases from the grate (A), which pass through the cylinder (B), on their way to the chimney (D). The hot

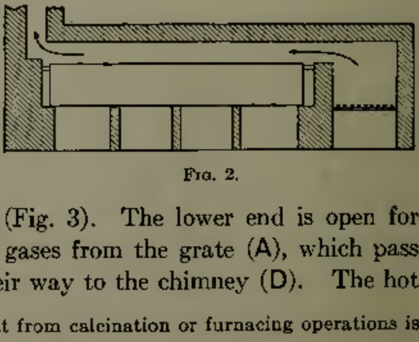

FIG. 2.

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* To save expense, the waste heat from calcination or furnacing operations is frequently utilized.

gases are often passed through the flues of a boiler (C), to utilize the waste heat. The solution to be evaporated is fed into the cylinder at the upper end in a small stream, and comes in direct contact with the flame. The water is evaporated, and the solid matter is delivered into the pit or wagon (E) at the lower end of the furnace, in a dry and calcined state. Such furnaces are frequently used for evaporating waste liquors to recover the salts which they contain; and for the treatment of sewage and other liquid refuse.

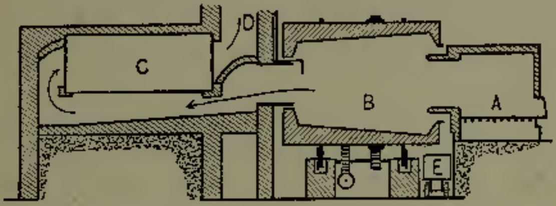

FIG. 3.

The third method of evaporation, by the use of steam heat, is very often employed where there is danger of injury to the product by overheating.

(*a*) Jacketed pans or kettles may be used. These are simply double-walled vessels, the steam being admitted between the walls.

(*b*) The steam may be allowed to circulate through coils of pipe, placed inside the vessel, which is sometimes made of wood. The temperature of the liquid depends on the steam pressure; very often exhaust steam is employed.

The fourth method, evaporation *in vacuo*, is merely a modification of either the second or third method, but is considered separately for convenience. The boiling point of a liquid may be very materially lowered by reducing the pressure within the vessel. Hence, solutions containing substances which would be injured by the heat necessary to boil them under the atmospheric pressure, or liquids boiling at very high temperatures, are evaporated in vacuum pans.

The different forms of apparatus used for vacuum evaporation vary much in their details, but all depend on the principle of reduced pressure. The essential parts of the plant are the vacuum pan or still, the pump for exhausting the air and steam from the pan and sending them to the condenser, and the heating apparatus. The vacuum pan is usually a globular copper or iron vessel, provided with a manhole, a pressure gauge, and a discharging valve. Very often a piece of heavy plate glass is set in the side to afford a view of the interior during evaporation. On the top of the pan is a dome or short tower, from which a pipe leads to a receptacle, called the "catch-all," that retains any *liquid* which may escape from the pan. A small pipe returns this liquid to the pan, and a larger one connects the "catch-all" with the vacuum pump, which is an ordinary double-cylinder air pump of large size, driven by an engine. An injector pump, which condenses the steam directly, may be used. The pan is generally heated by steam coils within it, or by a steam jacket, or by both.

A very efficient method of vacuum evaporation is that obtained by the use of **Multiple Effect Systems.** In these greater economy of fuel for heating is secured. The apparatus consists usually of two or more simple vacuum pans, so joined together that the steam from the boiling liquid in the first pan is made to pass through the coils and jacket of the second pan, and the steam generated in the second pan goes through the coils and jacket of the third, and so on through the system. The vacuum maintained in each pan of the series is greater than in the one preceding. Hence, notwithstanding its increased concentration, the boiling point of the liquid in the second pan is so low, that the steam from the first pan is sufficiently hot to boil it. Similarly the steam from the second pan is made to boil the liquid in the third, in which there is still less pressure, and so on to the last pan, in which the highest vacuum is maintained. As a rule only four pans are used, for it is very difficult to sustain the vacuum sufficiently to work another pan in the series. In many plants only three pans (triple effects) are used.

An effective modification of this method is the apparatus known as the **Yaryan evaporator** (Fig. 4). It is made in triple and quadruple effects, and each pan is exactly like its neighbors. It consists of an outside shell of iron, within which is a system of small tubes (A, A), joined together in groups of five or six, each group constituting a section or unit. The tubes in each unit are so connected at the ends as to form one continuous coil. *The liquor to be evaporated is run through the several coils* thus constructed in each pan. The tubes in the first pan are heated by steam, introduced into the shell directly from a boiler. As the liquid flows through the tubes, it is brought to boiling, and the steam generated mingles with it, converting the whole mass into foam, which runs through the coil and spurts against a baffle plate in the "separator" (B, B), which is an enlarged chamber at the end of the shell. The steam and liquid are separated, the liquid falling to the bottom and running off into the receiver (C), to be passed through the tubes of the next pan. The steam rises, passing through the steam dome and "catch-all" (D), and into the shell of the next "effect," through the coils of which the liquid is passing under still greater vacuum, and so on through the system. The apparatus is very economical in its use of fuel, and as the liquid is exposed in thin films to the heat, the evaporation is rapid; hence the liquid is subjected to a high temperature for only a short time.

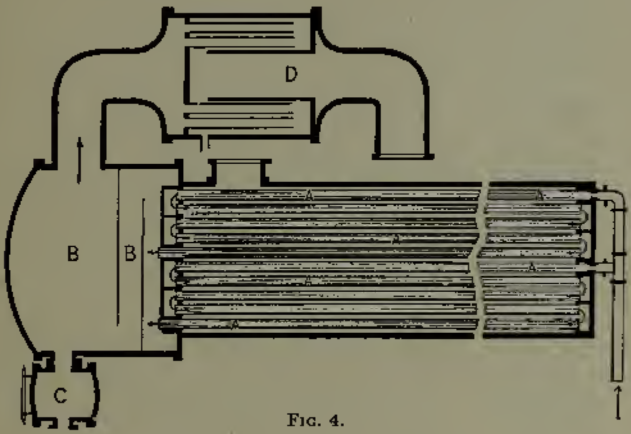

Fig. 4.

The apparatus is nearly automatic in its action, and needs little attention. It can be stopped and started quickly, since it contains only a small quantity of liquid at one time, and it occupies but little floor space when the several "effects" are placed one over the other.

The ordinary form of vacuum pan evaporates about 8½ lbs. of water per pound of coal, but it is said that the best forms of Yaryan apparatus evaporate from 23½ to 25 lbs. of water per pound of coal in a triple effect, and 30½ lbs. in a quadruple effect.*

The **Kestner evaporator** utilizes the "climbing film" principle, by which the liquid to be evaporated is automatically distributed over the heating surface, without the use of pumps. The apparatus is built in multiple effect and each pan (Fig. 5) consists of a narrow vertical shell (M) containing a number of small tubes (R) through which the liquor passes upward from the bottom. The tubes are tightly fixed into plates at top and bottom and are entirely surrounded and heated by steam in the shell (M). The tubes are about twenty-three feet long and are open at top and bottom. Liquor is fed in through the valve (V) and the supply so limited that a relatively

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* J. Soc. Chem. Ind., 1895, 112.

small quantity enters each tube, where it at once begins to boil: the vapor evolved rushes up the tube, carrying some of the liquor along and distributing it in a thin film on the hot tube wall. Emerging from the top of the tubes the foaming mixture of vapor and liquor is discharged against the vanes of a centrifugal separator (D) by which the concentrated liquor is whirled against the walls of the enlarged vapor space (S). The liquid flows down the walls and passes out at (L), while the vapor rises through (B) and passes to the shell of the next effect, or to the condenser. The separation of vapor and liquor is claimed to be so complete, that practically no entrainment results: only a small quantity of liquid is in the apparatus and the time of heating is short; only about two minutes being required for the passage through the tubes. The drop in temperature between any two pans of the series is small, ranging from 8° to 12° C. Thus four and five effects are often used in series. The apparatus occupies little floor space, gives little trouble from scaling of the tubes, and is easily washed out.

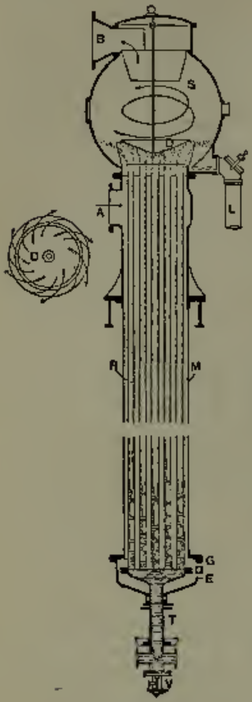

FIG. 5.

The **Lillie evaporator** is a very efficient type of multiple effect (Fig. 6). Slightly inclined straight tubes (A) tightly fastened at one end in the thick plate (C) open into the steam space (B). The other ends of the tubes are closed, except for a small air vent, and are unsupported. Thus they expand and contract freely, preventing strains and resulting leaks. In the upper part of the effect is a row of distributing pipes (D), each having a longitudinal slot on its upper side. These pipes are closed at one end; the other opens into a distributing box (E). The liquor to be evaporated enters through (G), passes into (D), and

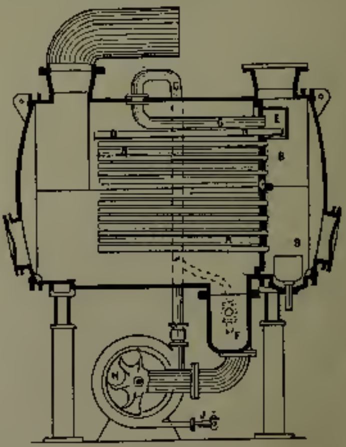

FIG. 6.

flowing from the slots in thin films, is showered uniformly over the hot tubes (A), from whose outer surface the evaporation takes place. The liquor drips from tube to tube, collecting in the float box (F), from which the suction pipe of the centrifugal pump (H) draws it, to again pass over the tubes. The float in the box (F) operates a valve which allows fresh liquor to enter the effect just fast enough to replace that vaporized and what passes from the discharge pipe (J) as concentrated liquor. On (J) is a regulating valve governing the level of the liquor in (F) and thus controlling the rate of feed; the slower the discharge, the greater the concentration. The float completely closes the feed valve when the liquor rises to a definite height in (F); the discharge valve in the last effect thus automatically controls the flow of the liquor from effect to effect, by influencing the action of the feed valves. The tubes (A) are heated by live or exhaust steam, or by vapor from the preceding effect, which enters the steam chamber (B); the hot water condensed in (A) collects in the bottom of (B), and passing the steam trap goes to the steam space of the next effect; thus being under great vacuum, it gives up part of its heat as steam, which assists in the heating of this effect. The vapor from each effect also enters the steam space (B) of the next.

DISTILLATION

Distillation is the process of vaporizing a liquid and recovering it by condensing the vapors. The liquid formed by this condensation is called the distillate. Distillation is chiefly employed to separate a liquid from non-volatile matter dissolved or suspended in it; or to separate one liquid from a mixture of liquids of different boiling points; that one having the lowest boiling point being the first to begin to pass off as vapor.

The separation of two miscible liquids by distillation depends on the difference between the composition of the vapor and of the boiling liquid from which it comes;* and while never perfect is more complete the greater the difference in composition. Most liquid mixtures evolve a vapor containing more of the low-boiling constituent than does the liquid itself; but in some cases the reverse is true between certain limits of composition, and such liquids always give

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* The vapor pressures of the pure liquids, or what is practically the same thing, their boiling points, are not the essential factors; thus both glycerine and water, and hydrochloric acid and water, differ widely in vapor pressures and boiling points, but glycerine and water are easily separated by distillation while the separation of hydrochloric acid and water by this means is impossible.

mixtures of maximum or minimum boiling point, which cannot be separated by distillation as the vapor and liquid compositions are in these cases the same.*

During a distillation the boiling point gradually rises, and at the end there remains in the still a relatively small amount of the high-boiling liquid very free from the other component, or else a mixture of maximum boiling point. While the distillate has been enriched in the low-boiling constituent, it is far from pure, but repetition of the distillation improves the separation. In general it is easier to secure the high-boiling liquid free from the other than the reverse.

If a mixed vapor be slowly cooled, the liquid to condense is that in equilibrium with the vapor; thus it is largely the less volatile component which separates first. By abstracting only enough heat to condense a part of the vapor, the remainder is greatly enriched in the volatile constituent; this *fractional condensation* is attained by using a condenser with relatively hot cooling medium, the uncondensed vapors passing to a cold condenser for complete condensation. From the fractional or partial condenser, the condensate returns to the still for reboiling, to remove the remainder of the volatile component. Fractional condensation is equivalent to a redistillation, *without the consumption of additional heat.*

The chief parts of every distilling apparatus are the boiler or still and the condenser. The still is usually iron or copper, and may be heated directly by a furnace, or by a steam-jacket, or a coil. The condenser is a coil of pipe, or a system of tubes, or a double-walled chamber, submerged in a tank of cold water. Condensers are usually made of iron or copper, but lead, silver, earthenware, or glass tubes are sometimes used. The fractional condensation apparatus is placed between the still and the final condenser; it may consist of a series of chambers, or of pipes or U-tubes, surrounded by a water-bath or other liquid at a temperature between the boiling points of the liquids to be distilled.

The condensate from a fractional condenser is richer in the volatile component than is the liquid in the still; it is, therefore, not in equilibrium with the vapor from the still, and if brought into contact

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* Thus water and alcohol have a mixture of minimum boiling point at 96 per cent alcohol, a mixture more volatile than either component; water and hydrochloric acid containing 28 per cent hydrochloric acid have a maximum boiling point; mixtures containing more acid than this evolve vapors richer in hydrochloric acid; if less than 28 per cent acid is present, more water in proportion is given off; in either case there is finally left in the still this constant boiling mixture which cannot be separated by further boiling.

with that vapor, an interchange of heat results, accompanied by a volatilization of the low-boiling constituent and a condensation of the high-boiling one, which further enriches the vapor and improves the separation, *without any additional expenditure of heat.* This process is called **dephlegmation**, and to secure the maximum efficiency, must be repeated a number of times. The mixed vapors from the still are bubbled through a series of shallow layers of liquid, through which passes in counter-current flow, the partial condensate from the fractional condenser; this condensate, with its low-boiling constituent removed as completely as possible, finally flows back into the still. The apparatus for this, called the **dephlegmator**, or "column," usually consists of a tall tower (Fig. 8, B, B) set above the still, and divided by a number of perforated horizontal plates into many shallow chambers, through each of which the returning liquid must flow on its way to the still. The vapors from the still pass up through the openings in the plates, bubbling through the shallow layers of the liquid and give up heat to it, causing vaporization of its volatile constituents. The boiling of the liquid in all of the chambers is done by the heat in the vapors entering the lowest chamber: any condensation in the tower results in greater coal consumption to restore the heat thus lost. The chief object of the dephlegmator is to boil the liquid in the several chambers, and deliver the enriched mixed vapors to the fractional condenser. As radiation from the walls of the column causes condensation and loss of heat, the column should be covered or lagged.

In an ordinary distillation, even with use of fractional condenser and dephlegmating column, it is only at the end of the operation that there remains in the still the high-boiling component in a practically pure state; at any earlier stage in the process, however, it is possible to dephlegmate the low-boiling component from the liquid in the still, by using a dephlegmating column *below the still.* This is done in practice by admitting the liquid mixture to be distilled into the middle of a long column, the overflow from which passes down to the still in which there is only pure high-boiling liquid; the rising vapors carry the low-boiling constituent. The original mixture can now be admitted and the distillate and high-boiling residue withdrawn *continuously* from the apparatus. Also, the column, below the point of admission of the liquid to be distilled, accomplishes the redistillation of the overflow from the apparatus above, *without further consumption of heat;* in addition to the great advantage of continuity of operation, this type of column gives the best heat economy of any method of distillation, and is generally employed except where special conditions render it inadvisable. The heat economy can be still further improved if the feed liquor be heated by using it as cooling medium in the fractional or final condensers.

In Coupier's still (Fig. 7) a tower (A) is placed on top of the boiler (B); between the tower and the condenser is a series of chambers (C, C) surrounded by a water bath, which may be kept at any desired temperature. While the mixed vapors are passing through the chambers, the high-boiling constituents are condensed, and the vapor of the more volatile liquid passes through (E) to the condenser (F). A pipe (D) returns the condensed heavy liquid to the tower, to be redistilled or dephlegmated.

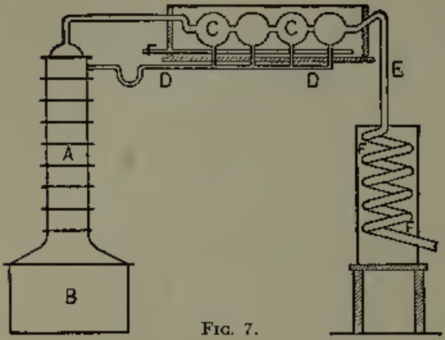

FIG. 7.

The **French column** apparatus (Fig. 8) has a series of U-tubes (C) surrounded by a water bath. The column or dephlegmator (B) is divided into chambers by plates, each of which has a central opening covered by a dome; a small overflow pipe passes from each plate to the next. The vapors from the boiler (A) pass up through the central openings and bubble out under the edges of the domes through the layer of liquid on each plate. The liquid thus condensed flows down through the overflow pipes, and returns to the boiler.

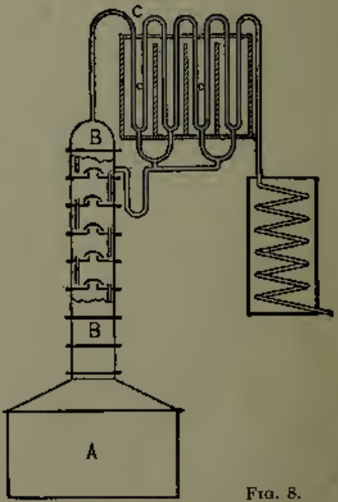

FIG. 8.

The **Coffey still** (Fig. 9) is much used for alcohol and gas liquor distillation. This consists of two towers, one, called the "analyzer" (E), receiving free steam from the boiler, and the other, called the "rectifier" (G), containing a long coil of pipe (C, C), through which the liquid to be distilled flows on its way to the analyzer. The analyzer is divided into a series of chambers by horizontal, perforated plates (A); from each plate an overflow pipe (F) passes down and dips into a shallow cup (H) on the next plate below and holding liquid enough to form a hydraulic seal at the lower end of each overflow pipe. These pipes project about an inch or so above the plate in which they are set, thus determining the depth of the liquid layer on each plate. The rectifier is divided into chambers by perforated plates, but has overflow pipes in its lower half only. In the chambers lie the coils of pipe (C) through which the liquid to be distilled passes on its way to the analyzer. This still works as follows: Steam from the boiler is blown through (K) into the analyzer, and passes from the top of the analyzer through the pipe (L) to the rectifier. The liquid to be distilled is pumped through the pipe (B) and the coil (C) in the rectifier, and is delivered at the top of the analyzer through the pipe (D). The cold liquid is heated by the steam surrounding the coils, and is delivered hot into the analyzer.

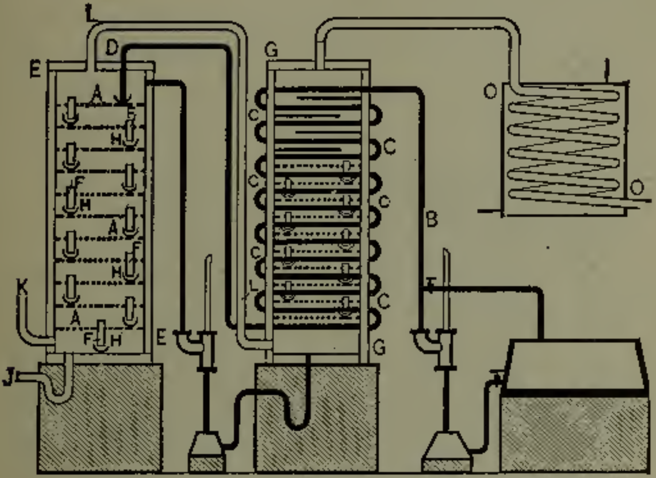

Fig. 9.

Since steam is being forced up through the perforations, the liquid cannot pass down through them, but is forced to spread out over the plate, and run down the overflow pipe (F) to the next plate, and so through the analyzer. The steam, bubbling up through the thin layers of liquid, heats it very hot, and causes the volatile substances to distil off with the steam. This mixture of steam and volatile matter passes from the top of the analyzer, through (L), to the bottom of the rectifier. During its passage up the rectifier, the steam is condensed by coming into contact with the cold pipes (C, C), through which the liquid is flowing to the analyzer. Thus only the more volatile matters pass out at the top of the rectifier, and go to the condenser (O). The water condensed in the rectifier contains some volatile matter, so it is pumped to the top of the analyzer and mixes with the fresh liquor to be distilled. From the bottom of the analyzer a waste pipe (J) carries off the spent liquor which has been deprived of its volatile matter. The rectifier (G) is a combination of fractional condenser and dephlegmator; the analyzer (E) is strictly a dephlegmating column.

Distillation with use of a dephlegmating column is sometimes called *rectification*, but this term should be reserved for such an operation conducted so as to eliminate one or more undesirable constituents. (See Alcohol, p. 459.)

Distillation in vacuum is sometimes employed, and will be described in connection with the industries in which it is used.

SUBLIMATION

Sublimation is the process of vaporizing a solid substance and condensing the vapors to again form the solid directly, without passing through an intermediate liquid state. There are very few substances which vaporize without melting, but in all cases of sublimation, the change from the vapor to the solid state is direct, and without any formation of liquid. The sublimed body is recovered unchanged chemically, but its physical properties are often more or less altered. In most cases, the temperature does not exceed a low red heat. Dissociation often occurs in the process.

FILTRATION

Filtration is the process of separating suspended solid matter from a liquid, by causing the latter to pass through the pores of some substance, called a filter. The liquid which has passed through the filter is called the filtrate. The filter may be paper, cloth, cotton-wool, asbestos, slag- or glass-wool, unglazed earthenware, sand, or other porous material.

Filtration is very frequently employed in chemical technology, and it often presents great difficulties. In most technical operations, cotton *cloth* is the filtering material, but occasionally woollen or hair cloth is necessary. The cloth may be fastened on a wooden frame in such a way that a shallow bag is formed, into which the turbid liquid is poured. The filtrate, in this case, is cloudy at first, but soon becomes clear, and then the turbid portion is returned to the filter. Filtration is often retarded by the presence of fine, slimy precipitates, or by the formation of crystals in the interstices of the cloth, from the hot solution. Any attempt to hasten filtration, by scraping or stirring the precipitate on the cloth, will always cause the filtrate to run turbid.

A better form is the "bag-filter," which is a long, narrow bag of twilled cotton, supported by an outside cover of coarse, strong netting, capable of sustaining a considerable weight and hydrostatic pressure. These bags are often five or six feet long, and eight inches or more in diameter. The open end of the bag is tied tightly around a metallic ring or a nipple, by which the whole is suspended, and through which the liquor to be filtered is introduced. When hot liquids are filtered, the bags are often hung in steam-heated rooms, the temperature being nearly that of the liquid.

In pressure filtration, the liquid is forced through the interstices of the filter by direct atmospheric pressure, the air being exhausted from the receiver; or by hydrostatic pressure, obtained either by means of a high column of the liquid, or by a force pump. By the first method, called suction filtration, the liquid may be forced *downward* through the filter into a receiver; the precipitate collects on the top of the filter and becomes a part of the filtering layer. This sometimes causes difficulty, for the particles of certain precipitates unite to form an impervious layer. Or the filtrate may be drawn *upward* through the filter, which is suspended in the liquid to be filtered; thus clogging does not occur so easily, as a large part of the precipitate settles to the bottom of the vessel and does not come in contact with the filter until most of the liquid has been drawn off.

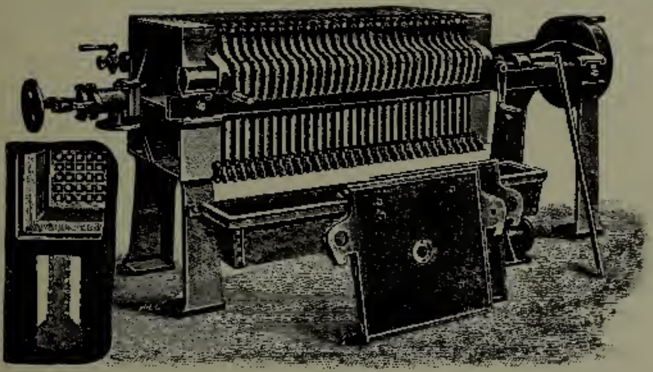

Fig. 10.

In technical work, pressure is usually obtained by the filter press (Figs. 10 and 11). This is a strong iron frame, in which a number of cells of iron or other metal are supported and tightly clamped by the screw (H). Each cell is made up of two flat metal plates (A), with planed edges, which are separated by a hollow "distance frame" (B). Between the filter plates (A) and the "distance frames" (B) are stretched the filter cloths (C), which are held in place by the clamping of the edges of the plates and frames. The face of each plate is channelled by grooves leading to an outlet (D) at the lower edge of the plate. In a corner, or at one side of each plate, distance frame, and filter cloth is a hole (E) in such a position that when clamped in the press the holes form a continuous channel (E, E, E) through the series of cells. This forms the feed channel through which the material to be filtered enters the cells; a side opening from this channel in *each distance frame* admits the material to the space between the plates. The liquid passes through the filter cloth (C) into the grooves leading to the outlet (D) and escapes through the cocks (F), while the sediment retained by the cloth accumulates in the distance frames, forming a solid cake, which finally fills each cell completely.

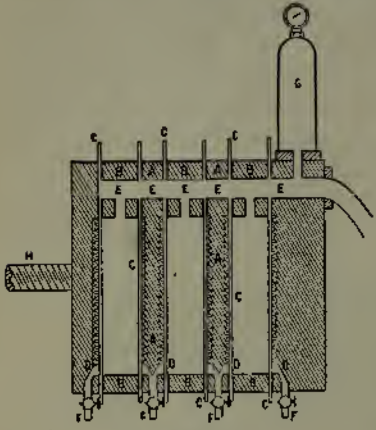

FIG. 11.

A powerful pump supplies a continuous stream of the liquid and forces the sediment into the cells, where it collects in a cake and offers increasing resistance to the passage of the liquid. The limit of pressure employed to force the liquid through depends on several factors, and is usually determined by experiment for each material to be filtered. When this pressure limit is reached, the process is stopped, the cell taken apart, and the cake of sediment removed; then the cells are returned to the press frame, clamped in position, and the operation repeated. The air chamber (G) equalizes the pressure during the working of the pump.

Another type of press is the central feed machine in which the feed channel (E, E) passes through the middle of each plate (see Fig. 10). In each filter cloth, to correspond with this opening, there is a hole, around which a small clamping ring makes a tight joint.

The number of cells in a single press may range from half a dozen to a couple of hundred, according to the amount of material to be filtered. The average sizes of frame are from 18 to 36 inches in diameter, and the width of the frames, which determines the thickness of the cake, may be ½ inch to 3 inches. The proper size and thickness of cake must be determined by experiment for each material. Very often the filter press is fitted with special arrangements for washing the cake to remove the soluble matter. This is usually accomplished by a special feed channel from which the wash-water is forced through the cakes as they rest in the cells. Sometimes the cells are surrounded with jackets for steam heating, or refrigeration, for filtration at high or low temperatures.

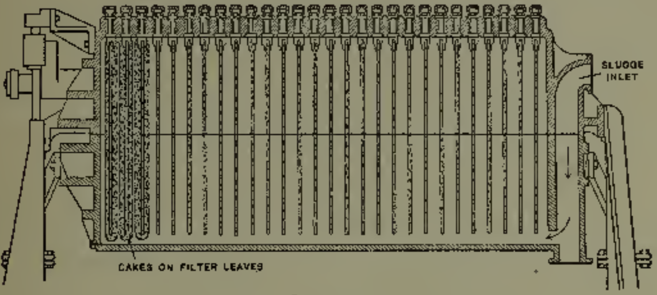

Fig. 12 *a*.

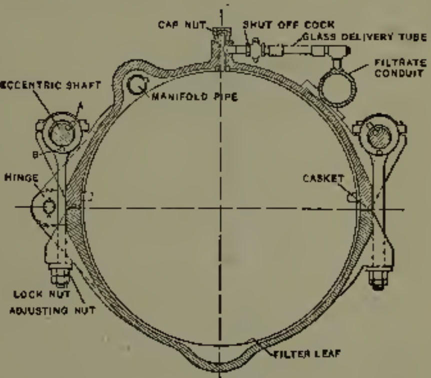

Fig. 12 *b*.

The leaf filter consists of a closed chamber containing numerous filter leaves, made of thin wood slats or metallic wire webbing, covered on both sides by the filter cloth; the cloth is stitched or clamped around the edges of the leaf. A nipple at the top or side of the leaf, connecting with its interior, serves as the means of suspending the leaf in the chamber, and also as exit for the filtrate, which passes into the filtrate conduit. A shut-off valve is placed between the nipple and the conduit.

In Fig. 12 * is shown a leaf filter of the "clam shell" type, in which the chamber consists of two semi-cylindrical castings, the upper one fixed in suitable supports, and the lower one so hinged that it can swing away from the top half, permitting the dumping of all the cakes at once, without disturbing the filter leaves. A rubber

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* Jour. Ind. Eng. Chem., **1914**, (VI) 143.

gasket renders the joint tight when the filter is closed. A short glass tube between the outlet nipple and the filtrate conduit makes it possible to detect a broken filter cloth by the turbidity of the liquid passing.

The chamber is filled under pressure with the liquid to be filtered and the leaves are thus entirely submerged; the liquid passes through the cloth into the interior spaces of the filter leaf, and thence out by the nipple to the filtrate conduit. The solid matter is retained on the cloth and coats both sides of the leaves, forming cakes of uniform thickness on each. When the cakes are sufficiently thick, the feed is stopped and the cakes washed without disturbing them, by introducing water through the sludge inlet, or by a special manifold pipe delivering into the spaces between the cakes. After the washing, the residual liquor is drained out of the chamber, and the cakes freed from most of the retained liquor by compressed air admitted to the chamber. The cakes are then loosened from the cloths by introducing compressed air, steam, or water through the filtrate outlet; this passes into the space inside the leaf frames, and escapes through the cloths, forcing the cakes from the filtering surfaces.

Another type of leaf filter has the frames suspended longitudinally in the chamber, and the outlets for the filtrate pass through the press head. The press head and frame carrying the filter leaves are supported on a carriage, by which they can be moved out of the chamber for discharge of the cakes. This press is set at an incline of 8° to 9°, to facilitate movement of the carriage when the leaves are all covered with cakes.

Fig. 13.

The **centrifugal machine** (Fig. 13) is much used to separate liquid from solid matter. It works rapidly and leaves the substance almost dry. It is a cylindrical cage or basket (A) of wire gauze or perforated sheet metal, fixed on a vertical shaft (B) which rotates at very high speed. The contents of the cage are thrown against the perforated wall by the centrifugal force, the solid matter being held by the screen; the liquid passing through impinges upon the fixed casing (C) surrounding the rotating cage. These machines vary in size from 12 to 60 inches diameter, and 8 to 30 inches depth of basket. Two forms are in use: the over-driven type, in which the driving pulley (P) is fixed at the upper end of the shaft, above the basket; and the under-driven type, in which the cage is placed on the upper end of the shaft, and the pulley below. In the over-driven type, the shaft is usually hung in flexible bearings, so the cage may adjust itself to any change of the centre of gravity, caused by unequal loading, and runs without vibration.

Sand filters are sometimes used for work on a large scale. These are made as follows: Into a box having a perforated bottom is put a layer of coarse gravel; this is covered with finer pebbles; these by sand, and a jute or canvas cloth covers the whole. A wooden or iron grating is added to protect the filter when the sediment is shovelled out. The filter is often placed over a receptacle from which the air may be exhausted, thus affording pressure filtration if necessary.

CRYSTALLIZATION

Crystals are chemically homogeneous bodies, usually having regular polyhedral forms, and whose molecules have arranged themselves regularly according to definite laws. The tendency to form crystals is common to almost all chemical compounds under certain conditions, the forms of the crystals being characteristic of the substance.

Crystals may form from a fusion, or by sublimation; but crystallization almost always takes place from solution.

In general, the solubility of a substance increases as the temperature of the liquid rises; when the boiling point is reached, under atmospheric pressure, the rise in temperature ceases, and no more of the substance dissolves. When a liquid has dissolved all of a solid that it can hold in solution at a certain temperature and pressure, it is said to be *saturated for that temperature.* Any decrease in the temperature results in the separation of a part of the substance usually as crystals. There are a few instances where the maximum solubility is reached at temperatures much below the boiling point of the solution, the most notable of these salts being sodium carbonate and sodium sulphate, both reaching the maximum solubility below 35° C. During the formation of the crystal, there is a tendency to exclude from it all matter not homogeneous with it; hence this is an excellent method of purifying salts. But if a concentrated solution, which is very impure, is allowed to crystallize, the impurities may become enclosed in or entangled among the crystals as they form, producing an impure product. This can often be prevented by stirring the solution while crystallizing, thus causing the formation of very fine crystals or "crystal meal," which may be more readily washed free from mother-liquor and impurities. The liquid from which the crystals have deposited, is called the *mother-liquor;* it contains the greater part of the soluble impurities present in the original solution, and also a considerable quantity of the salt, which has not deposited as crystals. The amount of the latter depends upon the temperature at which the crystallization took place. By further evaporation more crystals may be obtained, but they are less pure than those first separated. Thus the impurities accumulate in the mother-liquor, and in many cases, being valuable salts themselves, are recovered, and add to the profits of the industry. On the other hand, the mother-liquors from some processes are the cause of much annoyance and expense to the manufacturer, since from their corrosive, poisonous, or offensive nature, they cannot be run into the streams or sewers, and their disposal in some other way becomes necessary.

If a concentrated solution is allowed to stand quietly while crystallizing, especially if there is a considerable quantity of the liquid and the temperature falls very slowly, the crystals formed are usually large and well defined; on the other hand, if it be stirred, the crystals are small and imperfectly developed, constituting the crystal meal above mentioned. Since large crystals are compact and offer a relatively small surface to the action of water, they dissolve very slowly, unless pulverized. Crystal meal dissolves more readily, and for this reason is becoming more and more popular with manufacturers.

CALCINATION

Calcination is the process of subjecting a substance to the action of heat, but without fusion, for the purpose of causing some change in its physical or chemical constitution. The objects of calcination are usually: (1) to drive off water, present as absorbed moisture, as "water of crystallization," or as "water of constitution"; (2) to drive off carbon dioxide, sulphur dioxide, or other volatile constituent; (3) to oxidize a part or the whole of the substance. There are a few other purposes for which calcination is employed in special cases, and these will be mentioned in their proper places. The process is often called "roasting, "firing," or "burning," by the workmen. It is carried on in furnaces, retorts, or kilns, and the material is often raked over or stirred, during the process, to secure uniformity in the product.

The furnaces used for calcining substances vary much in their construction, but there are three general classes: reverberatory, muffle, and shaft furnaces or kilns.

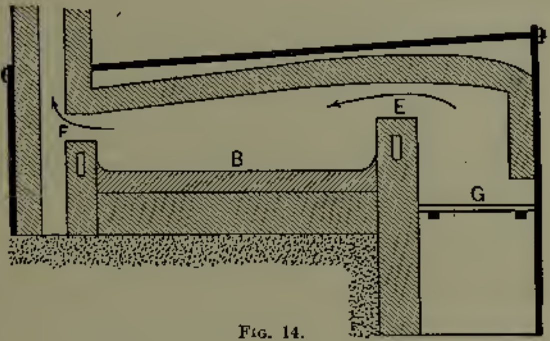

Fig. 14.

Reverberatory furnaces are built in many forms, but in all cases the flames and hot gases from the fire come in direct contact with the material to be calcined, but the fuel is separated from it. The simplest and most common form is shown in Fig. 14. The fire burns on the grate at (G), and the flames, passing over the bridge at (E), are deflected downward by the low sloping roof of the furnace, and pass directly over the surface of the charge in the bed of the furnace at (B), finally escaping through the throat (F) into the chimney. The charge is spread out in a thin layer on the bed (B), and may be either oxidized or reduced, according to the method of firing and the amount of air admitted.

The **revolving furnace** (Figs. 3 and 47) is a very important modification of the reverberatory furnace. This consists of a horizontal or slightly inclined cylinder (B) of iron or steel plates, lined with fire-brick or other suitable fire-resisting material, and open at each end. The flames from a grate (A) at one end pass through it on their way to the chimney (D). The cylinder is revolved about its longitudinal axis by means of a gear. It is turned until a manhole in the side is brought directly under a hole in the floor above, the bolted cover is removed, and the charge dumped in. The revolution of the cylinder stirs the charge thoroughly, and brings it into intimate contact with the flame. To discharge the contents, the manhole cover is removed, the cylinder is rotated, and the material drops out upon the floor or into a car placed for it. To facilitate discharging, the lining usually slopes from all sides towards the manhole. The speed varies from about two revolutions a minute to one revolution in five or ten minutes. These furnaces are extensively used, their advantages being the intimate mixing and even heating of the charge, and the large quantities, amounting often to several tons, which can be worked at one time.

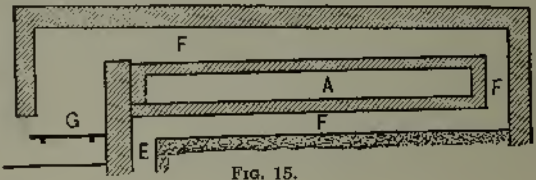

Fig. 15.

Muffle furnaces (Fig. 15) are so constructed that neither the fuel nor the fire gases come in direct contact with the material to be calcined. A retort (A) of iron, brickwork, or fire-clay is placed over the fire grate (G). Flues (F, F) are built around the retort, and through these the hot gases from the fire pass on their way to the chimney (E).

Shaft furnaces and **kilns** are of two general classes, periodic and continuous. After a charge has been calcined, the periodic furnace (p. 175) or kiln is allowed to cool before it is emptied and recharged. In the continuous variety (p. 176) this is not necessary, and the calcined substance is withdrawn and fresh material added without loss of time or waste of heat. The furnaces may be charged with alternate layers of fuel and material to be calcined. By this method, known as "burning with short flame," the material to be calcined is in close contact with the fuel, and is of course more or less contaminated with ashes. In other forms of shaft furnaces (Fig. 74) the fuel is burned on a separate grate, and only the flames and hot gases pass into the shaft; consequently, no ashes are left in the product. This process is called "burning with long flame."

Any of the various forms of furnace here mentioned may be heated by natural gas, generator gas, or oil. This is very advantageous in the matter of cleanliness and of regularity of temperature. (See Fuels.)

REFRIGERATION

Since refrigerating machines have made artificial cooling of rooms and of material possible, industries which were formerly only carried on in cold weather are now operated at all seasons. The manufacture of ice is also a large and increasing industry, and is apparently forcing the natural product from the market more and more each year.

The principle involved in a refrigerating machine is the rapid absorption of heat by the rapid evaporation of a volatile liquid. The substances most used are liquefied ammonia, sulphur dioxide, carbon dioxide, and the very volatile liquids derived from petroleum, chiefly *cymogene* and *rhigolene.* In this country by far the greatest number of machines employ liquid ammonia.

The gas is heavily compressed and then liquefied by passing it into a coil over which a large amount of cold water flows; the liquid is then forced through a small opening into a large chamber or coil of pipe, from which the gas formed may be rapidly exhausted by a pump. The rapid expansion and conversion of the liquid to a vapor here absorbs much heat from the walls of the coil or chamber, whose temperature consequently falls considerably below the freezing point of pure water. In order to increase the external surface of the expansion coils, cast-iron disks are placed at frequent intervals on the pipe perpendicular to its line of direction. Only a comparatively small amount of ammonia or other volatile liquid is necessary for the continuous working of the machine. Since the gas is returned to the compressor, it is only necessary to supply that lost by leakage.

It is often customary to surround the expansion coils with a brine or calcium chloride solution, which is then pumped through coils or pipes in rooms to be cooled. For making ice, galvanized iron boxes are filled with water and immersed in the cold brine.

In the system shown in the diagram (Fig. 16) a certain amount of oil is injected into the compressor along with each charge of ammonia. This insures complete emptying of the compressor at each stroke, lubricates the piston, prevents the gas escaping behind the piston, and absorbs part of the heat evolved in the cylinder by the compression of the gas. This oil is separated from the liquefied ammonia by gravity in separating tanks and returned to the compressor.

The machines above described are called "compression machines," because the volatile substance is compressed directly to be used again. Another class of refrigerating apparatus depends for the recovery of the volatile substance upon *absorption* of the vapors in some liquid from which they can again be set free. The cooling effect in this case is also produced by rapid evaporation of the liquefied gas, the difference in the two classes of machines being in the method of recovering the vaporized liquid for use again. In the Carré ammonia absorption apparatus very concentrated *aqua ammonia* is heated in an iron retort or generator; the ammonia gas is driven out through a condenser, chilled by running water over the coils; the ammonia is liquefied by its own pressure, and the liquid passes through an expansion valve into the *refrigerator coils*, which may be surrounded with brine. The expanded ammonia vapor then passes to the *absorber*, containing weak ammonia water from the generator, which has been cooled by running through coils immersed in water. Reabsorption of the ammonia vapors to form concentrated *aqua ammonia* takes place, and the solution is returned to the generator to repeat the cycle. Another style of absorption machine evaporates water in a vacuum apparatus, and absorbs the vapor in concentrated sulphuric acid. The dilute acid thus produced is concentrated in open pans by evaporating the water, and is used again.

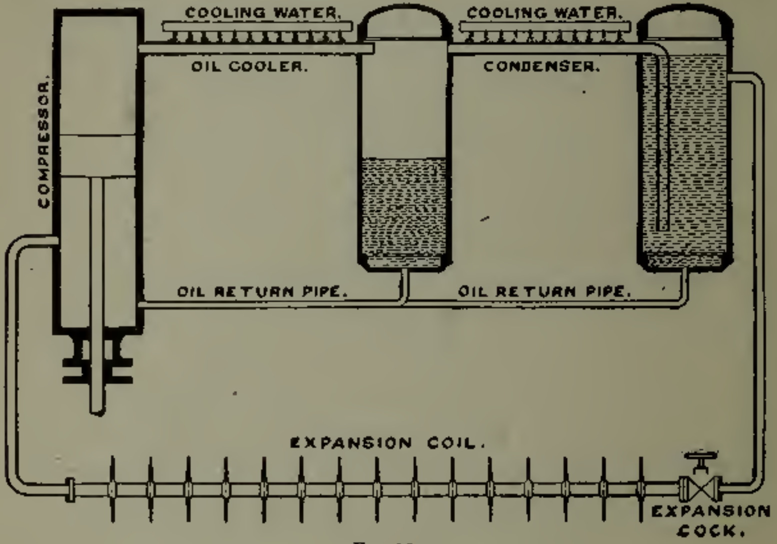

FIG. 16.

The absorption machines require a large quantity of cooling water, and are generally more complicated and expensive than the compression machines.

A third class of machines are those depending on the sudden expansion of highly compressed air or other gas, which does not liquefy at the temperature and pressure used. These machines are large and complicated and are not adapted to making ice, but find limited use for cooling and ventilating on board war vessels where any traces of ammonia or other vapor would be dangerous.

Refrigeration, Cold Storage, and Ice-making, A. J. Wallis-Taylor. London, 1902. (Lockwood & Son.)

SPECIFIC GRAVITY

By the specific gravity of a liquid is meant its relative weight compared with the weight of an equal volume of pure water at a definite temperature. This determination is one of the most frequent operations in chemical work and may be done with a pyknometer when very exact results are required, but in technical operations, sufficient accuracy for all practical purposes may be attained by the hydrometer. This is usually a glass instrument, consisting of a cylindrical bulb, weighted at the lower end, and drawn out at the upper end to a long, slender tube, carrying a scale. The gradations of the scale begin at the top and read downward, the numerically greater reading being at the bottom, except in one instance, — that of Baumé's scale for liquids lighter than water. Since the specific gravity of a liquid varies as its temperature changes, the scale is adjusted to a certain temperature, usually about 15° C., at which determinations must be made.

When the hydrometer is placed in a liquid, it sinks sufficiently to displace a volume of the liquid equal *in weight* to the weight of the instrument, and floats in an upright position. Should the hydrometer sink so deeply into the liquid that the scale is entirely below the surface, the specific gravity is less than the spindle is intended to measure, and one having lower* numerical readings should be used. If, on the contrary, the spindle does not sink deep enough to bring the scale into the liquid, an instrument having higher numerical scale readings is necessary.

Three systems of hydrometer scales are in common use, besides a great number of special scales intended to give one particular factor in the specific gravity of a liquid; *e.g.* the per cent of alcohol in a mixture of alcohol and water, or the amount of sugar in a syrup, etc.

The direct specific gravity hydrometer is so constructed that the reading on its scale shows the specific gravity of the liquid directly as compared with pure water at the same temperature (15° C.). Its

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* Baumé's hydrometer for liquids lighter than water is an exception (p. 27).

scale is adapted to liquids heavier or lighter than water. The point to which it sinks in pure water at 15° C. is marked 1.000. As usually furnished, a set of these hydrometers consists of four spindles, the scale being thus divided into four sections. The first spindle, with gradations from 0.700 to 1.000, is for liquids lighter than water, and the others are for those heavier than water. The scale is usually divided about as follows: 1.000 to 1.300 on the second spindle, 1.300 to 1.600 on the third, and 1.600 to 2.000 on the fourth.

The gradations at the top of each spindle are farther apart than those at the bottom of the stem,* rendering the reading somewhat more difficult in dense liquids than in those of lighter gravity.

Twaddell's hydrometer is also a direct-reading instrument. The system consists of a series of spindles (usually six in number) carrying gradations from 0 to 174. The reading in pure water, at 15.5° C., is taken as 0, and each subsequent rise of 0.005 sp. gr. is recorded on the scale as one additional division. Thus 10 Twaddell becomes 1.050 sp. gr. The gradations on this scale are also closer together as the specific gravity increases, but as its total length is divided among six spindles, the readings are not so difficult even at the highest gravities. The instruments are small, and may easily be used in an ordinary 100 cc. measuring cylinder. For the reasons that it is easy to read, requires but a small quantity of liquid to be tested, and permits a ready conversion of its readings into specific gravity by a very simple calculation, this is a convenient hydrometer for ordinary factory or laboratory use. It is, however, not adapted to liquids lighter than water.

Twaddell readings are converted into specific gravity as follows: Multiply the reading by .005 and add 1.000 to the product. Thus 15 Twaddell becomes 1.075 sp. gr. $(1.000 + [15 \times .005] = 1.075.)$

Baumé's hydrometer is largely used in technical work, but its readings bear no very direct relation to true specific gravity. Baumé dissolved 15 parts of pure salt in 85 parts of pure water at 12.5° C. The point to which his instrument sank in this solution was marked 15; the point to which it sank in pure water was marked 0. The distance between these points was divided into *fifteen equal parts*, and the entire stem marked off in divisions of this width. This produced an instrument for liquids heavier than water.

For liquids lighter than water, the point to which the instrument sank in a 10 per cent solution of salt was marked 0, and that to

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* For the explanation of this fact consult any of the larger works on physics.

which it sank in distilled water was marked 10; the distance between these points was divided into 10 equal parts, and this gradation continued the entire length of the spindle. The 0 thus being placed at the bottom of the stem, the *lighter the gravity* of the liquid tested, the *greater numerically* is the reading of the scale. For instance, a liquid reading 70 Bé. is of less gravity than one of 50 Bé., which in turn is lighter than water at 10 Bé.

To further complicate matters, the instrument makers have produced instruments with erroneous scales. A test made a few years ago disclosed thirty-four different scales, none of which was correct! *

The conversion of Baumé readings to specific gravity involves some calculation and is usually accomplished by reference to tables. The formulæ for this conversion are as follows: —

$\text{Bé.}^\circ = 145 - \dfrac{145}{\text{sp. gr.}}$ (for liquids heavier than water. Temperature 60° F.).†

$\text{Bé.}^\circ = \dfrac{140}{\text{sp. gr.}} - 130$ (for liquids lighter than water. Temperature 60° F.).

The pyknometer is not often used in technical work, but a brief description of it may not be out of place here. It consists of a small bottle, having ground into its neck a capillary tube enlarged at its upper end, to form a reservoir which is closed by a stopper. The tube is removed and the bottle filled with the liquid to be tested; the tube is then inserted tightly, the liquid displaced rising through the capillary to the enlarged part of the tube. The stopper is then loosely inserted and the bottle placed in a bath at the temperature at which the gravity is to be taken. When the bottle and contents have reached this temperature, the stopper is taken out and the liquid in the reservoir removed by means of absorbent paper, until the level of the liquid recedes within the capillary to a mark thereon. The stopper is then tightly inserted and the bottle removed from the bath, and after cleaning and drying its outside, allowed to stand until it reaches the normal temperature of the room. It is then weighed, and the specific gravity of the liquid is calculated from its known volume, previously determined by calibration of the bottle. (For determining specific gravity by means of the pyknometer, see T. E. Thorpe's Dictionary of Applied Chemistry, Vol. V, pp. 107–114.)

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* C. F. Chandler, Proc. Nat. Acad. Sciences, **1881**.

† J. Am. Chem. Soc. **21 (1889)**, 119. J. Soc. Ind., **1905 (24)**, 786. European instrument makers use the formula $\text{Bé.} = 144.3 - \dfrac{144.3}{\text{sp. gr.}}$. See Alkali-makers' Handbook (Lunge and Hurter), p. 175.

Westphal's balance is used to determine the specific gravity of *liquids*. A glass plummet of known weight and volume, suspended from the beam by a fine platinum wire, is submerged in the liquid. The weight which the plummet loses by this submersion is the weight of the volume of liquid it displaces. The decimal graduation of the beam, with the use of riders of 0.1, 0.01, and 0.001 part of the weight of the water displaced by the plummet, permits the actual specific gravity to be read off on the beam, as soon as the latter is brought to equilibrium with the plummet suspended in the liquid in question.

SURFACE PHENOMENA AND COLLOIDS

Particles in the interior of solids and liquids are greatly influenced by the presence in their immediate neighborhood of other particles; this is indicated by describing solids and liquids as "*condensed phases*." Particles on the surface are free from such action on one side, but not on the other. Hence the properties of the surface of a condensed phase are different from those of the interior; thus an aqueous soap solution contains more soap in its surface layer than in its interior, but with most inorganic salts the reverse is true. The surface layers are so thin, however, that these differences become appreciable only when the ratio of surface to volume is enormous. This obtains when a substance is in the form of extremely small, separate particles; since the voids between the particles are necessarily filled with something, such a system consists of at least two phases. The whole is called a *disperse system* — the separated particles the *disperse phase*, and the void-filling substance the *dispersing medium*. Surface phenomena are usually of importance only in such disperse systems. The following table illustrates the phenomena: —

	Dispersing Medium	Disperse Phase	Illustration
1	Gas	Liquid	Fog
2	Gas	Solid	Smoke
3	Liquid	Gas	Whipt Cream (Air emulsified in oil.)
4	Liquid	Liquid	Emulsions — Cream (Oil emulsified in water.)
5	Liquid	Solid	Suspensions — Colloidal solutions, as gold in water.
6	Solid	Gas	Bread
7	Solid	Liquid	Frozen Cream — Gels
8	Solid	Solid	"Milk" Glass

When the size of the dispersed particles is small, the friction between them and the gaseous or liquid dispersing medium becomes very great, and relative motion is difficult. Hence separation by decantation is difficult or impossible, filtration fails except through the densest filtering media, and the separation of the phases is a serious problem. Frothing in evaporators, dust production in furnacing and grinding operations, the "fume" from storage batteries and pickle baths, are cases in point. The solution of the problem is found either in increasing relative motion by the application of an external force, (as in centrifugal separators for dust, cream, etc.), or in causing coalescence of the particles. This may be brought about by enmeshing them in a mass of larger particles (as in the use of iron or aluminum hydroxides in water purification), by impinging upon surfaces, wet or otherwise (as in " catch-alls " and gas washers), or by electrical discharge, or by mutual co-precipitation. These last two methods are based on the fact that in general there exists at the surface between two phases an electrostatic potential difference. The particles of the dispersed phase are therefore charged with reference to the dispersing medium and hence are capable of electrolysis (movement in an electric field followed by discharge on reaching the electrode). Also the particles are often held apart and prevented from coalescing to form larger aggregates, by the mutual repulsion of the charges on the particles; when discharged, coagulation or precipitation results. Discharge may be caused* (*a*) by electrolysis; (*b*) by neutralization with the charge of a disperse phase of opposite sign; (*c*) by the adsorption of ions of opposite sign.

A characteristic property of such disperse systems is the power possessed by the surfaces between the phases to condense upon themselves large quantities of gases and of solutes from liquid phases. This condensation is called **adsorption**; the amount adsorbed x, on the surface m, is given by the expression $\frac{x}{m} = kC^{\frac{1}{n}}$, where C is the

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* An illustration of (*a*) is the **Cottrell Process** for precipitating smoke and dust from smelters, cement works, etc.; the gas containing the fine solid particles in suspension is passed through a cylindrical metal tube or chimney, at the axis of which is a fine wire. Between this wire and the chimney a high direct-current potential difference (100,000 volts and over) is maintained, which causes the charged dust particles to move rapidly to the surface of the stack, discharge, and coalesce. Owing to the small ratio of charge to weight of dust particle, the current consumption (hence the cost) is small. The efficiency of dust removal and the gas-handling capacity are high. A technical application of (*b*) is in the tannage of leather (p. 577), while (*c*) is illustrated in the use of certain electrolytes to coagulate fine precipitates (the use of salt in washing white lead, p. 225, and the addition of NH_4NO_3 to aid in filtering phosphomolybdate precipitate).

concentration of the substance adsorbed, while k and n are constants, n being greater than unity, seldom less than 2 or more than 20. Adsorption at low concentration is relatively far greater than at high, and this can be used to remove small amounts of impurities from solutions, as in water purifying (p. 49), sugar refining (p. 429), decolorizing oils (p. 342), etc. The adsorbing agent may be brought in contact with the liquid by admixture or by use of the counter-current principle, the solid being held in a suitable container through which the liquid passes, thus forming an *adsorption filter*. Adsorption is generally greater the lower the temperature and the higher the molecular weight and complexity of the substance adsorbed. Certain materials, notably bone-char and fuller's earth, have high adsorptive power, while others, such as animal and vegetable fibres, are very specific in the substances they adsorb.

Where the dispersing medium is a liquid, the disperse phase is called a colloid, if exceedingly small, so that separation by filtration is very difficult; if somewhat larger, it is called *colloidal*, or a colloidal precipitate or suspension. Solid colloids vary much in their capacity to combine with the solvent; the following aqueous colloids are approximately in the order of their degree of hydration in colloidal solutions: (1) glue, caseinogen, dextrins, etc.; (2) hide substance, starch; (3) ferric hydroxide, aluminium hydroxide, silicic acid; (4) clay; (5) arsenic sulphide, sulphur; (6) colloidal metals (gold, etc.). When highly hydrated, the colloid acquires many of the properties of a liquid, and the colloidal solution resembles an emulsion. Such colloids are called *emulsion colloids* or *emulsoids;* the less hydrated ones are called *suspensoids*. A sharp distinction cannot be drawn between them.

The value of a solid colloid depends on its possession of emulsoid characteristics. Solid emulsoids when treated with a solvent first swell (glue, rubber, starch), due to combination with the solvent, but finally dissolve, *i.e.* the individual particles separate and stay in suspension in the solvent. By lowering the temperature, the solvent in combination with the colloid increases at the expense of that in the dispersing medium, and if the latter be not too great in amount, it finally becomes so small relative to the colloidal phase that the two change functions, *i.e.* the system becomes a suspension of small drops of liquid dispersed in a solid, much swollen with solvent. This is called a *gel* or jelly, and the transformation temperature is the jellying point.

Solid colloids are substances whose individual particles or molecules are very large and complex molecular aggregates. They are in general chemically inert and little affected by solvents; when heated, or when swollen with a suitable solvent (in gel form), they are "plastic," *i.e.* they can be moulded, and separate pieces pressed together coalesce so they can be shaped at will. Some possess great strength and hardness and are important as materials of construction. Such colloids consist of one or several units U, a number, n, of which are associated into an aggregation U_n. Thus in starch the unit is the dextrose radical, association resulting from elimination of water from dextrose; in rubber the unit is isoprene or polyprene; in albumens the units are a number of amido-acids. In general the larger the aggregate U_n, the stronger and harder the solid colloid, the more inert chemically, the less soluble in solvents, and the less ductile and plastic the material becomes. Mechanical manipulation, heat, and the action of solvents tend to decrease the size of the aggregate by decreasing n.

Many important solid colloids (cellulose, hair, wool, and silk) are natural products, any chemical treatment of which causes disintegration of the aggregate to a greater or less extent, with results on the physical properties as indicated (pp. 489, 494, 499, 505, 511, etc.). Many others are made by first forming the colloid as a plastic and then destroying the plastic condition. The important industrial methods of doing this are: (1) producing the plastic state by means of heat and hardening by cooling (as in glass, p. 196, and asphalt, p. 347); (2) rendering plastic with a solvent and solidifying by evaporation of the solvent (as in artificial silk, p. 496, and sun-dried bricks); this may be succeeded by chemical changes essentially modifying the character of the solid (drying of varnish, p. 397; burning of ceramics, p. 212); (3) increasing the chemical and physical resistance and decreasing the plasticity, by increasing the size of the molecular aggregate U_n, by (*a*) co-precipitating two emulsoids to give a more complex and stable mass (as in tanning leather, p. 573); (*b*) by increasing the number of units, n, in each aggregate (as in the manufacture of bakelite, p. 585); (*c*) by increasing the complexity of the unit U by chemical addition (as in vulcanizing rubber, p. 588).

FUELS

Fuels are substances which, when burned with air, evolve heat with sufficient rapidity and in sufficient quantity to be employed for domestic or industrial purposes.

There are three classes of fuel: *solid, liquid,* and *gaseous.* In the majority of these the essential constituent is carbon, but in many of them hydrogen is also an important ingredient. In rare cases sulphur, phosphorus, silicon, or manganese may take part in the combustion; but for the purposes for which fuel is ordinarily used these constituents are deleterious. Oxygen is sometimes regarded as advantageous, but not always. Nitrogen may cause a direct loss of calorific power, owing to its dilution of the combustible gases, but in most solid fuels the percentage of nitrogen is so small that its effect is negligible.

SOLID FUELS

The solid fuels are wood and other matter containing cellulose, peat, lignite or brown coal, bituminous coal, anthracite, charcoal, and coke.

Wood consists of cellulose $(C_6H_{10}O_5)_n$, lignine, resins, various inorganic salts, and water. The quantity of water present has great effect on the heating value and ranges from 25 to 50 per cent in green wood, and from 10 to 20 per cent in air-dried wood. Wood cut in the spring and summer contains more water than that cut in the early part of the winter. A cord of hard wood, such as ash or maple, is about equal in heating value to one ton of bituminous coal; soft woods, such as pine and poplar, have less than half this amount. Wood burns with a long flame and makes comparatively little smoke; but its calorific power is low, averaging from 3000 to 4000 Cal. per kilo of air-dried wood. It is, however, easily kindled, the fire quickly reaches its maximum intensity, and a relatively small quantity of ash is formed. Wood is too expensive for industrial use, except in a few special cases, where freedom from dirt and smoke is necessary.

Of other cellulose materials, shavings, sawdust, and straw are used for fuel in some places. They are bulky and difficult to handle, while their heat value, which depends on the amount of moisture they contain, is seldom more than from one-third to one-half that of good coal. Such waste matter as spent tan-bark and *bagasse* (crushed sugar cane), and the pulp from sugar beets is sometimes used for fuel for evaporation or for steam, but owing to the large amount of moisture they contain, the heat value is very low.

Peat is the product of slow decay of mosses, especially *Sphagnaceæ,* under water. It is of little importance in this country, but is extensively used in parts of Europe where it is found. Since it contains a large amount of water and inorganic matter, its calorific power is not high, averaging from 4000 to 5000 Cal. per kilo. One pound of peat evaporates about 4.5 lbs. of water. It is dug from the bogs and dried in the air, sometimes being heavily compressed to reduce its bulk. As thus prepared, it contains from 15 to 20 per cent of moisture and from 8 to 12 per cent ash. It is used considerably as a packing material, owing to its soft and spongy consistency.

Lignite or **brown coal** is intermediary between peat and bituminous coal. It was probably formed from swamp plants which decomposed under water, and is geologically of more recent formation than true coal. It is dark brown or black in color, and its texture is fibrous, earthy, or sometimes vitreous. It usually contains from 15 to 20 per cent of moisture, a large quantity of ash, and often a considerable amount of sulphur. It burns freely with a long flame, producing much smoke, and its calorific power varies from 4000 to 6500 Cal. It is extensively used for heating steam boilers and evaporating pans, and for domestic fires.

Bituminous coal is the most important of all fuels. There is a great variety in the kinds of coal classed under this name, but they differ chiefly in the amount of volatile matter, which ranges from 20 to 50 per cent. They were all formed from similar sources, the varieties having resulted from pressure and from exposure to heat. The specific gravity varies from 1.25 to 1.75. They are classified according to their behavior when burning, as fat, caking, and non-caking. Fat coals usually have a dull lustre, are very rich in volatile matter, sometimes containing as much as 50 per cent, and burn with a long, smoky flame, sometimes caking in the fire. Non-caking coals are those which burn freely, with little smoke, and do not cake. The caking coals burn with a smoky flame and fuse or sinter together.

The formation of coal is probably due to a slow decomposition of cellulose matter, under fresh water, by which marsh gas (CH_4) and carbon dioxide (CO_2) were eliminated. The composition of a typical coal, as shown by the analysis of good samples, may be represented by the symbol ($C_{26}H_{20}O_2$), and assuming this, the change of cellulose may be represented by the equation : —

$$6\ (C_6H_{10}O_5) = 3\ CH_4 + 7\ CO_2 + 14\ H_2O + C_{26}H_{20}O_2.$$

Various changes were afterwards brought about by the heat and pressure within the earth's strata, and the character of the coals modified in many cases. Thus, more or less of the volatile constituents were removed, and the coal itself compressed to a very hard, compact mass. When this process went to the extreme, nearly the whole of the volatile constituents were expelled, and the resulting product is the hard coal known as anthracite.

Anthracite coals are nearly pure carbon, are very hard and dense, have a very high lustre, and contain but little hydrogen or volatile matter. They burn with a slight flame, form no smoke, have no caking properties, and are difficult to ignite. Their specific gravity is high, being nearly 1.75 in good Lehigh coal. They have a calorific value of from 7500 to 8500 Cal.

Between bituminous and anthracite coals are a number of semi-anthracites, which cannot be classed in either variety.

Coal deteriorates considerably when stored, owing to the escape of some of its volatile constituents. There is a popular idea that wetting coal before burning increases its heating capacity; but this is a fallacy, for a loss of heat results.

The average composition of various coals is here tabulated for comparison : — *

	TOTAL CARBON	FIXED CARBON	VOLATILE MATTER	ASH	MOISTURE	CALORIES
Brown coal (Wyo.) . .	58.41	39.56	37.96	4.79	17.69	5753
Bituminous (Ill.) . . .	63.85	44.31	37.70	12.80	5.13	6496
Bituminous (Pa.) . . . (Connellsville)	76.34	60.85	29.09	9.09	0.97	7751
Semi-bituminous (W. Va.) (Pocahontas)	79.12	70.80	16.90	11.50	0.80	7761
Anthracite (Pa.) . . .		84.28	3.27	9.13	3.33	7417

Charcoal is made by the dry distillation of wood, at a temperature of from 400° to 450° C. This is done in heaps, or in closed retorts. All the volatile matter is driven off, and the residue consists of carbon and the inorganic constituents of the wood. Good charcoal is porous, brittle, with conchoidal fracture, and retains the

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* U. S. Bureau of Mines, Bul. No. 29.

form of the wood, but has only about three-fourths of the volume and usually about 20 per cent of the weight of wood. It burns with but slight flame, without smoke, and is easily ignited. Containing but little sulphur or phosphorus, it is especially useful in making some high grades of iron and steel. Its calorific power is about 7100 Cal.

In this country much of the charcoal is made by burning wood in "charcoal pits." The wood is heaped in a hemispherical pile around a central opening, and covered with earth and sod, leaving only a few small draught holes near the bottom. Then it is ignited at the centre and allowed to burn until the whole pile is on fire. A smouldering combustion takes place, largely at the expense of the oxygen and hydrogen of the wood fibre, forming water, carbon dioxide, and volatile hydrocarbons, which escape. The draught holes are then all closed and the pit is kept carefully covered until the fire smothers and the charcoal is cold. By carbonizing in pits nearly all the volatile matter is lost, or at best, only a part of the tar is saved and the yield of charcoal is only 20 per cent by weight of the wood. But if the process is carried on in retorts, a large amount of gas, pyroligneous acid, and tar is collected (see p. 301), and about 30 per cent of charcoal is obtained, together with nearly 40 per cent of pyroligneous acid and 4 per cent of tar.

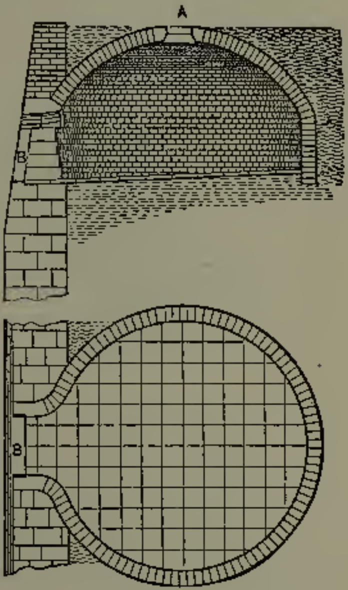


Fig. 17.

Coke is made by the destructive distillation of coal. It has a silvery white lustre, an open, porous structure, and a metallic ring when struck. It contains all the ash-forming materials of the coal, but nearly all volatile matter and sulphur have been eliminated. For metallurgical purposes it must be sufficiently strong to sustain the weight of the charge in the furnace without crushing. The calorific value is from 7600 to 8100 Cal. It burns without smoke and with but little flame and does not cake. It is made in kilns of two general types: The "**bee-hive**" coke oven (Fig. 17) is made of brick, with a circular opening (A) at the top and a door (B) at the side, through which the coke is drawn. A part of the coal is burned, in order to carbonize the remainder. As a rule, no attempt is made to save the volatile products or the tar. The yield of coke amounts to only 60 or 65 per cent of the weight of the coal.

Coking ovens in which the by-products are saved are much used abroad, and to an increasing extent in this country. There are several kinds, but the Otto-Hoffmann, the Simon-Carvès, and the Semet-Solvay ovens are much used. In these, the ammonia and coal tar are recovered, and a coke suitable for metallurgical purposes is obtained. The waste gas is employed to heat the retorts.

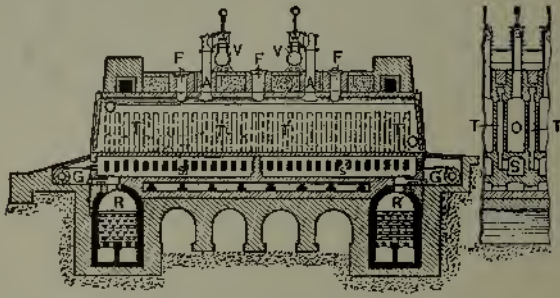


Fig. 18.

The **Otto-Hoffmann oven** is shown in Fig. 18. The retorts are narrow chambers (O) about 40 feet long, 5 feet high, and 22 inches wide, having doors at each end, and heated by vertical flues (T, T) in the walls. Coal is charged through (F, F) while the gases and tar pass off through (A, A) to the hydraulic main (V, V). The gas for heating enters from pipe (G), mixes with hot air from the regenerator (R), and burns in the flue (S) under the retorts, the flame passing up through the flues (T, T), and down through (T′, T′) to (S′), from which the products of combustion pass through the regenerator (R′) and heat it. After a time, the flow of gases is reversed, the producer gas enters through (G′) and air through (R′), burning together in (S′), while the products of combustion escape through (R). The volatile matter given off from the coal passes through (V) to washers and scrubbers (see Illuminating Gas), which remove tar and ammonia, while the gas is stored in a holder, to be led, later, through (G, G′), and burned under the retorts.

The **Simon-Carvès oven** (Fig. 19) is also a long, narrow retort (A) with doors at each end, but the heating flues (F, F) are set horizontally in the retort walls. The volatile matter escapes from the retort through (B), passes to the washer and scrubber, whence the purified gas goes to the holder, from which it is drawn as needed, through (G), and burned with hot air.

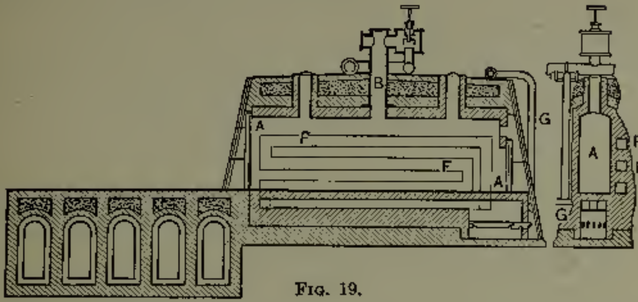
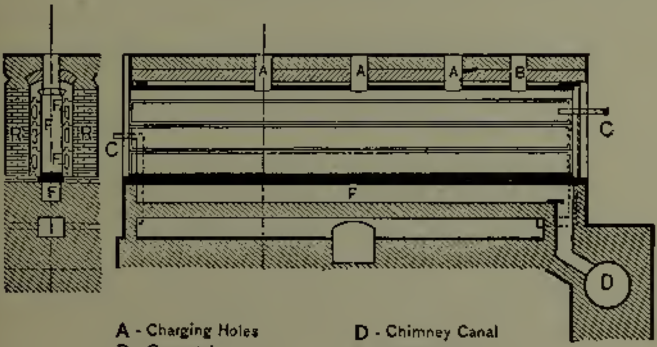


Fig. 19.

The **Semet-Solvay oven** (Fig. 20) also has horizontal flues, but deeper and narrower retorts than the two just mentioned. Each retort has an independent set of flues which are placed in the retort lining and backed by a heavy brick retaining wall; this supports the weight of the roof arch, and also holds the heat during the drawing and charging of the retort. Thus the flue walls can be made much thinner than in the ovens previously mentioned, and the oven works more rapidly, giving a larger yield of coke, and will coke coals which are low in volatile matter. The lining can easily be replaced without rebuilding the entire oven. The retorts are usually about 30 feet long by 16 inches wide, and $5\frac{1}{2}$ feet deep, and hold about $4\frac{1}{2}$ tons of coal at each charge. No regenerative heating is used, the heat being retained in the walls between the retorts. A number of these ovens have been recently introduced into this country and give excellent results.



A - Charging Holes
B - Gas uptake
C - Gas Inlet to Heating Flues
D - Chimney Canal
F - Heating Flues
R - Wall between Retorts

Fig. 20.

LIQUID FUELS

The most important liquid fuels are crude petroleum and various oily residues obtained in distilling petroleum, shale oil, and coal tar.

Crude petroleum, especially the Texas and California oils, and the residuum from the manufacture of burning oils and lubricators, are the chief sources in this country. The residuum from Russian petroleum, called "*astatki*," is very extensively used in southern Russia.

Crude petroleum is easily regulated so as to burn without smoke or soot, giving a steady heat and requiring no stoking. It is less bulky, and from two to two and a half times as efficient as anthracite coal. Its heat value is about 11,000 Cal., and it evaporates about 15 lbs. of water to one pound of oil. One pound of coal-tar residue evaporates 13 lbs. of water.

Liquid fuel is coming into more general use every year, especially where long flame and high temperature are desired. It is usually burned as spray, being forced into the furnace by a large atomizer supplied with an air blast or superheated steam.

GASEOUS FUELS.

Gas fuel is important industrially, because of the cleanliness, economy of labor, and exact control of the heat it affords, and of the much greater efficiency obtained in the conversion of energy into work, or the development of power, by the use of internal-combustion engines. Since combustible natural gas is found only in restricted areas, artificial fuel gas is largely prepared; but always from solid fuels. Liquid fuel is itself nearly as satisfactory as gas, and is too expensive as a material for gas making.

Natural gas exists already formed in the earth, and is obtained by boring tube wells similar to petroleum wells. Its essential heat-producing constituents are methane (CH_4) and hydrogen. It is the cheapest and most efficient of all fuels, when properly burned, having a heat value of about 9400 Cal. per cubic metre; but it requires a large amount of air for its combustion, and special burners must be used.

Destructive distillation of solid fuels containing a large proportion of volatile matter is the simplest method of obtaining combustible gases. This is done with both wood and soft coal, but in the case of the former the expense precludes its use for gas production alone.

Coal gas (p. 314) is made by distilling bituminous coal in retorts at such high temperature that the hydrocarbon constituents break down, chiefly into methane and hydrogen (about 40 per cent of each), with small amounts of carbon monoxide, carbon dioxide, nitrogen, and unsaturated hydrocarbons which give luminosity to the flame. It is primarily made for illumination, but is often used for power and heating, where cheaper gas is not available.

Gas formation is important in the burning of soft coal, since distillation results from the heat of the fire, and the gases set free in the furnace burn with a "long flame," developing their heat of combustion uniformly along the entire length of the furnace.

Besides the gas from the volatile constituents, the carbon of coal may be converted into a combustible gas, carbon monoxide, by burning the carbon with a limited air supply. A disadvantage of the process lies in the fact that the large heat of formation of carbon monoxide (29.0 Cal. per Mol), is developed as sensible heat in the gas and is lost if the gases are cooled previous to their combustion. But if the hot gas can be used immediately without cooling, as is often done in lime kilns, etc., there is much economy attained. This may be considered as a type of "long-flame burning" of the coal.

Water gas contains much carbon monoxide and is made by the action of steam on carbon at high temperature: —

$$C + H_2O = H_2 + CO - 29.0 \text{ Cal.}$$

There is, however, a very large absorption of heat (29.0 Cal.) in this operation. But the gas has high calorific value, and after "enrichment" (*i.e.* saturation with low-boiling, unsaturated hydrocarbons), is much used in this country as an illuminant (p. 312).

It appears that carbon when burned with oxygen first forms carbon dioxide with evolution of 97.0 Cal., but in the presence of excess carbon, the dioxide is partially reduced to monoxide, thus: —

$$C + CO_2 = 2\ CO - 39 \text{ Cal.}$$

The lower the temperature the less complete is the reduction. By the mass action law, at any given temperature, the partial pressure of the carbon dioxide, divided by the square of that of the carbon monoxide, is at equilibrium a constant, which is, however, a function of the temperature; *i.e.* $\frac{p_{CO_2}}{(p_{CO})^2} = K_1 = f_1(t)$. In the table below the value of this constant for various temperatures is given, and it appears that a large reduction of dioxide with carbon is only possible at high temperatures. The proportion of carbon dioxide in the gases at a given temperature is generally greater than the figures indicate, since the rate of reaction between carbon dioxide and carbon is relatively low: but it decreases rapidly with the temperature. If the gases are in contact with carbon for a sufficient time, at the given temperature, the ratio of dioxide to monoxide corresponds to the equation, independently of the presence of other gases.

EQUILIBRIUM RELATIONSHIPS OVER CARBON *

(Pressures in Atmospheres)

Temperature of Carbon, C°	$\frac{p_{CO_2}}{p^2_{CO}}$	$\frac{p_{H_2O}}{p_{CO} \cdot p_{H_2}}$
700°	1.37	0.769
800	0.189	0.165
900	0.0357	0.0446
1000	0.00855	0.0143
1100	0.00246	0.00524
1200	0.000824	0.00213
1400	0.000129	0.000449

The mass action law for the water-gas reaction requires that $\frac{p_{H_2O}}{p_{H_2} \cdot p_{CO}} = K_2 = f_2(t)$; this second constant is also shown in the table above. From this it appears that at high temperatures only does the reduction of the steam approximate completion. Since the carbon monoxide formed by this reaction is necessarily accompanied by carbon dioxide corresponding to its equilibrium with carbon, it is seen that at high temperatures only will the gas coming from the producer be satisfactory, while at lower temperatures much undecomposed steam and carbon dioxide will be present. This is shown in the table below.

THEORETICAL COMPOSITION OF WATER-GAS

(Equilibrium of Steam and Carbon)

Temperature of Carbon, C°	% CO	% H_2	% H_2O	% CO_2
800	35.03	39.67	22.98	2.32
1000	49.51	49.93	0.35	0.21

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* Haber, Thermodynamics of Technical Gas Reactions.

The water vapor will largely separate on cooling the gas, but the carbon dioxide remains as an undesirable diluent. Furthermore, a commercial producer, especially when forced in capacity, owing to incomplete reactions, gives lower yields of monoxide and hydrogen than is shown; it should not be run at less than 1000° C.

In operation, the fuel is brought to white heat by an air blast, which is then cut off and steam injected; the formation of water gas now proceeds until the temperature falls below 1000° C., owing to heat absorption; then the steam is cut off, and the air blast turned on until the fuel is again incandescent, and the cycle of operations repeats. During the air blow, the gas formed is sent to the chimney but during the steam blow, the water gas is cooled and sent to the holder. As the fuel bed is deep and above 1000° C., the air blow forms a large amount of carbon monoxide, which may be collected for use; but it is often run to waste, in which case the air supply should be large to secure a maximum formation of carbon dioxide, which is not in contact with the fuel a sufficient time for reduction to carbon monoxide. Even under the best conditions, a serious loss of heat results from the incomplete combustion of the fuel.*

The waste of energy of the coal in this intermittent process can be largely avoided by combining the two reactions; the air and steam being regulated so the heat of combustion of the carbon with the air just compensates the heat of formation of the water gas; the mixture of gases so obtained is called **producer gas.** The product contains much free nitrogen, but the simplicity of the process causes this artificial gas to find use on a large scale.

Since the fuel must be kept at about 1000° C. to secure complete reaction between the carbon and steam, and ensure low carbon dioxide content of the gas, the product leaving the generator carries very high sensible heat. In theory it is possible to recover this by using it to heat the air and steam supply, thus saving energy which must otherwise be furnished by burning more coal, but owing to the complications of the system, this heat recovery is not usually practised.

The use of steam in a producer to lower the temperature results in smaller loss of sensible heat in the gas, and theoretically should increase the efficiency of the gas producer. But in fact the gain is

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* Anthracite produces a higher content of hydrogen and methane than does coke, but the latter yields some methane, due to the action of hydrogen on the carbon at the high temperature. The gas also contains some nitrogen from the air blast and often a little oxygen due to leaks.

offset by the large heat loss due to undecomposed steam, which escapes reduction by the carbon, owing to the slow rate of reaction between steam and carbon; much heat is wasted in bringing this steam up to the temperature of the producer. Since lowering the temperature avoids clinkering of the ash and decreases the wear and tear on the apparatus, steam is, however, always used in excess.

In the **Siemens gas producer**[*] (Fig. 21), the coal is introduced at (E), falls upon the step grate (B, B), and is brought to incandescence by air entering through the openings while steam is injected from the pipe (C), and the gas formed escapes through (A, A). The ashes fall through the grate (G) into the pit, which is kept closed except when cleaning. A more modern producer (**Taylor's**) is shown in Fig. 22. The coal rests on a bed of ashes (A, A), and air is forced through the blast pipe (F), raising the fuel to incandescence. The gas formed passes out by the pipe (E). The grate (G) is made to revolve by the crank at (B), and the ashes fall over the edge of the grate at (H). The bed of ashes is kept about 3 feet deep on the revolving bottom. Steam from the pipe (D) is introduced with the air through the blast pipe, which is provided with a hood to disseminate them through the fuel. In all plants burning producer gas the regenerative or recuperative heating system is used.

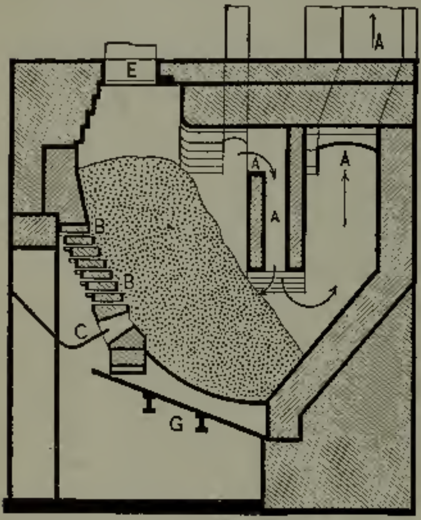

FIG. 21.

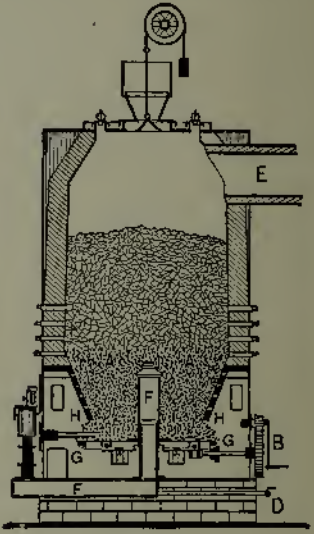

FIG. 22.

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[*] Jour. Soc. Chem. Industry, **1885**, 441.

Mond gas is producer gas made from coal slack and with a very large excess of steam in the blast. Much undecomposed steam passes out with the gas and the temperature in the producer is kept low (exit gas about 500°) so that the major reaction taking place is,

$$C + 2\ H_2O = CO_2 + 2\ H_2.$$

This avoids destruction of the ammonia content of the gas, which is higher than in water gas, and by scrubbing with water and sulphuric acid, ammonium sulphate is obtained as a by-product. The gas has, however, rather low calorific value (140 B. T. U. per cu. ft.) and because of its high hydrogen content is not well suited for open-hearth steel furnaces.

Blast furnace gas. — The waste gases from iron blast furnaces contain about 30 per cent of carbon monoxide and 58 to 60 per cent of nitrogen. About one-half of the gas is used for heating the air blast and the rest under boilers, or in large gas engines to generate power for driving the blowers and other purposes. The gas has to be carefully purified from dust before delivery to the gas engine.

The efficiency of the internal-combustion engine is much greater than that of the steam engine; thus the use of producer gas in gas engines is the most efficient method of converting the energy of coal into power. But this high energy efficiency is largely offset by the greater cost of installation and maintenance, and by lack of "overload" capacity of the engine. Thus with the exception of conditions of unusual constancy of load, or of very high cost of fuel, the steam plant is the cheapest method of developing power.

To secure high temperatures by gas combustion, preheating of both gas and air before they enter the combustion chamber is necessary. This avoids the cooling effect they otherwise exert, and is most economically done by recovering the waste sensible heat in the reaction products, by means of the **Siemens regenerative furnace,** which is shown in its simplest form in Fig. 23. The material to be heated is placed on the furnace hearth (A). Four passages (B, C, D, and E), filled with loosely piled fire-brick are called the "checker work." On their way to the chimney, the hot gases from the furnace pass through and heat two checker works, *e.g.* (B) and (C). When they are sufficiently heated, the flow of furnace gases is turned into (D) and (E), through which they pass to the chimney. Then fuel gas is conducted through the hot passage (B), to the furnace (A), where it mixes with air which has been heated by passing through (C). The temperature of (A) is thus much higher than if the air and gas arrived at (A) cold. While (B) and (C) are being thus cooled, (D) and (E) are heated by the waste gases, and after a time the dampers are turned, the gas made to pass through (E), and the air through (D), while the combustion products pass through (B) and (C) to the chimney. Hence the process is an alternating one, the checker works on one side being heated, while those on the other are giving up their heat to the gas and air respectively. The interstices between the bricks of the checker work often become clogged with ashes and soot.

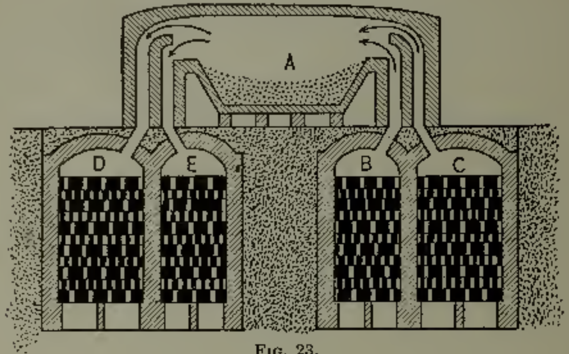

Fig. 23.

Recuperative heating involves the counter current flow of the hot combustion gases through or around flues, on the other side of which the cold gas and air pass to the furnace. This method has the disadvantage of low heat conductivity of the flue walls, but avoids all intermixture of the in-coming and out-going gases. The flow of the gases through the recuperator is continuous and there is no periodic changing of valves as in the other system.

An average composition of various fuel gases is as follows: —

	H_2	CH_4	C_2H_6	CO	CO_2	N_2	O_2
Natural gas (Ohio)* . .	2.3	92.6	0.3	0.5	0.3	3.5	0.3
Coal gas†	49.8	29.5	3.2	8.5	1.6	3.2	0.4
Water gas†	50.8	0.2	—	40.9	3.4	3.5	0.9
Producer gas (coal)† . .	10.4	6.3	—	17.6	7.3	58.1	0.7

When burned with 20 per cent excess of air, and assuming that the escaping gases have a temperature of 500° F., 1000 cubic feet

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* Gas and Fuel Analysis for Engineers, A. H. Gill.

† Industrial Chemistry, Rogers and Aubert, 2d ed., p. 404.

of gas will evaporate the following number of pounds of water, at from 60° F. to 212° F.: —

Natural gas	893 pounds *
Coal gas	591 pounds
Water gas	262 pounds
Producer gas	115 pounds

REFERENCES

Liquid Fuel. B. H. Thwaite, London, 1887. (Spon.)
Chemical Technology. Groves and Thorp. Vol. 1, Fuel, by Mills and Rowan, Phila., 1889. (Blakiston.)
Feuerungsanlagen. F. Fischer, Karlsruhe, 1889.
Liquid Fuel. E. A. B. Hodgetts, London, 1890. (Spon.)
Die Feuerung mit flüssigem Brennmaterialien. I. Lew, 1890.
Fuels. H. J. Phillips, London, 1891.
Fuels. C. W. Williams and D. K. Clark, London, 1891.
Die Chemie der Steinkohle. F. Muck, Leipzig, 1891. (W. Engelmann.)
Die Gasfeuerungen für metallurgische Zwecke. A. Ledebur, Leipzig, 1891.
Taschenbuch für Feuerung stechniker. F. Fischer, Stuttgart, 1893. (Enke.)
Contribution à l'étude des combustibles. P. Mahler, Paris, 1893.
Die chemische Technologie der Brennstoffe. F. Fischer, Braunschweig, 1896.
A Treatise on the Manufacture of Coke and the Saving of By-Products. John Fulton, Scranton, Pa., 1895.
Mineral Industry, **1896**, 215, W. H. Blauvelt. (By-Product Coke Ovens.)
Grundlagen der Koks-Chemie. Oscar Simmersbach, Berlin, 1895. (J. Springer.)
The Calorific Power of Fuels. Herman Poole, New York, 1898. (Wiley Sons.)
Gas and Fuel Analysis for Engineers. A. H. Gill, New York, 3d ed., 1902.
Modern Power Gas Producer Practice. H. Allen, 1908.
Kraftgas. Dr. F. Fischer, Leipzig, 1911. (Otto Spamer.)
Oil Fuel. S. H. North and Ed. Butler, 2d ed., London, 1911.

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* Orton, Geology of Ohio, Vol. VI, p. 544.

WATER

Water for industrial use is chiefly obtained from: —

1. Surface waters, consisting of,
   (*a*) Flowing waters (streams).
   (*b*) Still waters (ponds, lakes).
2. Ground waters, furnished by,
   (*a*) Springs.
   (*b*) Shallow wells (usually penetrating but one geological stratum).
   (*c*) Deep wells (passing through several geological strata).

Sea water, aside from some use for condensers and for supply to marine boilers, finds but little direct use. Rain water collected from clean roofs or other surfaces furnishes excellent soft water in limited amount, but little is so obtained industrially.

The impurities contained in water may be derived from the ground with which it has been in contact, or by contamination with sewage or factory wastes. In general the impurities in water constitute four classes: —

I. Dissolved gases, such as oxygen, carbon dioxide, hydrogen sulphide, etc.
II. Soluble crystalloids, consisting of definite chemical compounds which cannot be removed by sedimentation or filtration.
III. Soluble colloids, consisting of material of very high molecular weight which will not settle or separate, and can be filtered only through semi-permeable membranes.
IV. Suspended matter which will settle or can be filtered.

I. **Dissolved gases** may comprise two groups: (*a*), those whose solubility diminishes sufficiently with increase of temperature in the solution, and which may thus be removed by merely heating the water in open heaters, or in closed vessels with the aid of vacuum; (*b*) those requiring chemical treatment. Acid gases may be neutralized (with calcium hydroxide or sodium carbonate), resulting in precipitation, or not, according to individual circumstances. Oxygen may be removed by passing the water over metallic iron, which is readily oxidized to the ferric state and precipitated, owing to hydrolysis.

II. The **soluble crystalloids** include most of the impurities occurring in natural waters, and their removal generally involves precipitation by chemical treatment. The presence of these substances in greater or less amounts imparts to the water those properties which render it *hard, soft, saline,* or *alkaline.* Some of these substances may be partially or wholly removed by merely heating the water. Here two groups are distinguished: (*a*) those which evolve a gas at higher temperatures and form insoluble bodies; (*b*) those whose solubility decreases as the temperature increases in the solution; thus hydrated salts in solution lose water of hydration as the temperature rises and pass into less hydrated and less soluble forms.

The more common soluble crystalloids are the bicarbonates, sulphates, and chlorides of calcium and magnesium; sodium chloride, sulphate, and carbonate; iron salts; and silica. These are the substances which cause the most difficulty in technical work, and especially when the water is used in steam boilers.

Hard water contains salts of calcium, magnesium, or iron, and is defined as one which precipitates soap from solution. Thus hardness is determined by titration with a standard soap solution. *Temporary* hardness is due to the presence of *bicarbonates* of iron and the alkaline earth metals; the neutral carbonates are insoluble but dissolve in water containing free carbon dioxide, forming $CaH_2(CO_3)_2$, $MgH_2(CO_3)_2$, etc. *Permanent* hardness is due to the presence of soluble neutral sulphates and chlorides of calcium and magnesium.

Soft water usually contains very little mineral matter. Rain water as it falls is very soft, and if collected from clean surfaces is suitable for most purposes. Natural waters collected from ground containing little calcium or magnesium in soluble form is fairly soft as a rule; but if the water has percolated through soil containing peat or decaying vegetable matter, it is often discolored by dissolved organic matter, and may contain organic acids which cause corrosion of iron or other metals.

Saline and alkaline waters contain the sulphates, carbonates, or halogen salts of the alkali metals, in rather large amounts. Sea water and many ground waters (springs, wells) are characteristically saline (mineral waters). Alkaline waters are high in carbonates and sulphates; as, *e.g.* the "alkali" waters of the western states.

III. **Colloidal substances** have very large molecular weight, and are characterized by the tendency to *adsorb* or condense on the boundary surfaces of precipitated matter, if these surfaces are relatively large. Thus to remove colloidal matter from solution, a flocculent or finely divided amorphous precipitate may be produced in the water, which adsorbs the colloidal matter and attaches it to the precipitate. Crystalline precipitates have relatively small surfaces, and do not serve well for removing colloidal matter.

Colloidal substances in water form two groups: (*a*) Suspension colloids, consisting of small particles of suspended *solid matter*, which may be easily coagulated and precipitated by adding some electrolite. (*b*) Emulsion colloids consisting of minute particles of insoluble matter *probably liquid*, suspended in the water, *e.g.* emulsified oils, gelatine, gums, and certain hydrated compounds mostly of complex structure, such as some varieties of clays, tannic acids, humus bodies, etc. Emulsion colloids are usually difficult to coagulate, and only when much precipitating agent is added, can it be done. Thus if emulsion colloids predominate in a water, purification may be impracticable, owing to the large quantity of precipitant needed; but these colloids can often be *adsorbed* on the surfaces of suitable materials, such as alumina, iron hydroxide, charcoal or bone-char.

Some substances present in natural waters may impart to it corrosive properties, making its use objectionable for industrial purposes. Dissolved oxygen and carbon dioxide, hydrogen sulphide, free acids, either mineral or organic, and easily hydrolized salts, as $MgCl_2$ and $FeSO_4$, are very liable to cause corrosion or "pitting" in a boiler. Some of these may be derived from factory wastes, or from swamps and peat bogs, or from mine sumps and drainage from culm or refuse dumps.

The **purification of water** for industrial use consists in the partial or complete removal of the objectionable substances suspended or dissolved in it. This is often difficult, owing to the nature of the impurities; the size of the plant required for large works is also an item of concern. The quality of the water available should be considered in locating the works.

Water containing suspended matter only may be purified by sedimentation, followed by sand filtration; but this is often combined with chemical treatment, by which a precipitate is formed in the water. This precipitate acts *mechanically* to entangle the suspended matter; and it also acts as an *adsorption agent* on emulsion colloids, such as dissolved organic coloring matter, grease or oils, glutinous substances, and many kinds of factory wastes. Aeration by spraying into the air, or by trickling in thin films over large surfaces, accelerates the escape of carbon dioxide, or hydrogen sulphide, while absorption of oxygen aids precipitation of iron from solution. Bacteria and other organisms are frequently destroyed in sewage effluents, and in municipal supplies, by treatment with hypochlorites, ozone, or copper sulphate. Generally the raw water is mixed with some soluble salt, such as aluminum or ferrous sulphate, which is precipitated as aluminum or iron hydroxide by the action of the alkaline substances in the water, or added to it later. This gelatinous precipitate encloses suspended matter, and combines with soluble organic coloring matter by adsorption; by filtration on sand filters (p. 19) it is removed, carrying with it the impurities. But this increases the soluble impurity by the alkaline sulphates left in the water. Sulphuric acid and iron sulphate are removed from Allegheny River water for the Pittsburgh city supply, by adding calcium chloride.* The calcium sulphate precipitate aids in removing the suspended silt and coloring matter.

Water for boiler supply is generally treated to reduce the hardness or to neutralize its corrosive properties; the operation is called "softening." *Temporary* hardness is removed by some of the following methods: —

1. Boiling the water, usually in "feed-water heaters," to decompose the bicarbonates: —

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2.$$

Feed-water heaters are heated by exhaust steam, or waste flue-gases, and may be "open," when working under atmospheric pressure, or "closed" if under internal pressure (as economizers), or under vacuum. Open heaters permit the ready escape of dissolved gases and decomposition of bicarbonates, with precipitation of iron, calcium, and magnesium, but for *complete* separation of the alkaline earths, a small amount of sodium carbonate must be added to the water in the heater, to decompose any permanent hardness. Closed heaters working under pressure (economizers) afford less complete separation of hardness, since the gases cannot readily escape. In vacuum heaters the gases are removed, and the water is purified.

Heaters employing waste flue gases are known as "economizers," the water being heated in tubes set in the furnace flue. The conditions are essentially those prevailing in the boiler and the scale deposits inside of the tubes, which need to be frequently cleaned.

2. Treatment with calcium hydroxide ("milk of lime"): —

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + 2\ H_2O.$$

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* Hoffmann, J. Ind. Eng. Chem., VI (**1914**) p. 52.

The clear calcium hydroxide solution obtained by letting the undissolved lime settle is preferable for this, but frequently unsettled "milk of lime" is used. The required amount of quicklime is slaked in a little water, and the "milk" thoroughly mixed with the water to be purified. This is Clarke's process. The sludge of calcium carbonate is removed by settling in suitable tanks, or by a filter-press.

3. Treatment with sodium carbonate (soda-ash): —

$$CaH_2(CO_3)_2 + Na_2CO_3 = CaCO_3 + 2\ NaHCO_3.$$

The *permanent* hardness is less easily remedied, for in these cases treatment of the water leaves some substance more or less deleterious in solution: —

1. $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$
2. $CaSO_4 + Ba(OH)_2 = BaSO_4 + Ca(OH)_2.$
3. $CaCl_2 + Na_2C_2O_4 = 2\ NaCl + CaC_2O_4.$

Much care is necessary to avoid an excess of the chemical added.*

When natural water containing soluble impurities is used in a boiler, a more or less coherent deposit, called **boiler scale**, forms on the plates and tubes. This is chiefly composed of carbonate and sulphate of calcium; but in some cases magnesium hydroxide and sulphate, iron hydroxide or oxide, silica and organic matter, are present. The decomposition of bicarbonates of calcium and magnesium by heat, as above indicated, also takes place in the boiler. Calcium carbonate alone forms a porous, non-adherent scale or sludge, which is largely removed by "blowing off" or washing out the boiler. Calcium sulphate is rendered less soluble by the heat and pressure within the boiler, and is deposited as a hard, compact scale, adhering firmly to the plates and tubes. Magnesium sulphate, if present, is deposited as monohydrated salt ($MgSO_4 \cdot H_2O$), and is strongly adherent.

Scale formation is very detrimental; being a poor conductor of heat, the evaporative capacity of the boiler is reduced and much

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* Besides the methods given above, many other substances have been proposed, and are used to some extent, usually within the boiler itself, for water purification. Among these are sodium hydroxide, phosphate, aluminate, fluoride, oxalate, silicate, and bichromate; also barium hydroxide and aluminate. But in general these are too expensive for large works.

1. $MgH_2(CO_3)_2 + 2\ NaOH = MgCO_3 + Na_2CO_3 + 2\ H_2O.$
2. $CaH_2(CO_3)_2 + Na_2Cr_2O_7 = CaCrO_4 + Na_2CrO_4 + 2\ CO_2 + H_2O.$
3. $MgSO_4 + Na_2Cr_2O_7 = MgCrO_4 + Na_2SO_4 + CrO_3.$

J. Am. Chem. Soc. **1899**, 655. Eng. Min. Jour. LX, 220.

more fuel is consumed. The scale separates the water from the boiler plates and tubes, which thus are overheated and rapidly burn out. The tubes also become clogged and their efficiency is much impaired.

Magnesium chloride is especially troublesome, for it not only forms scale, but causes rapid corrosion of the iron, possibly thus: —

$$MgCl_2 + Fe + 2\,H_2O = Mg(OH)_2 + FeCl_2 + H_2.$$

Dissolved oxygen and carbon dioxide, and hydrogen sulphide, are strongly corroding, the latter probably because of oxidation to sulphuric acid. Manganese sulphide in the boiler plates assists depolarization of the hydrogen; it may also be oxidized and hydrolized to form sulphuric acid, and thus accelerate corrosion.

As a rule the water should be treated before it goes into the boiler, but if the scale-forming impurity does not exceed 170 parts per million, the purification may be done in the boiler itself, followed by a daily "blowing off." A good circulation of water in the boiler tends to keep the precipitated matter loose so it may be easily blown out.

In some cases scaling may be prevented by introducing colloidal substances into the boiler; possibly the particles of incrusting matter become coated with a thin film of the colloid by adsorption. Coalescence of the particles of the crystalloids is thus prevented and they form a loose sludge, or are kept in suspension in the water, until removed by "blowing off," or washing out the boiler. The use of kerosene, of tannins, and of other organic substances in the boiler is based upon this action.

Many proprietary "anti-scale" preparations are sold, some of which are of no particular value. These are generally intended for use inside of the boiler, and may act by direct precipitation of mineral matter, or by preventing adhesion to the boiler plates. They often contain soda-ash, caustic soda, sodium silicate or phosphate, barium hydroxide, tannins or vegetable extracts, or petroleum products.

Saline or alkaline waters, or those whose content of alkali sulphates and chlorides has been artificially raised by purification methods as above, may give trouble in steam boilers by causing "*priming*," *i.e.* the passage of water particles, mixed with the steam, from the boiler. Priming is associated with *foaming*, resulting from much dissolved matter, or due to finely divided suspended particles. When water contains a great number of suspended fine solid particles, each serves to release steam bubbles in its immediate vicinity, and this increases the space occupied by the water in the boiler, *i.e.* foaming is caused.* The presence of large amounts of alkaline chlorides and sulphates, along with much calcium or magnesium sulphate, may render a natural water useless for steam raising, since it will foam after chemical treatment. No satisfactory method of purifying such waters has yet been proposed. Frequent blowing off of the boiler is the only preventive of foaming. In locomotives foaming may occur when the dissolved salts amount to 1700 parts per million; but stationary boilers will permit four times as much.

Grading of natural water for steam raising is often difficult, owing to the local conditions in the region where the water is to be used. A water containing 250 parts per million would be considered poor in some parts of New England, but would rank as good in Dakota or Iowa. A classification proposed † for locomotive supply is shown below: —

	Incrusting or Corroding Constituents. Parts per Million.		Foaming Constituents. Parts per Million.	
	More than	Not more than	More than	Not more than
Good	—	90	70	150
Fair	90	200	150	250
Poor	200	430	—	—
Bad	430	680	250	400
Very bad	680	—	400	—

The character of the water available is very important in some manufacturing processes. Hard water is objectionable for laundries, bleacheries, and soap works, since the insoluble lime soaps are precipitated, causing loss of considerable soap, and injury to the goods, owing to the insoluble soaps adhering to them.

The permutite process ‡ for water softening is used somewhat in dye works and bleacheries. Permutite is an artificial zeolite (hydrated silicate of sodium and aluminum) made by fusing together feldspar, kaolin, and alkali carbonates, and lixiviating the pulverized mass with hot water. The composition is given as $2\ SiO_2 \cdot Al_2O_3 \cdot Na_2O \cdot 6\ H_2O$, and the substance is practically insoluble in water. Upon contact with water containing bicarbonates or sulphates of calcium or magnesium, or iron or manganese

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* Railroad Gazette, Oct. 12, 1900. C. H. Koyl.

† Proc. Am. Ry. Eng. and Maintenance of Way Assoc. V (1904), 595; IX (1908), 134.

‡ Textile World Record, Nov. 1912.

salts, an interchange takes place between the sodium of the permutite and the metal of the dissolved salts; thus:—

$$Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2 \cdot 6\,H_2O + CaH_2(CO_3)_2 = CaO \cdot Al_2O_3 \cdot 2\,SiO_2 \cdot 6\,H_2O + 2\,NaHCO_3.$$

$$Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2 \cdot 6\,H_2O + MgSO_4 = MgO \cdot Al_2O_3 \cdot 2\,SiO_2 \cdot 6\,H_2O + Na_2SO_4.$$

Thus by simple filtration through a layer of granular sodium permutite, a hard water can be softened. When the permutite becomes inactive through deposition of alkaline earth metal and removal of the sodium, the material can be regenerated *in situ*, by washing for 8 to 10 hours with a 10 per cent sodium chloride solution; thus:—

$$CaO \cdot Al_2O_3 \cdot 2\,SiO_2 \cdot 6\,H_2O + 2\,NaCl = Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2 \cdot 6\,H_2O + CaCl_2.$$

Hard waters may cause unevenness of color deposition in dyeing; they also lower the quantity of extract matter taken up from malt in brewing and distilleries. Iron in any form is very bad for dyeing, tanning, paper making, bleacheries, laundries, and for brewing; it causes dark color in the material. Moderate hardness due to sulphates is of advantage in paper making; for tanning sole leather, owing to its swelling effect on the hides, and for brewing pale beers, since it decreases the extraction of coloring matters and protein substances from the malt. Chlorides are injurious in nearly all cases where the water comes in direct contact with the material, as in foods, in the brewing and distilling industries, in sugar making, and in tanning.

Suspended matter, either of mineral or organic nature, and dissolved organic coloring substances, may cause discoloration, or spots in goods with which they come in contact: thus paper-mills, dyeworks, bleacheries, and starch factories require a perfectly clear and colorless water. The presence of organic dirt may cause decomposition or putrefactive changes in food products, in the fermentation industries, in starch and sugar making.

REFERENCES

Die Chemische Technologie des Wassers. F. Fischer, Braunschweig, 1880.
Die Verhutung und Beseitigung des Kesselsteins. W. Storck, Halle, 1881.
A Treatise on Steam Boiler Incrustations. C. T. Davis, Washington, 1884.
Water Supply. William R. Nichols, 1886.
Report on Boiler Waters of the C. B. & Q. R.R. W. L. Brown, Chicago, 1888.
Die Verunreinigung der Gewässer. K. W. Jurisch, Berlin, 1890.
Das Wasser. F. Fischer, Berlin, 1891. (J. Springer.)
Das Reinigen von Speisewasser für Dampfkessel. A. Rossel, Winterthur, 1891.

L'Eau dans l'Industrie. P. Guichard, Paris, 1894. (Bailliere.)
Report of the Filtration Commission of the City of Pittsburg, 1899.
American Machinist, **22** (1899). A. A. Cary. (Use of Boiler Compounds.)
L'Eau dans l'Industrie. De la Coux, Paris, 1900.
Boiler-Waters. Wm. W. Christie, New York, 1906. (Van Nostrand.)
Clean Water and How to Get It. Allen Hazen, New York, 1907.
Stream Pollution in Potomac River Basin. H. N. Parker. U. S. Geol. Survey, Water Supply Paper, No. 192 (**1907**).
Disinfection of Sewage and Sewage Filter Effluents. E. B. Phelps. U. S. Geol. Survey, Water Supply Paper, No. 229 (**1909**).
Proc. Western Railway Club, **1903**, 241.
Eng. Min. Jour. **1895**, 220. F. Wyatt. **1899**, 443. J. H. Parsons.
J. Soc. Chem. Ind. **1884**, 51. J. H. Porter. **1886**, 267. Macnab and Beckett. 416. A. Steiger. **1887**, 178. V. C. Driffield. **1888**, 795. A. H. Allen. **1891**, 511. Archbutt and Deeley.
Eng. News. **60** (**1908**), 355. H. Stabler.

SULPHUR

Most of the sulphur used in the industries is derived from the native mineral, which is found in many places, but usually in volcanic regions. It is always impure, being mixed with gypsum, aragonite, clay, or other matter, in the interstices of which the sulphur is deposited. The formation of sulphur beds may have occurred by the reaction of gases, such as hydrogen sulphide and sulphur dioxide, with each other or with oxygen; or by the decomposition of metallic sulphides through the agency of heat; or by the reduction of sulphates, especially of calcium sulphate, which has probably caused the formation of some stratified deposits.

The first is probably the most frequent mode of deposition, and may be observed at the present time in many volcanic districts where hydrogen sulphide and sulphur dioxide are escaping. The reactions are the following: —

$$SO_2 + 2\,H_2S = 2\,H_2O + 3\,S;$$
$$H_2S + O = H_2O + S;$$
$$H_2S + 3\,O = H_2O + SO_2.$$

The largest part of the world's supply of sulphur comes from Sicily, but some is obtained in Japan, Italy, Greece, and in the United States, particularly in Louisiana, in Wyoming, in Utah, and near Humboldt, Nevada. The Louisiana deposit is now yielding a sufficient supply for our domestic consumption and shipment abroad has been introduced.

In Sicily it is disseminated through the matrix, sometimes in considerable masses of nearly pure sulphur, but usually in fine seams or grains. The methods of obtaining it are very crude and wasteful. The mines are for the most part open pits, ranging from 200 to 500 feet in depth, and the ore is carried to the surface in baskets or sacks by laborers, who ascend by inclined paths on the walls of the pit. In some of the better mines, however, hoisting machinery is now used, but only after overcoming the determined opposition of the laborers. The ore is generally refined in a very simple manner, the process being carried on in kilns called "*calceroni.*" As usually constructed, these are shallow pits, about 30 feet in diameter, with walls about 10 feet high, made tight with mortar. They are generally built on a hill-side, and the sloping bottom is beaten smooth. The ore is arranged in the *calcerone* so as to leave a few vertical draught holes from top to bottom of the heap, which is fired by dropping burning brush or straw into these openings. The sulphur, forming from 25 to 40 per cent of the ore, burns freely, and when the heap is well on fire, the draught holes are closed, the *calcerone* covered with spent ore, and the whole left for several days. The heat given out by the burning of part of the sulphur is sufficient to melt the remainder from the gangue, and it collects in a pool near a tap-hole, made in the wall at the lowest point. At intervals of a few hours, the melted sulphur is drawn off into moulds. If the temperature rises above 180° C., there is a large formation of plastic sulphur, which will not flow from the tap-hole. To burn out a *calcerone* requires 35 to 80 days, depending on its size, the amount of gypsum in the ore, and the weather. From a quarter to a third of the sulphur is lost as sulphur dioxide, and as this damages vegetation, *calcerone* burning is prohibited during the spring and summer months.

Of recent years the Gill kiln, patterned after the Hoffmann furnace (p. 185), has been introduced. This uses part of the sulphur as fuel and consists of four to six chambers, the air for combustion entering that chamber where the melting has just been finished. The air thus warmed enters the second chamber, where combustion is at its highest point and the sulphur is melted out of the ore; the hot gases pass to the next chamber, filled with fresh ore, which is thus heated to the fusion point of the sulphur before combustion begins. The waste gases finally pass to the chimney. The yield of sulphur is considerably better than by the *calcerone* method.

Processes for extraction of the sulphur by means of carbon disulphide or other solvents have proved too expensive for industrial use. Extraction with superheated steam* yields an excellent quality of sulphur without formation of sulphur dioxide, and is used in this country and Japan to some extent.

In Wyoming, sulphur occurs as irregular deposits or pockets in limestone. The ore is broken to small size, loaded into steel cars having perforated sides, and run into a retort where steam at 60 lbs. pressure is admitted; the sulphur melts, flows to the bottom of the retort, leaving the gangue rock in the car.

By boiling the ore in a concentrated solution of calcium chloride † at 125° C., the sulphur can be melted from the gangue, with no formation of sulphur dioxide, and no nuisance is caused. This has been tried in Sicily, but is not in general use.

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* J. Soc. Chem. Ind. **1887**, 439, 442; **1889**, 696.

† Vincent, Bull. Soc. Chim. **40**, 528. Am. Chem. Jour. VI, 63.

In Louisiana, sulphur is obtained by the method devised by Hermann Frasch,* which has been very successful. Driven wells are sunk into the deposit, which lies at a depth of about 450 feet, and is about 100 feet thick. In each well are four concentric lines of pipe, ranging in diameter from 10 inches to 1 inch. Superheated *water* (165° to 170° C.) is forced down between the 10-inch and 6-inch pipes, and passing into the crevices of the sulphur-bearing rock, melts the sulphur, which runs into the sump at the foot of the well. Through the 1-inch pipe, compressed hot air is forced to the bottom of the well, where it mixes with the melted sulphur, forming an aerated mass, which the water and air pressure cause to rise through the 4-inch pipe, to the surface; the mixture of melted sulphur, hot water, and air is discharged into large open vats made of boards. The solidified sulphur goes direct to market without further refining, and is of better quality than that from Sicily, which it has practically displaced from the American market.

A small part of the sulphur of commerce is recovered sulphur, chiefly obtained from the calcium sulphide waste of the Leblanc soda process (p. 103 *et seq.*), and from the residues from the purification of illuminating gas by iron oxide (p. 321). The residues containing 50 to 60 per cent of free sulphur are heated in a retort and the sulphur distilled off. It seems improbable that recovered sulphur will ever become much of a factor in the market.

The sulphur obtained by the above described processes is generally pure enough for manufacturing and agricultural uses. But in a few industries, a refined sulphur is needed. This is produced by distillation from an iron retort, the vapors being condensed in brick chambers. If the temperature of the chamber is not above 110° C., the vapors condense at once to a fine powder, called "flowers of sulphur"; but if the temperature in the condensing chamber rises much above 110° C., the vapors condense to a liquid, which is drawn into moulds to form the "roll brimstone" of commerce.

The chief uses for crude sulphur are: for combating *Oidium tuckeri*, a fungus causing the vine disease (this disposes of a large part of the yearly production); for making sulphuric acid; for sulphurous acid and bisulphite solutions; for carbon disulphide; and for making ultramarine. Refined sulphur goes mainly for gunpowder, matches, and for vulcanizing rubber.

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* U. S. Pat. Nos. 461429, 461430, 461431. Mining World, **1907**, 1049. Eng. Min. J. **1907** (**84**), 1107. Mineral Resources of the United States, **1907**, (Pt. II), 674.

Sulphur melts at 115°–120° C., and has a specific gravity of 1.98–2.04; it is a poor conductor of heat and electricity, dissolves easily in carbon disulphide, and less readily in chloroform, benzol, turpentine, and other oils.

Sicily, owing to its favorable situation as a shipping point, the abundance of cheap labor, and its rich deposits, was long the dominating factor in the sulphur market. But recent competition with the American and Japanese production of sulphur has caused the closing of many of the mines, and those which have continued working have met with large losses. Only by greatly improving their methods of mining and refining the ore can the industry be restored to a satisfactory condition. At the present time the American sulphur industry in Louisiana is in a flourishing condition.

SULPHUR DERIVATIVES

Sulphur dioxide (SO_2) is the most important sulphur compound and is made on a large scale by roasting iron pyrites (p. 66) for the sulphuric acid manufacture: for producing smaller quantities of sulphur dioxide direct combustion of brimstone is customary. Brimstone burners may be simple brick ovens, or long iron retorts, in which the sulphur is ignited and a regulated supply of air admitted to ensure complete combustion. Too much heat in the retort may cause distillation of sulphur into the flues and other parts of the apparatus. Mechanical sulphur burners afford more uniform combustion and high concentration of the sulphur dioxide gas. A modern type is the **Wise sulphur burner** (Fig. 24), consisting of a cast-iron bowl (B), with an agitator (A) whose ploughs dip into the melted sulphur (C) in the bowl. Air enters by openings (D) in the wall just above the surface of the burning sulphur. In the annular trough (E) is placed brimstone, which is melted by the heat of the burner itself, and flows through the inlets (F) into the bowl, replacing that which is burned to sulphur dioxide. Above the sulphur pot is a combustion box (G), in which is a horizontal baffle plate with slots

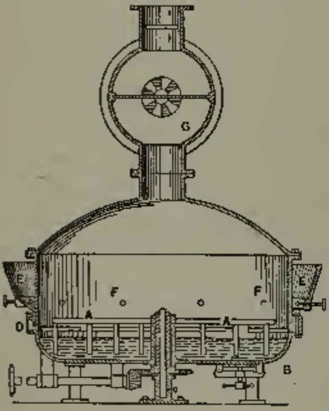


Fig. 24.

at each end. Opposite each slot is a damper in the end of the combustion box, to admit air for completing the combustion of any sulphur vapor. Thus sublimation of the sulphur is avoided and the sulphur dioxide concentration in the gas is high, 18 to 19 per cent by volume being claimed.

The **Tromblee-Paull burner** is a rotary, horizontal iron cylinder, 8 feet long and 3 feet in diameter, having conical ends; it makes one revolution in two minutes, and consumes about 5500 lbs. of sulphur per day. The sulphur, melted by the heat of the burner, flows into the cylinder, coating the interior of the shell in consequence of the rotation. Air entering through suitable dampers in one end of the cylinder burns the sulphur on the inner surface of the shell, and the gases pass into a combustion chamber to complete the burning of any volatilized sulphur.

Much sulphur dioxide is produced in the roasting and smelting of copper and lead ores (p. 594 *et seq.*) and recently attention has been given to the condensation of these fumes for the making of acid or other purposes, but chiefly with the object of abating the nuisance and damage they cause in the surrounding country.

Pure sulphur dioxide is made by dissolving the crude gas from sulphur burners in water by use of counter-current washing towers, and recovering it from the solution by heating. The gas is dried, compressed to liquid, and put on the market in steel cylinders.

Sulphur dioxide is used for making sulphuric acid; for the acid sulphite liquor used in making wood pulp; for preparing sodium bisulphite as a bleaching agent for wool, hair, straw, and other tissues; as a disinfectant and germicide; and in the liquid state in ice machines.

Substances such as wool and straw, when bleached by exposure to sulphur dioxide gas, slowly regain their original color on exposure to the light. The coloring matter is not destroyed, but probably unites with the sulphur dioxide to form a colorless compound, which slowly decomposes.

Sodium bisulphite ($NaHSO_3$) is formed by saturating sodium carbonate solution with sulphur dioxide: —

$$Na_2CO_3 + H_2O + 2\ SO_2 = 2\ NaHSO_3 + CO_2.$$

It forms a strong-smelling solution occasionally used as an "antichlor" to remove excess of chlorine from the fibres of bleached cotton or linen goods. Its reaction is probably as follows: —

$$\begin{aligned} Ca(ClO)_2 + 2\ NaHSO_3 &= 2\ NaCl + CaSO_4 + H_2SO_4;\ \text{or,} \\ &= Na_2SO_4 + CaSO_4 + 2\ HCl; \\ 2\ Cl + NaHSO_3 + H_2O &= NaCl + H_2SO_4 + HCl;\ \text{or,} \\ &= NaHSO_4 + 2\ HCl. \end{aligned}$$

It also finds some use in other industries, such as chrome tannage, brewing, glucose and starch making. The solution of bisulphite decomposes on evaporation, giving off part of the sulphur dioxide, and forming neutral sulphite of sodium.

Calcium bisulphite [$CaH_2(SO_3)_2$] is made by passing sulphur dioxide into milk of lime. It is probably a solution of neutral sulphite in an excess of aqueous sulphurous acid. It is used in much the same way as the sodium salt.

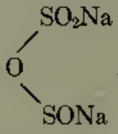
Hydrosulphurous acid ($H_2S_2O_4$) and **sodium hydrosulphite** are important bleaching and reducing agents. The acid results from the action of iron or zinc on aqueous sulphurous acid: —

$$2\ H_2SO_3 + Zn = ZnO + H_2S_2O_4 + H_2O.$$

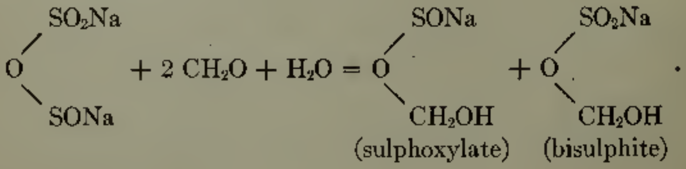
The zinc oxide unites with another molecule of sulphurous acid, forming zinc sulphite.

Sodium hydrosulphite ($Na_2S_2O_4$)* is made by dissolving zinc in sodium bisulphite: —

$$4\ NaHSO_3 + Zn = Na_2Zn(SO_3)_2 + Na_2S_2O_4 + 2\ H_2O.$$

The zinc-sodium sulphite is precipitated with milk of lime, and the hydrosulphite is left as a solution, which is very unstable, rapidly absorbing oxygen from the air. The hydrosulphite can be precipitated from the solution by adding salt, and cooling the liquid, when crystals of $Na_2S_2O_4 \cdot 2\ H_2O$ separate. By treatment with hot alcohol, the water of crystallization is removed, and the anhydrous powder is fairly stable if kept dry; its formula is  $O\begin{cases}SO_2Na\\SONa\end{cases}$. It can also be made by treating metallic sodium with sulphur dioxide (gas or liquid) in the presence of petroleum ether.

Hydrosulphite combines with formaldehyde, producing a stable mixture of formaldehyde compounds of sodium sulphoxylate, and sodium bisulphite: —



$$O\begin{cases}SO_2Na\\SONa\end{cases} + 2\ CH_2O + H_2O = \underset{\text{(sulphoxylate)}}{O\begin{cases}SONa\\CH_2OH\end{cases}} + \underset{\text{(bisulphite)}}{O\begin{cases}SO_2Na\\CH_2OH\end{cases}}.$$

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* Bernthsen, Ber. **13**, 2277; **14**, 438; **33**, 126.

This mixture is much used under various trade names, *hydrosulphite* NF, *rongalite* C, *hyraldite, decroline, blanchite,* etc., as reducing, bleaching, and discharge agents in textile industries. By treatment with zinc dust, the bisulphite-formaldehyde is converted into the sulphoxylate-formaldehyde ($NaHSO_2 \cdot CH_2O \cdot 2\ H_2O$), which is sold as *hydrosulphite* NF, *conc.*; *hyraldite* C, *extra,* etc.

Sodium thiosulphate ($Na_2S_2O_3 \cdot 5\ H_2O$), sold under the trade name "*hyposulphite of soda,*" is made by digesting sulphur with a solution of neutral sodium sulphite, or sodium hydroxide: —

$$Na_2SO_3 + S = Na_2S_2O_3.$$

$$6\ NaOH + 12\ S = Na_2S_2O_3 + 2\ Na_2S_5 + 3\ H_2O.$$

It is also obtained from the waste sulphide liquors of the Leblanc soda process (p. 104). It is largely used in chrome tannage, in photography, in wet silver-extraction processes, as antichlor in paper bleaching (p. 562), in textile dyeing and printing, for bleaching straw, wool, ivory, etc., and in iodometry.

SULPHURIC ACID

Sulphuric acid is probably the most important of all chemicals, because of its extensive use in a very large number of manufacturing operations. Of the immense quantities made yearly, the greater part does not come upon the market; for, being expensive and difficult to ship, consumers of large amounts generally make their own acid.

The commercial grades of acid have special names. A moderately strong acid (50°–55° Bé.), such as condenses in the lead chambers, is known as "*chamber acid.*" It contains from 62 to 70 per cent of H_2SO_4, and is strong enough for use in the manufacture of fertilizer, and for other purposes requiring a dilute acid. By concentrating this chamber acid, an acid of 60° Bé. is obtained, containing about 78 per cent of H_2SO_4, which is sufficiently strong for most technical uses. Further evaporation in platinum or iron pans yields an acid of 66° Bé., containing 93.5 per cent of H_2SO_4, and known as *oil of vitriol,* while the strongest acid that can be made by direct evaporation contains about 98.5 per cent of H_2SO_4, and is called *monohydrate. Fuming* or *Nordhausen* acid, which is still more concentrated, is prepared by special means, and it is essentially a solution of sulphuric anhydride (SO_3) in sulphuric acid; this is the acid which was prepared by the alchemists in the Middle Ages.

In about the year 1740, Ward, an Englishman, began to make sulphuric acid on a moderately large scale. He burned sulphur and nitre (KNO_3) together, and condensed the vapors in glass vessels containing a little water. The dilute acid so formed was then concentrated in glass alembics or retorts. In this way an acid was produced at a lower price than the fuming acid could be made, and the industry was soon established on a commercial scale.

Sulphuric acid is now made by two important methods: the old chamber process yielding dilute chamber acid (p. 74) directly, and the newer contact processes yielding sulphuric anhydride (SO_3) as first product, from which any desired strength of sulphuric acid may be made by dissolving in weak acid or water. For producing concentrated acid the contact method has proved generally more economical, and is slowly displacing the old chamber process with its concentrating plant. But for acid of 50°–60° Bé., the advantage is not so decidedly in favor of the newer method. It is probable that the lead chamber will not be entirely given up for many years to come.

The reactions involved in Ward's process are those of the present chamber process for sulphuric acid. This consists in bringing together, under suitable conditions, sulphur dioxide, oxygen, and water vapor, in the presence of certain oxides of nitrogen. The latter probably act catalytically, causing the oxygen to unite with the sulphur dioxide and water to form acid. The apparent reaction is: —

$$SO_2 + H_2O + O = H_2SO_4.$$

But this does not represent the actual process, which is more complicated than it at first appears. Several theories have been advanced to explain the reactions occurring in the lead chambers, and the part taken by the nitrogen oxides, but the most generally accepted one, that of Lunge, regards nitrous anhydride (N_2O_3)* as the essential factor.† According to this view, the principal reactions involved are as follows: —

1) $2\ SO_2 + N_2O_3 + O_2 + H_2O = 2\ SO_2 \cdot (OH) \cdot (ONO)$ (Nitrosylsulphuric acid);

2) $2\ SO_2 \cdot (OH) \cdot (ONO) + H_2O = 2\ SO_2(OH)_2 + N_2O_3$; or,

3) $2\ SO_2(OH)(ONO) + SO_2 + O + 2\ H_2O = 3\ SO_2(OH)_2 + N_2O_3$.

First there is a union of sulphur dioxide, nitrous anhydride, oxygen, and water, to form nitrosylsulphuric acid, which probably separates as part of the mist or fog seen in the lead chambers. But in the presence of water vapor or of dilute sulphuric acid, this nitrosylsulphuric acid is at once decomposed, according to reaction (2), sulphuric acid being formed, and nitrous anhydride regenerated; or if sulphur dioxide and oxygen are concerned in the process, then reaction (3) occurs. This cycle of reactions repeats an indefinite number of times. But in the first lead chamber, where the temperature is rather high and an excess of water vapor is usually present, the following secondary reactions probably occur to a greater or less extent: —

4) $2\ SO_2 \cdot (OH) \cdot (ONO) + SO_2 + 2\ H_2O = 3\ H_2SO_4 + 2\ NO$,

this reaction being only momentary.

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* Ramsey and Cundall (J. Chem. Soc., **1885**, 672) maintain that N_2O_3 exists only as a *liquid*, and on heating, it decomposes into NO and NO_2; accepting this view, N_2O_3, as such, cannot be present in the lead chambers, where the temperature is over 60° C.

† Hurter (J. Soc. Chem. Ind., **1882**, 49 and 83) supports the theory that nitrogen peroxide (NO_2) plays an important part in the process.

Since there is usually an excess of oxygen present, however, the nitric oxide here formed is at once brought into action again, thus: —

5) $2\ SO_2 + 2\ NO + 3\ O + H_2O = 2\ SO_2 \cdot (OH) \cdot (ONO)$.

If there is a deficiency of oxygen, the nitric oxide is not returned to the process, but passes through the several chambers and, since it is not absorbed by the concentrated acid in the Gay-Lussac tower, it escapes into the atmosphere and is lost.

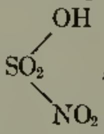
The nitrogen oxides are derived from nitric acid, or by the action of sulphuric acid on sodium nitrate in the nitre pots. When nitric acid is used, it must be introduced in the form of vapor, or at least as a very fine spray, whereupon it reacts as follows: —

6) $2\ SO_2 + 2\ HNO_3 + H_2O = 2\ H_2SO_4 + N_2O_3$.

Perhaps this reaction really occurs in two stages, thus: —

(*a*) $SO_2 + HNO_3 = SO_2 \cdot (OH) \cdot (ONO)$;

(*b*) $2\ SO_2 \cdot (OH) \cdot (ONO) + H_2O = 2\ H_2SO_4 + N_2O_3$.

The formula assigned to the nitrosylsulphuric acid may perhaps be written  $SO_2 \begin{matrix} \diagup OH \\ \diagdown NO_2 \end{matrix}$, and the compound would then be called nitrosulphonic acid. But in either case the existence of the substance is only transitory, it being broken up at once by the steam and sulphur dioxide present when the process is working properly. In case there is a deficiency of water vapor in the chambers, and especially if the temperature falls too low, the nitrosylsulphuric acid may separate as crystals, which deposit at various points on the walls, forming "*chamber crystals.*" This is an undesirable accident, for when steam or water come in contact with them, they decompose into sulphuric acid, nitric oxide, and nitrogen peroxide (N_2O_4): —

$$4\ SO_2 \cdot (OH) \cdot (ONO) + 2\ H_2O = 4\ H_2SO_4 + N_2O_4 + 2\ NO.$$

Then the nitrogen peroxide unites with some of the water,

$$N_2O_4 + H_2O = HNO_2 + HNO_3,$$

forming nitrous and nitric acids directly on the walls, corroding the lead at the point where the cluster of crystals was attached. To prevent this separation of "chamber crystals" or retention of nitrogen oxides in the sulphuric acid an excess of steam in the lead chambers is often preferred, although it dilutes the acid somewhat.

Raschig,* after an extended study of the process, maintains that nitrous acid (HNO_2) is present dissolved in the mist of sulphuric acid droplets filling the chamber. In the presence of air, water, and excess sulphuric acid, the sulphur dioxide and nitrous acid combine to form nitrosisulphonic acid, $HO \cdot SO_2 \cdot NOHO$; this then decomposes into sulphuric acid and nitric oxide. Finally the nitric oxide, reacting with water and air, is oxidized to nitrous acid. The cycle of reactions thus becomes continuous, regenerating nitrous acid to react with new portions of sulphur dioxide, as follows: —

1) $2\ HNO_2 + SO_2 = H_2NSO_5 + NO.$
2) $H_2NSO_5 = H_2SO_4 + NO.$
3) $2\ NO + H_2O + O = 2\ HNO_2.$

If, from any cause, the proportion of nitrous acid present falls below the quantity required by reaction (1), there is probably formed some nitrososulphonic acid, thus: —

4) $HNO_2 + SO_2 = ONSO_3H$ or $(NO \cdot SO_2 \cdot OH).$

This may be one of the regular cycle of reactions of the process, but if an excess of nitrous acid is present, the nitrososulphonic acid passes over at once to nitrosisulphonic acid: —

5) $HNO_2 + ONSO_3H = H_2NSO_5 + NO.$

But with an excess of water vapor present, the nitrososulphonic acid is hydrolized to form sulphuric acid and nitrous oxide: —

6) $2\ (ONSO_3H) + H_2O = 2\ H_2SO_4 + N_2O.$

Since nitrous oxide is not absorbed in the Gay Lussac tower,† there is here a possible cause of the steady loss of nitrogen oxides (nitre) observed in every chamber system.

The occasional formation of chamber crystals when water is deficient in the chambers is due to the formation of nitrosulphonic acid ($HO . SO_2 . NO_2$), by the oxidation of nitrosisulphonic acid by the nitric acid produced through reaction between excess oxygen and nitric oxide present in the chamber gases, thus: —

$2\ NO + 2\ O = N_2O_4.$
$N_2O_4 + H_2O = HNO_2 + HNO_3.$
$H_2NSO_5 + HNO_3 + HNO_2 = HNSO_5 + H_2O + HNO_2 + NO_2.$

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* Zeitschr. angew. Chem., **1905**, 1301; **1907**, 701.

† J. Soc. Chem. Ind., **1906**, 149.

The manufacture of chamber acid is shown in the diagram in Fig. 25.

The acid may be made from brimstone, pyrites, blende, hydrogen sulphide, or the sulphur dioxide produced in metallurgical processes. Crude **sulphur** gives a pure acid free from arsenic, iron, copper, or zinc, and much smaller condensing chambers may be used for a given yield than when pyrites or blende is employed. Various types of brimstone burners are in use (see p. 58).

Pyrites, or natural disulphide of iron (FeS_2), is a dense, hard mineral of crystalline structure and pale yellow color. Large deposits in the United States are in Virginia, at Mineral City, and at Charlemont in Massachusetts. Of the foreign deposits, those in Spain* are the most important. A pure pyrites contains 53.3 per cent of sulphur, but that commonly used for acid making carries from 43 to 48 per cent. It seldom pays to use an ore with less than 35 per cent of sulphur, for it will not support its own combustion.

The first proposal to use pyrites originated with an Englishman named Hill, who took out a patent for the process in 1818. But it was not until 1838, when the Sicilian government sold the monopoly of the sulphur export to a French firm which nearly trebled the price of crude brimstone, that pyrites began to find favor with acid makers. At the present time, because it is cheap and easily obtained, pyrites has almost completely replaced sulphur for acid making. The product from pyrites is usually contaminated with arsenic, and often with zinc, copper, and selenium.

By the oxidation of pyrites in a suitable furnace, the sulphur is converted to dioxide, and iron oxide remains. The reaction may be written as follows: —

$$2\ FeS_2 + 11\ O = 4\ SO_2 + Fe_2O_3.$$

This is not exact, however, as some sulphur remains in the ore and some sulphur trioxide is formed. The proper regulation of the pyrites burners is one of the problems of the manufacturer. If the ore contains over 35 per cent of sulphur, the burning, once started, generates sufficient heat to maintain the combustion, and no fuel is necessary. But zinc sulphide and the "mattes" from metallurgical processes must be heated by fuel.

The complete burning of pyrites is difficult. With lump ore there is apt to be a kernel in the centre of the lump, from which

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* Spanish pyrites containing copper is much used in England and to some extent in this country, the burned cinder being afterwards treated to recover the copper.

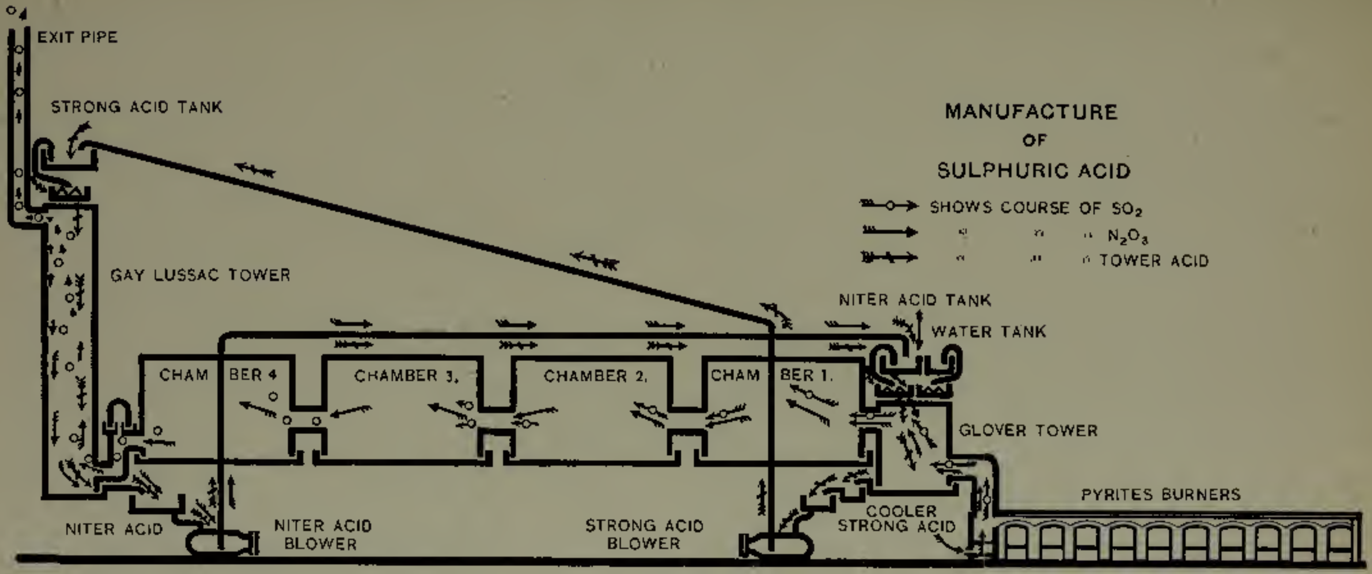
MANUFACTURE
OF
SULPHURIC ACID
SHOWS COURSE OF SO_2
" " " N_2O_3
" " " TOWER ACID
EXIT PIPE
STRONG ACID TANK
GAY LUSSAC TOWER
NITER ACID TANK
WATER TANK
CHAM BER 4
CHAMBER 3.
CHAMBER 2.
CHAM BER 1.
GLOVER TOWER
PYRITES BURNERS
NITER ACID
NITER ACID BLOWER
STRONG ACID BLOWER
COOLER STRONG ACID

Fig. 25.

the sulphur is not burned out. If the temperature rises too high, the charge fuses together, forming clinkers or "scar," and choking the furnace. If too much air is admitted, the furnace cools below the temperature at which fresh pyrites will ignite, and the gases leaving the burner are so diluted that the desired reactions do not take place in the lead chambers. With "smalls" the tendency to fuse is more marked than with lump ore, and the fine ore packs together so densely that the air will not penetrate it, and unless it is constantly stirred only the surface is burned. (The lump ore is that which has been broken to about the size of a goose egg, the "smalls" constituting what will pass through a half-inch screen.)

Pyrites burners are usually built in benches containing from three to thirty furnaces, in order that the supply of gas may not be broken while charging or cleaning one furnace.

A burner for lump ore (Fig. 26) consists of a brick furnace, containing a grate formed of single loose iron bars (B, B) having a square section, and resting in grooves at each end. These bars may be turned parallel with their longitudinal axes, but have no lateral motion. They are so adjusted that their sides are at an angle of 45° to the vertical. After a charge is burned, the bars are given several quarter turns by means of a key, to allow the cinders on them to drop through into the ash pit. Air is admitted by dampers beneath the grate. When properly working, the cinders resting on the bars are nearly cold, the hottest part of the fire being eighteen inches above the grate. The furnaces are lined with fire-brick, and to prevent any access of air except through the dampers, the doors (D, K) for charging, cleaning, raking, etc., are made to fit closely, and are generally luted with clay.

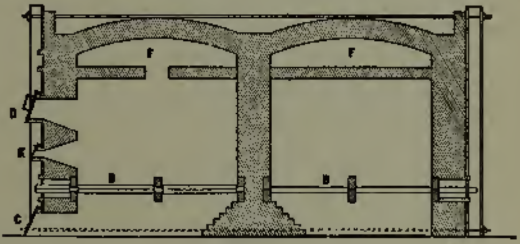

Fig. 26.

All the burners in one bench deliver their sulphur dioxide gas into a common, wide flue, or "dust box" (F), where any fine dust carried along by the gases may settle before they enter the Glover tower. This dust consists of unburned pyrites, arsenic, antimony or zinc oxides, iron oxide, etc.

In one or more of the burners a cast-iron "**nitre pot**" may be set, in which nitrous gases are generated by the action of sulphuric acid on sodium nitrate. Or the pots may be placed in a small chamber built into the flue (F), and heated by the waste heat of the burners. Sometimes, however, the pots are placed in separate furnaces.

A lump burner of average size has a grate area of 15 to 25 square feet. The furnace is sometimes made slightly hopper-shaped inside, so that it is larger at the level of the charging doors than at the grate bars. About 40 pounds of pyrites, containing 48 per cent of sulphur, are burned per square foot of grate area in 24 hours, a larger quantity of such high-grade ore being liable to cause fusion, unless great care is exercised. A larger quantity of poorer ore may be burned daily, without danger of fusion.

A number of burners for fines have been invented, of which the Maletra burner (Fig. 27) is an early type. It consists of a series of shelves, about 5 by 8 feet in size, arranged in a tall furnace. The smalls, introduced through a hopper, fall on the top shelf and are spread out by rakes, introduced at the door (A); they can be dropped through an opening (B), upon the next shelf, to be again spread in a thin layer, and so on, each shelf being hotter than the preceding. The spent cinders are taken out at (C). In starting the furnace, the shelves are heated by burning brimstone or fuel, until the walls are hot enough to ignite the pyrites, which by their combustion evolve heat enough to continue the burning, as long as the furnace is properly regulated, and fresh ore supplied as needed.

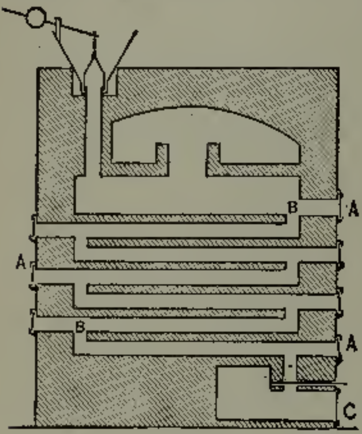

FIG. 27.

In Spence's furnace, fines are put into long muffles, externally heated by waste heat from lump burners, or by generator gas, or a fire; this furnace is used for roasting zinc blende, copper mattes, or concentrates, in which the sulphur is too low to burn, without external heat; the sulphur dioxide gas is fairly concentrated.

Raking shelf burners by hand is heavy labor and permits the entrance of undue amounts of air; mechanical raking obviates this largely, and several appliances are in use.

The **Herreshoff burner** * for fines has been largely introduced.

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* This burner is a modified form of the McDougall furnace (see p. 552). Mineral Industry, Vol. VI, 236; XII, 267. J. Soc. Chem. Ind., **1899**, 459.

It is a steel cylinder about 11 feet in diameter, 9 to 10 feet high, and raised 3 feet from the ground on iron posts. It is lined with fire-brick and contains five slightly arched shelves, the top one having holes at the outer edge; the next has a central opening; the third at the outer edge, and so on. The cinders are discharged at the outer edge of the lowest shelf. A hollow cast-iron shaft, 14 inches in diameter, passing through the centre of the furnace, contains sockets into which the cast-iron rakes for moving the ore are fitted and locked by a simple lip catching in a notch. The shaft is steadied by a side bearing at the top of the furnace and is turned by a gear beneath the furnace bottom. From the upper end of the shaft a pipe extends into the open air; at the bottom of the shaft, cold air is drawn in, and passing up through it and out by the pipe at the top, keeps the iron from becoming heated sufficiently for the sulphurous gases to act on the metal. As the shaft is rotated continuously, the rakes scrape the fines down from shelf to shelf, fresh ore being fed in, to maintain the combustion. Air for burning the pyrites is admitted through dampers near the bottom of the furnace, and the hot gases pass under and over each shelf as they ascend to the outlet at the top. The rakes may be easily replaced when broken, with only a few minutes' delay (compare Fig. 125, p. 597).

The **Wedge furnace** (Fig. 28) is a recent development of the mechanical burner. It is much larger than the previously mentioned and has five to seven shelves. A steel central shaft, four or five feet in diameter and protected from the action of the hot gases by a fire-brick covering, carries the stirring arms set in cast-iron holders riveted to the shaft. This shaft is supported on, and rotated by a large gear about 12 feet in diameter, which runs on heavy rollers beneath the furnace, and is driven by a pinion and pulley. The hollow cast-iron arms are divided by a partition, which causes the cooling water or air to circulate through them, thus giving some control of the temperature on the separate hearths. Special shaped fire-brick are used in the shelves, which are flat on top, so the ploughs scrape the hearths clean. The top arch is used to dry the

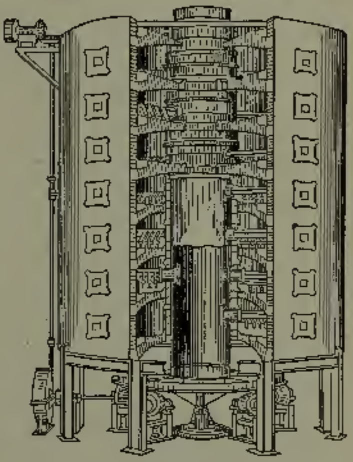
Fig. 28.

material, which is then delivered at the centre on to a cast-iron feed plate, so arranged that the ore forms an air-tight lute, preventing any escape of sulphurous gases. The large size of the central shaft permits of workmen entering same to make repairs, without cooling down the furnace. These furnaces are built in several styles, some with muffle hearths, for desulphurizing, chloridizing, sulphatizing, etc. (see p. 594).

The **Glover tower**, used in nearly all sulphuric acid works, is placed next to the burners. Its functions are to set free the nitrogen oxides from the Gay-Lussac tower acid; to cool the burner gases to 50° or 60° C. before they enter the lead chambers; to furnish part of the steam needed in the lead chambers; and in many works to concentrate the dilute acid from the lead chambers to a specific gravity of 1.75. It also increases the yield of acid from a plant of given lead chamber capacity, for, in addition to that condensed in the chambers, some acid is formed in the tower itself. The tower (20 to 30 feet high and about 10 feet across) is made of sheet lead, joined as described below, and supported on a framework of timbers or steel. It is lined with acid-resisting brick or segments of Volvic lava,* laid without mortar, and is filled with quartz lumps, flint stones, or vitrified brick. At the top is an apparatus for distributing the acid, which is to run through the tower.† The burner gases enter at the bottom, and pass out at the top, by a pipe leading to the **lead chambers**. These form the most important part of a sulphuric acid plant, since in them the reactions involved in the formation of the acid take place. They are immense boxes, made by joining sheets of lead, and are supported from a strong timber or steel framework, by means of lugs or strips of lead attached to the outside of the sheets. The joints cannot be made with solder, but the edges of the sheets are fused together by means of an aero-hydrogen flame, and the process, called "lead burning," is both difficult and slow. Steam or atomized water is introduced into the chambers to supply water vapor as needed. Each chamber is suspended above a large lead pan in such a way that the acid collecting in the pan forms a hydraulic seal for the lower edge of the lead chamber. These pans are 6 or 8 inches wider than the chamber, and have sides from 14 to 24 inches high. There is much difference of opinion as to the best size and number of the lead chambers.‡ There are usually from 3 to 5, with a capacity of 140,000 to

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* An acid- and heat-resisting rock, found in the Puy de Dôme, France.

† The working of the Glover tower is described in connection with the Gay-Lussac tower.

‡ The so-called "tangential" chambers of Meyer consist of large cylindrical lead chambers, the inlet pipes placed tangentially on the sides and the outlet leading

200,000 cubic feet in the system.* As a rule, the first chamber is the largest, and in it the greater part of the acid is formed. The individual chambers vary from 10,000 to 80,000 cubic feet (100 by 40 by 20 feet). In this climate they are enclosed in a building to avoid changes of temperature, which should not vary much from 50° to 65° C. in the first chamber, and 15° above that of the outside air in the last; † and they are usually elevated, so that the acid may flow from them by gravity to the evaporating pans often placed on top of the pyrites burners; and also that the bottoms may be better watched for leaks. To observe the working of each chamber, small lead dishes are fixed at various points on the inside of the chamber wall, and from these, pipes called "drips" lead to test glasses outside, where the density of the acid may be taken. A better method is to place the dish inside the chamber at a distance from the wall, supporting it above the level of the condensed acid, and connecting it by means of a pipe with a test glass outside. Glass panes are sometimes set at opposite points in the chamber walls, so that the color of the gases may be observed. In the first chamber the color is white and opaque, owing to the copious condensation of acid vapor, but in the succeeding chambers the color becomes more and more reddish, owing to the excess of nitrogen oxides. If the color becomes pale in the last chamber, there may be a deficiency of nitrous gases; or too much or too little steam ‡; or the draught may not be properly regulated, causing too much or too little oxygen to enter the chamber. The usual remedy is to introduce more nitre and then to locate the difficulty and gradually bring the system to its normal working condition.

From the last lead chamber the gases pass to the **Gay-Lussac tower,** whose purpose is to recover the oxides of nitrogen. Sometimes

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from the centre of the bottom and becoming the inlet to the next; thus the gases have a spiral movement which insures intimate mixing.

Eng. Pat. No. 18376, **1898**. Zeitschr. angew. Chem., **1899**, 656: **1900**, 739.

* The usual American practice is to allow 16 to 22 cubic feet of chamber capacity per each pound of sulphur burned per 24 hours. In English practice for each pound of sulphur burned per day, from 22 to 29 cubic feet of chamber capacity is provided.

† Attempts have been made to operate at higher chamber temperatures, since a larger yield per unit of volume of chamber space is obtained, but these methods have generally failed, doubtless on account of the increased corrosion of the lead. Since a large excess of sulphur dioxide is present in the first chamber, the reduction of the nitrogen oxides is practically instantaneous and the corrosion is correspondingly low. Thus the maintenance of higher temperature there is feasible though not in the later chambers where the sulphur dioxide is nearly gone.

‡ The steam is derived from a boiler, or from the evaporation of water from the diluted tower acid in the Glover tower.

two towers are used, the gases passing up through one and then to the bottom of the other, and up through this to the chimney. The tower is usually about 50 feet high, and 8 to 15 feet across. It is built of lead, supported on a frame, in much the same way as the Glover. It is lined with a double row of vitrified brick placed next to the lead walls, and inside of this is hard coke, or pottery rings, plates, saucers, or balls. At the top is a distributing apparatus to spread the acid evenly over the coke. The acid which flows down the Gay-Lussac tower is that which has been concentrated in the Glover tower to a density of from 60° to 62° Bé. (about 1.750 sp. gr.). Acid of this strength absorbs the nitrous anhydride (N_2O_3) and the nitrogen tetroxide (NO_2 or N_2O_4), but does not absorb nitric oxide (NO) or nitrous oxide (N_2O). With normal working of the process, only that part of the nitrogen oxides is lost which is reduced to nitrous and nitric oxide. When an excess of oxygen is present, some of the nitric oxide is converted to nitrous anhydride, and thus saved. These nitrogen oxides are only absorbed when strong acid is run through the Gay-Lussac tower; if the acid is of less than 1.50 sp. gr., it will not absorb them; for best results it should be 1.75 sp. gr. The solution of nitrous gases in sulphuric acid, known in the works as "nitrous vitriol," is run into the Glover tower, where it is diluted with water, or chamber acid, till its specific gravity is about 1.6. As it passes down the tower, coming in contact with the hot sulphur dioxide from the burners and steam from the lower part of the tower, the high temperature causes the dilute acid to give out its absorbed nitrous gases, which mix with the sulphur dioxide and pass back into the lead chambers. This process is called denitration of the tower acid. The heat in the lower part of the Glover tower evaporates a considerable portion of the water from the acid, thus concentrating it again to a strength sufficient for use in the Gay-Lussac, to which the required amount is returned, and the remainder is added to the acid which has been concentrated in the lead pans (p. 74). The hot burner gases are cooled by contact with the tower acid in the Glover tower to between 50° and 60° C., the best temperature to work the first chamber.

If the nitrogen oxides go to waste entirely, about 11 to 13 kilos of sodium nitrate must be used with each 100 kilos of sulphur burned. The recovery by means of the Glover and Gay-Lussac towers reduces the nitrate consumption to 4 kilos or less, per 100 kilos of sulphur, while a larger quantity of nitrous oxides is introduced into the chambers, causing the acid to form more rapidly and in greater quantities.

Some manufacturers supply the nitrogen oxides in the form of liquid nitric acid, introduced into the chambers. This is easily regulated, admits no excess of air, and causes no loss of sulphur dioxide, such as may happen during the introduction of the "nitre." But care must be taken that the nitric acid does not run down the chamber sides, nor collect in the acid on the floor, for then the lead is rapidly corroded. Frequently the nitric acid is introduced into the Glover tower with the tower acid. The cost of the liquid nitric acid must be balanced against the advantages gained by its use.

When sodium nitrate is decomposed by sulphuric acid in the nitre pots, the nitric acid vapor enters the bottom of the Glover tower with the sulphur dioxide. The vapors here coming in contact with steam begin to react at once, probably as follows: —

$$2\ SO_2 + 2\ HNO_3 + H_2O = 2\ H_2SO_4 + N_2O_3;$$

or,

$$3\ SO_2 + 2\ HNO_3 + 2\ H_2O = 3\ H_2SO_4 + 2\ NO.$$

Thus the process of acid making begins in the Glover tower, and continues in the chambers according to the reactions given on p. 63.

Sufficient sulphuric acid is used to form the acid sodium sulphate ($NaHSO_4$). This is liquid at the temperature prevailing and after the reaction is ended is easily run out through a tap in the bottom of the pot. On cooling, this acid sulphate solidifies, forming "nitre cake" (p. 138).

Compressed air is employed to force the concentrated acid from the Glover tower to the top of the Gay-Lussac, and the nitrous vitriol from the Gay-Lussac to the top of the Glover tower. The acid collects in a large oval vessel of cast-iron, called the **acid egg** (Fig. 29), and the compressed air from (B) forces it out through the pipe (A) to the Glover or Gay-Lussac tower.

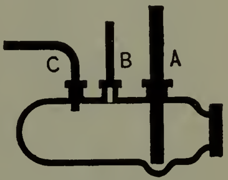

FIG. 29.

Kestner's acid elevator (Fig. 30) is much used; a cast-iron lead-lined vessel (B) has a vertical pipe (T) in which a rod hangs free, extending from the air-valve case (D) to the float (X). Acid enters through the valve (M) and the pipe (A), lifting the float (X), which opens the valve in (D) by the rod in (T), admitting compressed air from the pipe (P) to (B) through (T). The air compressed in (B) closes the valve (M) and forces the acid out through the pipe (O) to the desired elevation. As the acid level in (B) falls, the float sinks until it closes the air valve(D), while acid again flows in through (A). The apparatus is automatic, simple, and occupies but little space. Modified forms are used for hydrochloric and other acids. The acid in the cistern *supplying* the apparatus must never reach a higher level than the line (FG).

The "**air-lift**" pump (Fig. 31) is used to some extent to raise the acid to the top of the towers. A pipe (P) is sunk into the ground to a depth equal to the height to which the acid from (S) is to be raised; the air from (R) is forced in near the bottom of the pipe, the pressure causing a rush of air up the pipe, carrying before it some of the acid, which is thus thrown out into (T) in "slugs," and not in a continuous stream.

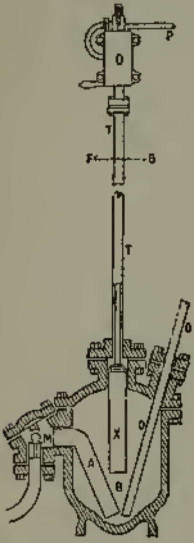

FIG. 30.

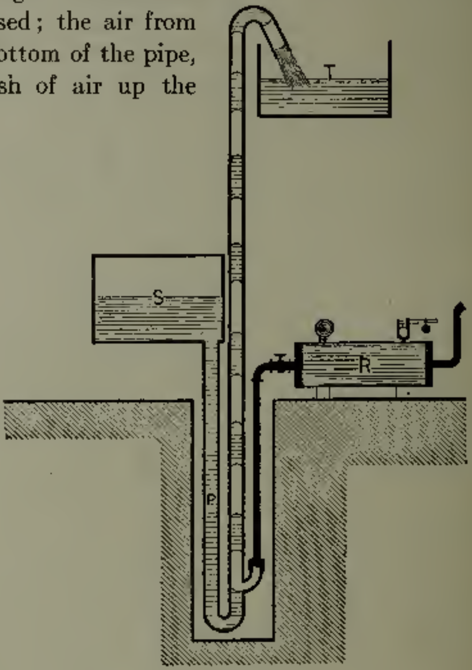

FIG. 31.

The acid condensed in the lead chambers varies from 1.5 to 1.62 sp. gr. If more concentrated, it absorbs oxides of nitrogen present in the chambers, and attacks the lead.

In the **concentration** of chamber acid it is first evaporated to 1.70 sp. gr. (60° Bé.) in shallow lead pans often heated by the waste heat from the pyrites burners. Since acid stronger than 1.70 attacks lead, "oil of vitriol" is made in glass balloons, or in platinum or iron stills, or by direct heating in the Glover tower, Kessler apparatus, or dishes of porcelain or fused silica.

Continuous acting concentrators, using **porcelain or fused silica** (Vitreosil, etc.) evaporating dishes set *en cascade* (Fig. 32) are considerably employed. Quartz dishes are bedded in asbestos rings on fire-clay supports, so the flame strikes directly on the lower part of the vessel, but is not in contact with the acid, nor with the fumes from the evaporation. The acid overflows from one vessel to the next, through a series of some 25 basins.

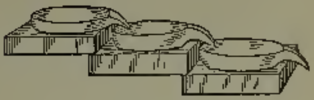

Fig. 32.

Glass stills set in sand baths and heated by a fire are used somewhat, and yield a very pure, colorless, and strong acid; but owing to breakage there is much loss and some danger.

Platinum stills (Fig. 33) are shallow platinum dishes (S, S) covered with a lead hood or bell (B), which is kept cool by a water jacket. The vapors condensing in this hood as a dilute acid do not fall back into the still, but collect in a narrow trough around the lower edge of the bell, and are usually returned to the lead pans. When the acid in the still has reached 1.835 sp. gr. (66° Bé.), it is drawn off through a platinum or lead cooling apparatus (C), as "oil of vitriol." The platinum stills are set directly over coke or coal fires on the grate (G), and are not allowed to cool except for repairs. Platinum stills may have a spiral partition in the pan which compels the dilute acid to flow a considerable distance over the hot still-bottom before it escapes through a tube from the central compartment. The rate of flow through the still determines the concentration of the acid.

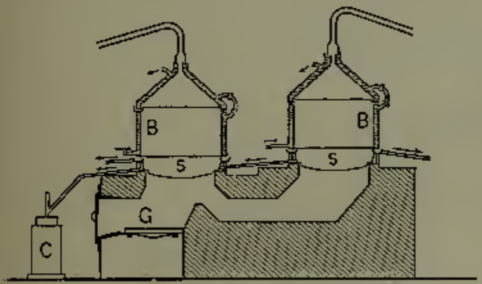

Fig. 33.

If the chamber acid contains nitrous vitriol, the platinum is often attacked. To prevent this, ammonium sulphate may be added to the acid during the concentration in the lead pans; the nitrogen oxides are destroyed, thus: —

$$N_2O_3 + (NH_4)_2SO_4 = 3\,H_2O + H_2SO_4 + 4\,N.$$

Platinum alloyed with iridium is more resistant to the action of nitrous vitriol. A still invented by Heræus * consists of platinum lined with a layer of pure gold rolled with the platinum, and not electroplated. It resists the action of concentrated acid, but is attacked by nitrous

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* J. Soc. Chem. Ind., **1891**, 460; **1892**, 36.

vitriol. The average loss of platinum in concentrating to "oil of vitriol" is about 1 gram per ton of acid produced.

Cast-iron stills for highly concentrated acid are much used in modern work. These are usually shallow iron retorts, from 6 to 8 feet long, by 2 to 4 feet wide, having a low cover provided with an outlet flue to carry off the vapors. The still is set so that it is entirely surrounded by the flame, thus preventing any condensation of dilute acid on the cover. Fins are often cast in the bottom to make the acid flow in a zigzag channel across the pan. Acid of 1.75 sp. gr. or over has very little action on chilled cast-iron, and the stills stand from two to six months' constant use. The chamber acid is first concentrated to about 64° Bé., in lead and platinum pans, or by running through the Glover tower, and then the hot acid enters the iron still and is brought up to the desired strength, ranging from 93 to 98 per cent H_2SO_4. One type of cast-iron still setting is shown in Fig. 34 *; the acid enters in a slow stream at (A), flows across the still and out at (B) into the vessel (C), where any sediment (sulphates, etc.) deposits. From (C) the concentrated acid flows into the coolers (E, E).

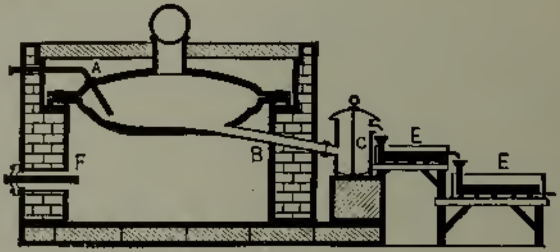

Fig. 34.*

Chamber acid is sometimes concentrated to 60° Bé. in open lead pans heated by steam in lead coils; this gives a clean product, but is not so economical as evaporation by waste heat from the burners. Over-surface evaporation (p. 4) in lead pans is occasionally practised, but yields a dark-colored acid.

Kessler's acid-concentrating apparatus † (Fig. 35) is a combination of over-surface heating with a tower evaporator. A chamber (G), built of siliceous materials enclosed in a lead case, is divided longitudinally by curtain partitions (P, P); over this chamber is a short tower (T), containing plates with overflow pipes (L) and porcelain

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* Trans. Am. Inst. Min. Eng., Vol. **16**, 517.

† J. Soc. Chem. Ind., **1892**, 434; **1900**, 246.

or fused quartz caps (J). The acid to be concentrated enters at (K), flows over the plates, and passes down by the pipes (L) from plate to plate, and finally to the chamber (G), where it lies about six inches deep on the floor; the curtain walls (P) just touch the surface of the acid. The hot gases from a coke fire enter at (E), pass under the lower edge of the curtain walls and into the channels leading to the tower. In passing under the walls (P) the hot gases bubble through the shallow layer of acid on the floor of (G), thus concentrating it; the vapors and hot gases then pass up the tower, bubbling through the layers of dilute acid on the tower plates, and pass off through the hood and vapor pipe (V).

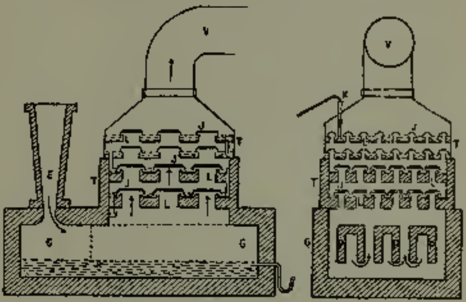

Fig. 35.

When chamber acid is concentrated by running through the Glover tower, it is contaminated with iron from the flue dust of the burners. It is better to further concentrate such acid in cast-iron stills, since, when the density reaches 64° or 65° Bé., a precipitate of ferric sulphate forms, which may cake upon the platinum and cause it to crack. The acid intended for oil of vitriol is usually drawn from the lead pans, while that which has been through the Glover tower is frequently not further concentrated.

To secure the intimate mixing of the gases essential in the lead chambers, Professor Lunge invented his **plate tower**,* a tall lead-lined tower divided into narrow chambers by transverse stoneware plates (Fig. 36) perforated by small holes, and so placed that the holes are not in line. By this arrangement the gases and liquids are brought into very close contact, and by placing such a tower between each pair of adjoining chambers, it is claimed that the chamber space for a given yield of acid can be much reduced. The plates are not practicable for the Glover tower, because the heat is liable to crack them, and the small holes become clogged with dust, but they may be used in the Gay-Lussac tower.

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* Zeitschrift für angewandte Chemie, **1889**, 385. J. Soc. Chem. Ind., **1889**, 774. It may be noted here that these Lunge-Rohrmann "plate towers" have found much favor for condensing hydrochloric acid, but are said to obstruct the draught in sulphuric acid making.

The "**pipe column**"* invention of Gilchrist and Hacker and the towers of Hart and Bailey† carry out the same idea of mixing and cooling the gases more thoroughly. They consist of towers containing a number of small lead pipes set horizontally, and open to the air at each end. The gases, in passing through the tower, impinge upon these tubes and are thus cooled and mixed, while air, passing through the tubes, cools them also.

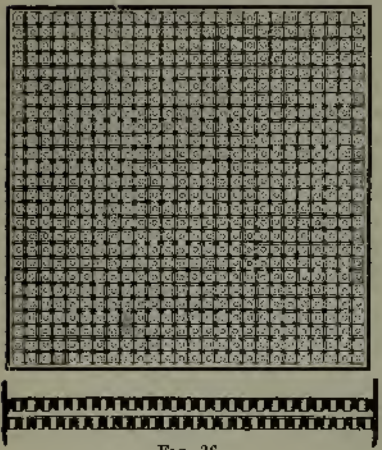

Fig. 36.

The **Barbier tower system**,‡ in which the lead chambers are abolished and a series of towers substituted, was carefully tested on a large scale in Italy, but the results were not satisfactory,§ probably due to excessive attack on the lead due to the high temperature (see footnote, p. 71). The advantages claimed for the system were: it occupies less ground and is cheaper to build than lead chambers; it works at high temperature (90° C.), hence is less influenced by atmospheric changes, and is suitable for either hot or cold climates; it gives a larger yield of acid per cubic metre of space than does the chamber system.

While tower systems may be further developed in the future, the most promising substitute for the cumbersome and expensive lead chambers will probably be found in some of the "contact" processes (see below).

To assist in the circulation and mixing of the gases in the chambers a fan of iron, hard lead, or earthenware is frequently placed in the inlet pipe, behind the Glover, or at the end of the system. This makes the working of the chambers uniform and independent of outside temperature and wind.

Atomized water instead of steam is often introduced into the lead chambers. This helps to abstract the heat liberated by the reactions, and increases the yield of acid per cubic foot of chamber space. The water must be in only the finest mist, made by directing a small jet, under high pressure, against a flat disk, or by using some type of spraying nozzle.

Very concentrated acid may be made by artificially cooling oil of vitriol of 66.3° Bé. considerably below 0° C., when crystals of sul-

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* J. Soc. Chem. Ind., **1894**, 1142; **1899**, 459.

† *Ibid.*, **1903**, 473.

‡ Bul. Soc. Chim., **11**, 726.

§ J. Soc. Chem. Ind., **1895**, 698.

phuric acid (monohydrate) separate, and are quickly freed from mother-liquor in a centrifugal machine. The crystals melt at 10° C., yielding an acid of 99.5 per cent H_2SO_4, with only a trace of water.

CATALYTIC PROCESSES

The **catalytic** or **contact processes** had their origin chiefly in some experiments by Professor C. Winkler,* on the conversion of sulphur dioxide into sulphuric anhydride by the action of certain catalyzers. The fact of this conversion has long been known (Phillips, Eng. Pat., **1831**), but no attempt to make practical use of it had been made. In 1878 Winkler patented a method for producing platinized asbestos to be used as a contact substance, and soon after other experimenters began work along these lines.

These processes attract manufacturers, since the plant occupies less ground area and does away with the costly lead chambers and the platinum-pan concentration; all strengths of acids, from the weakest to the most concentrated monohydrate of 98.5 per cent H_2SO_4, and even fuming acid, can be produced in the same works, and with comparative ease. Further, no nitre, with the accompanying recovery process, is necessary.

The raw materials are sulphur dioxide and oxygen from the air, to produce SO_3. By solution of the sulphur trioxide in water, any concentration of acid can be made.

The equation $2\ SO_2 + O_2 \rightleftarrows 2\ SO_3$ shows a characteristic gas reaction. The equilibrium constant $K_p = \frac{p_{SO_3}}{p_{SO_2}\sqrt{p_{O_2}}}$ is given in the following table; note that dissociation of the trioxide increases rapidly with the temperature: —

Degrees C.	450	528	579	627	680	727	789	832	897
K_p . . .	188	31.3	13.8	5.54	3.24	1.86	0.956	0.627	0.358

In the absence of a catalyzer the rate of reaction is negligible below 400° C.; with finely divided platinum, combination may be detected at 200° C., and becomes rapid above 400°; above 500° to 600° any surface is fairly active and burned pyrites cinder may be used. The reaction evolves 21.7 Cal., and unless the resulting rise of temperature is controlled by dilution of the gases, and radiation of the heat, reversal of the reaction and destruction of the apparatus results.

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* Dingl. J., **1875**, 296; **1877**, 232; **1879**, 384.

This necessary temperature control is secured by enclosing the reaction chamber within the flue, in which the *cold* mixture of sulphur dioxide and air is passing to the catalyzer, thus cooling the contact mass and apparatus, and warming the mixed gases to the initial temperature. Or regulated quantities of the *cold* mixture are passed into the contact chamber at different points. By use of spongy platinum, the reaction may be carried on at 400° to 450° C., with nearly quantitative conversion; with less active accelerators, higher temperatures (500° C., or more) are required, and oxidation is less complete, necessitating recovery of the residual sulphur dioxide from the exit gases.

The catalyzers most in use are spongy platinum and iron oxide from pyrites burners. The platinum mass may be platinized asbestos, or a sponge of metallic platinum disseminated through a porous mass of non-volatile soluble sulphates, oxides, or similar substance.

The presence of flue dust, sulphur vapors, or of arsenic, phosphorus, or mercury compounds in the mixed gases acts very injuriously upon the contact mass, soon rendering it inactive or causing rapid destruction of the apparatus. These substances must be entirely removed from the burner gases by cooling, scrubbing with water, injecting steam, or filtering.

Cast-iron has proved unsuited for the construction of the apparatus, since fuming acid makes it crack. The cause of this appears to be the formation of sulphurous acid in the pores of the iron, through the reduction of the acid by the action of the iron itself. Wrought iron seems to be passive to acid containing more than 27 per cent of sulphuric anhydride and is well suited to the purpose.

The contact process has entirely replaced the old dry distillation of iron sulphate for fuming acid; it has also largely affected the manufacture of monohydrate and oil of vitriol. In this country, for making acid of 50° to 60° Bé., the old chamber process appears to be economical, but in large plants, maintaining both processes, the expense of evaporating the chamber acid is avoided when making stronger grades, by adding contact sulphur trioxide to the weaker acid.

The process of the Badische Anilin u. Soda-Fabrik* at Ludwigshafen, Germany, was the first commercially successful one. In this, platinized asbestos is the contact material. The apparatus (Fig. 37) consists of several vertical iron tubes (R), containing perforated plates on which the platinized asbestos lies in thin layers, so that it does not offer too much resistance to the passage of the gases. The burner gases, cooled and purified, enter through (AA′), pass up the

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* Ber. deutsch. chem. Ges., **34** (1901), 4069.

space (S, S), between the tubes, thus cooling them, and thence through (O) and (F) to the chamber (D), from which they enter the tubes, pass down through the contact mass and out by (D′) and (C). The tubes are first raised to the initial temperature by gas burners at (H), the combustion gases passing out at (L); but once started, the heat of the reaction maintains the process. Thus the reaction heat is utilized to bring the mixture of SO_2 and air to the initial temperature, while the reaction products are cooled below the decomposition temperature.

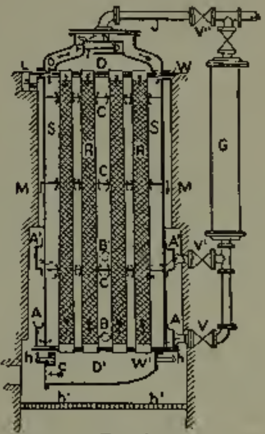

FIG. 27.

The **Grillo-Schroeder process** * employs platinized masses of soluble anhydrous salts, such as magnesium or sodium sulphate, as contact mass. This becomes inactive after a time, when the soluble salts are dissolved in water or acid and the platinum readily recovered.

Hasenbach and Clemm propose to use the iron oxide residue from pyrites burning as contact material. This is not so effective as platinum, and the formation of sulphur trioxide is not near the theoretical amount, but the cheap material offers inducement for experiment. The pyrites cinders are introduced, still hot, into the contact chamber, which is a vertical shaft, and the burner gases require no purifying. Dust, arsenic, and other impurities are retained by the iron oxide in the lower part of the apparatus, and the anhydride is formed in the upper part. The cinder is removed periodically, as it becomes inactive.

The difficulty of removing from the gas, dust and impurities (arsenic) which poison the catalyzer is very great, especially when burning pyrites. Frequently the gases are scrubbed in towers with strong sulphuric acid, or washed in spray chambers with a fine spray of acid; then they are filtered through layers of pulverized coke, slag, or asbestos wool, before admitting them to the contact chamber. This difficulty of purifying the gases is a large factor in limiting the extension of the contact process. The operation is more sensitive and a higher grade of labor is required than for the chamber process, in which the elaborate treatment of the gases is unnecessary. Thus despite the expensive lead chambers and high cost of nitre, the latter holds its own for dilute acid.

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* J. Soc. Chem. Ind., **1899**, 584; **1901**, 579.

FUMING SULPHURIC ACID

By absorbing the sulphur trioxide produced in the contact process in concentrated sulphuric acid, a brown, oily liquid is obtained, which fumes in the air, owing to the escape of some of the dissolved sulphur oxides. Sulphur trioxide fume cannot be dissolved in dilute sulphuric acid, and hence concentrated acid must be used, which is later diluted to the desired strength. Fuming acid ("Nordhausen acid") was formerly produced in Bohemia by the dry distillation of basic iron sulphates, obtained by weathering a kind of pyritiferous shale. When dried and heated in small retorts, decomposition ensues, thus: —

$$Fe_2(SO_4)_3 \cdot 2\ FeSO_4 = 2\ Fe_2O_3 + 4\ SO_3 + SO_2.$$

When absorbed in oil of vitriol, these vapors produced the fuming acid.

REFERENCES

J. Soc. Chem. Ind., **1882** +.
Progress in the Concentration of Oil of Vitriol. By W. H. Adams, Trans. Am. Inst. Min. Eng., **1887–1888**. Vol. **16**, p. 496.
Mineral Industry. **1892** +.
Schwefelsäurefabrication. Dr. K. W. Jurisch, Stuttgart, 1893.
Die Gegenwärtige Stand der Schwefelsäureindustrie. Gustav Rauter, Braunschweig, **1903**.
Sulphuric Acid and Alkali. Vol. I. 3d ed. G. Lunge, London, 1903.
Ber. deutsch. chem. Gesell., **34** (**1901**), 4069. R. Knietsch.
Zeitschr. angew. Chem., **1905** (**18**), 1253. (Chamber process.)
Thermodynamik Technischer Gasreactionen. F. Haber, Berlin, 1905.

SALT

The sources of salt are: —

1. Sea-water.
2. Rock salt.
3. Salt brines derived from springs, lakes, or wells.

Atlantic sea-water, except near the mouths of large rivers, averages about 3.4 per cent of solid matter, of which about 75 per cent is sodium chloride, the remainder consisting of chlorides, bromides, and sulphates of potassium, magnesium, calcium, lithium, etc., with minute amounts of other salts.

The concentration of **sea-water** for salt is carried on to some extent in warm, dry countries by solar evaporation, the water usually being exposed in shallow tanks or ponds to the sun's rays. Sea-water is seldom evaporated over fire because of the cost of fuel. In Russia it is allowed to freeze over the surface, and the ice, which contains but little salt, is removed. This is repeated until the brine is sufficiently concentrated to make the evaporation over fire profitable. Salt made from sea-water ("sea-salt") is coarse and is usually damp, owing to the presence of some magnesium chloride, which, being a deliquescent substance, attracts moisture from the air. It is of less importance in this country than that made from other brines.

Rock salt is found in many countries, and often very pure. In England, Austria, Germany, Spain, and Louisiana are large deposits, some so pure that it is only necessary to grind it for use, but in most cases it is contaminated with iron oxides, clay, sand, and other impurities, which often necessitate its purification. In this country it is mined in New York, Kansas, California, Utah, and Louisiana. As it does not dissolve so readily as finely crystallized salt, it is preferred for many purposes, such as curing meat, preserving green hides, and feeding to live stock.

The salt of principal interest in this country is derived from natural **brines**, found chiefly in New York, Michigan, Kansas, and Ohio, while West Virginia, Utah, Texas, and Pennsylvania produce lesser quantities.

The New York deposits are near Syracuse and in the neighborhood of Warsaw and Batavia. The Onondaga (Syracuse) deposit has been known since the middle of the seventeenth century, but that at Warsaw, opened in 1883, is now the most important. The

Michigan deposits are near Saginaw Bay and Manistee, a strong brine being obtained by boring. Large amounts of brine are evaporated near Salina, Kansas. The Ohio and West Virginia deposits are in the valley of the Ohio River, near Pomeroy and Wheeling.

Brines are obtained by bored wells, 8 inches in diameter, similar to those for petroleum (p. 336). The wells are lined with iron casings to exclude water from the over-lying strata. The brine as it comes from the well has some turbidity, due to clay or fine sand, together with minute bubbles of carbon dioxide, with which the brine is usually charged. Ferrous carbonate is also held in solution by the carbon dioxide, and on exposure to the air a yellowish red precipitate of ferric hydroxide separates. This is usually hastened by adding "milk of lime," or soda-ash, which also throws out some of the calcium and magnesium salts from the brine.

"**Solar salt**" was formerly made in large amounts at Syracuse, and is yet produced at Great Salt Lake in Utah, and in California, from sea-water. The brine was exposed to the sun's rays in shallow wooden vats, from 6 to 8 inches deep. During the early part of the evaporation, crystals of gypsum, $CaSO_4 \cdot 2\ H_2O$, separate in clusters, which are attached to the floor of the vat. After the gypsum is all separated, the brine is drawn into other vats, "salt-rooms," where evaporation causes the salt crystals to separate. These collect on the floor of the vat, and two or three times each season the salt is "harvested," *i.e.* raked up, freed from excess liquor in perforated drainers, and removed to the store house. Wooden covers over the vats, which may be rolled back in fair weather, serve to keep out rain. In foreign countries "ricks" (p. 4) are used to concentrate brines, prior to evaporation for crystallization.

Solar salt forms aggregates of the cubical crystals, which often take a "hopper" shape, and contain cavities in which small amounts of mother-liquor are retained, even after long draining. Since the liquors contain considerable amounts of calcium and magnesium chlorides, these contaminate the salt and cause it to become moist in damp weather.

Strong brines, purified with milk of lime or soda-ash, are generally concentrated by use of fuel, several types of evaporator being in use.

The old "**kettle process**"* (Fig. 38), in which the evaporation was carried on in cast-iron kettles (A, A) about 4 feet in diameter, set in rows of 16 to 25 over a flue leading from the fire-box (G) to the chimney, has

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* After Merrill, Bul. N. Y. State Museum, III, No. 11.

been generally abandoned. The brine was delivered through (P) to each kettle and the salt was raked out as it crystallized and drained in the basket (D), set over the kettle. A special-shaped "bittern pan" (B) was placed in the kettle at the start, and left until the salt began to crystallize, when it was lifted out, carrying much of the calcium and magnesium sulphates, or "bittern," which separates first as the brine evaporates.

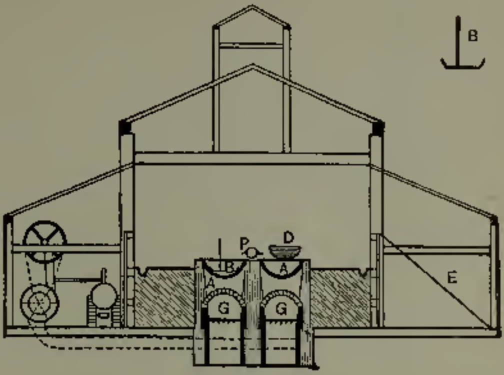

Fig. 38.

Sometimes the kettles are heated by steam jackets; as all have the same steam pressure, the temperature is uniform, and only one quality of salt is produced.

Salt is also made by the "**pan process**" (Fig. 39)* of direct evaporation over fire. Large wrought-iron pans (H, H), 24 feet wide, 100 feet long, and 12 inches deep, are used. These pans are divided into two sections by a loose partition, which allows the brine to flow slowly from the rear to the front section. A second smaller pan is set behind and slightly above the first, so that its contents may be syphoned into the front pan. Both are heated by flues from grates (G), but the rear one gets only the waste heat, before the gases pass into the chimney. The ends of each pan are made perpendicular to the bottom, but the sides are inclined, and sloping wooden platforms (F, F), called "drips," are joined to them; on these the salt is drained when removed from the pans. The brine is purified with "milk of lime," as in the kettle process.

The pan process permits an easy control of the size of the grain. For the preparation of a very fine grained product, called "factory-filled salt," it is customary to add a small amount of sodium carbonate to the brine; this decomposes the chlorides of calcium and magnesium and any excess of caustic lime from the "liming." Then a small quantity of butter, glue, or soft soap is added, and forms an insoluble calcium soap with the remaining traces of lime, and this is removed by skimming.

For both the kettle and the pan process, coal dust is used as fuel.

Strong brine boils at 105°–109° C., and thus the heat in the kettle and pan process is sufficient to dehydrate any calcium sulphate in the

* After Merrill, Bul. N. Y. State Museum, III, No. 11.

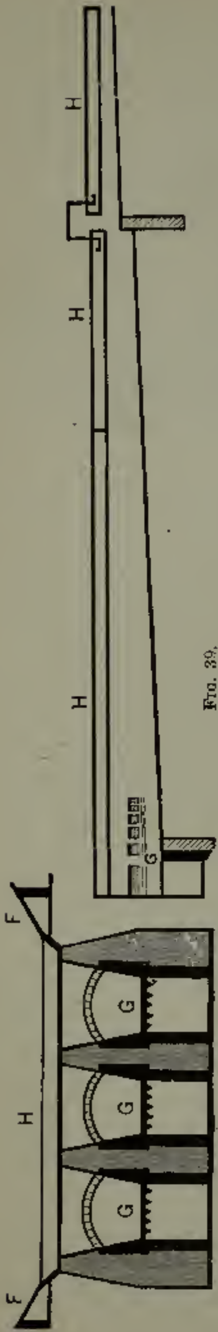

FIG. 39.

salt; when dissolved in water, such products cause a slight milkiness, which disappears after a time, owing to the hydration of the calcium sulphate and its solution in the water.

In Michigan and in western New York brine is evaporated in "**grainers**" (Fig. 40)*; these are long, shallow vats of wood or iron, containing steam pipes (P, P), through which live or exhaust steam is passed. The pipes are about 4 inches in diameter and are hung about 6 inches above the floor of the "grainer," which is some 20 inches deep. Once a day the salt is raked up and deposited on draining platforms over the grainers. The brine is purified before evaporation, as in the pan process, and is supplied to the grainer in just sufficient quantities to replace the water evaporated. When the mother-liquors become too highly charged with calcium and magnesium chlorides, they are drawn into special grainers, and a low grade of salt is made from them.

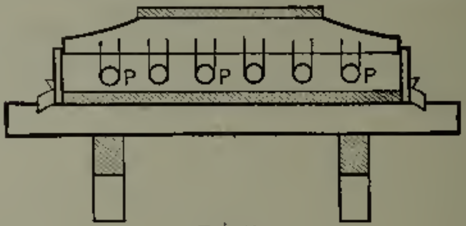

FIG. 40.

Brine is frequently evaporated in continuous-acting vacuum pans, and a finely crystalline product, the best grade of table and dairy salt, results. It is separated from adhering mother-liquor by the centrifugal machine.

Sometimes pure water is introduced into rock salt deposits through tube wells; when saturated with salt, it is pumped to the surface and evaporated. A much stronger brine than is found in nature is secured in this way.

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* After Merrill, Bul. N. Y. State Museum, III, No. 11.

In Michigan, West Virginia, Germany, and other places large quantities of bromine are recovered from the mother-liquors (also called "bittern") from the salt industry.

In Italy, Austria, and China the manufacture and sale of salt is a government monopoly. In France, Germany, and India salt used for seasoning food is subject to tax. When used for technical purposes, or in agriculture, the tax is very small. To prevent fraud, all German salt, not intended for table use, must be mixed with certain substances to render it unfit for eating. Some of these adulterants are iron oxide, crude petroleum, coal dust, pyrolusite, carbolic acid, mineral acids, sodium sulphate or carbonate, alum, soot, etc.

REFERENCES

Die Industrie von Stassfurt und Leopoldshall. G. Krause, Cöthen, 1877.
Report on Manufacture of Chemical Products and Salt. W. L. Rowland, United States Census, **1880**; Washington, 1884.
Mineral Resources of the United States. (**1882** +.)
Chemische Industrie. **1883**, 225. G. Lunge.
Report of the State Geologist of New York, **1885**, pp. 12–47. I. P. Bishop.
Jour. Soc. Chem. Ind., **1888**, 660. On the Tees Salt Industry. T. W. Stuart.
Die Salz Industrie von Stassfurt. Dr. Precht, 1889. (Weicke, Stassfurt.)
Bulletin of the New York State Museum, Vol. III, No. 11. Salt and Gypsum Industries of New York. F. J. H. Merrill, Albany, 1893.
Forty-seventh Report of the State Museum of New York, pp. 205–257. The Livonia Salt Shaft. James Hall, 1894.
Journal of the Society of Arts, **1894**. Manufacture of Salt. F. Ward.
Salt Deposits and Salt Industry in Ohio. J. A. Bownocker, Ohio Geol. Survey, Bull. 8, Vol. IX, 1906.
Gewinnung und Reinigung des Kochsalzes. Carl Riemann, Halle, a. S., 1909.
Louisiana Salt Mines. P. Wooten, Min. Eng. World, **1912**, 401.
The Salt Industry of Michigan. C. W. Cook. Mich. Geol. Survey, Pub. 8, 1912.

HYDROCHLORIC ACID AND SODIUM SULPHATE

Hydrochloric or muriatic acid is generally made by the action of sulphuric acid on common salt. It is a by-product of the Leblanc soda process, and in the early years of the industry was allowed to escape into the air, as the demand for it was small. But the nuisance caused by the acid fumes in the neighborhood of the alkali works became so great, that in England a very stringent law was enacted forbidding the soda makers to allow more than 5 per cent of the gas to escape into the atmosphere. This made it necessary to absorb the acid fumes in water. The provisions of the present " Alkali Act " permit only 0.2 grain of hydrochloric acid per cubic foot of chimney gas to be discharged into the atmosphere.

The Leblanc industry has declined in recent years, but there is an increased demand for hydrochloric acid, and at present this is one of the main products desired. Its chief use is for the generation of chlorine for the manufacture of bleaching powder; now nearly all soda makers also produce bleaching powder, and the profits derived from the latter have largely offset the decline in returns from soda-ash. Up to the present, no better method than the above has been devised for making this acid. The process may be represented by the equation: —

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$

But as actually carried out it takes place in two stages, according to the following reactions: —

1) $NaCl + H_2SO_4 = NaHSO_4 + HCl.$

2) $NaHSO_4 + NaCl = Na_2SO_4 + HCl.$

These reactions may be carried out by heating the mixture of salt and sulphuric acid either in an "open roaster," or in a muffle or " close roaster." These are both called " **salt-cake furnaces.**"

The **open roaster** (Fig. 41) consists of two parts, the cast-iron pan (A) and the reverberatory hearth (C). The salt and sulphuric acid (60° Bé., sp. gr. 1.72) are put into the pan (A), and are moderately heated by a fire on the grate (E). The first reaction takes place at a comparatively low heat, and the hydrochloric acid vapors escape through the earthenware pipe (B). Then the fused mass of sodium acid sulphate and undecomposed salt is raked up on the reverberatory hearth (C), where it is exposed to the high temperature of the flame from (D). This completes the second reaction, and a pasty mass of normal sodium sulphate is formed. The hydrochloric acid vapors, set free during the reaction, mix with the furnace gases from (D), and escape through the pipe (F) to the absorbing apparatus. The furnace gases dilute the acid vapors so much that a very concentrated solution of hydrochloric acid cannot be made with the open roaster; however, it yields acid strong enough for use in Weldon's chlorine process (p. 117). Moreover, the soot and dust from the furnace at (D) contaminate the acid, and may cause clogging in the passages and pipes of the absorption apparatus. The open roaster has the advantage over the close roaster that it yields more sodium sulphate with smaller consumption of fuel. The crude sodium sulphate, called "salt-cake," usually contains a little undecomposed salt and a slight excess of sulphuric acid.

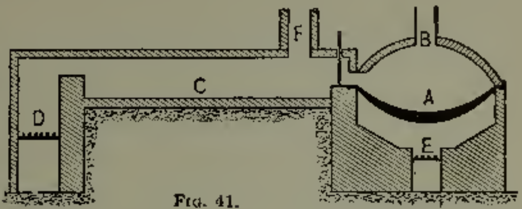

Fig. 41.

The **muffle** or "**close roaster**" is used very generally on the continent of Europe, and yields a stronger and purer acid than the open roaster. The usual form is shown in Fig. 42. The pan (A) is built very much as in the open roaster, but is heated by the furnace gases from the grate (D). The acid vapors set free in the pan escape by the pipe (C) to the absorption apparatus. The muffle (B) is made of fire-clay or brick, and is heated by the flames from the grate (D). The mixture of acid sulphate and salt is raked from the pan (A) into the muffle (B), where it is heated to a red heat, and the acid vapor liberated passes through the pipe (E) to the absorption apparatus. In this form of roaster the soot and dust from the grate are kept away from the acid vapor, and a concentrated acid vapor is obtained, which favors the formation of a concentrated solution of hydrochloric acid in the absorbers. But the muffles are expensive to build, yield a smaller output of salt-cake, and require more fuel than the open roaster. Moreover, they often crack, thus permit-

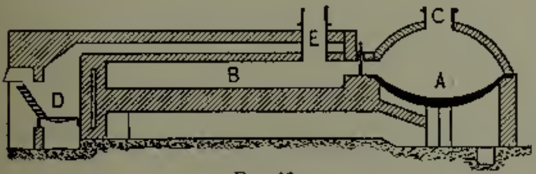

Fig. 42.

ting acid vapors to escape into the flues and chimney, causing loss and creating a nuisance. It is customary to maintain a slight pressure ("plus pressure") in the flues and chimney, so that if the muffle cracks, the flue gases force their way into it. This may cause a slight contamination of the acid, but no nuisance is created. Cheaper fuel may be used with these furnaces, but repairs are apt to be expensive.

The pan (A) in both furnaces is about 10 feet in diameter, 7 inches thick at the centre, and 3 inches thick at the sides. After a charge is drawn, the pan is cooled somewhat before introducing another, for cold salt, coming in contact with the hot pan, might crack it. The sulphuric acid is generally heated to 100° or 130° C. for the same reason.

During the second reaction, the charge is constantly stirred with a "rabble," a large hoe-shaped tool, to prevent "crusting" or burning on to the hearth or retort. The stirring is very heavy work and the workmen are sometimes careless, and allow a crust to form, which may crack the muffle. Hence, many attempts have been made to construct mechanical stirrers. Of these, the **Mactear furnace** * is most successful, but the difficulty of protecting the driving mechanism from the acid fumes, and the cost of building and heavy up-keep charges, have caused general abandonment of mechanical furnaces.

If salt-cake free from iron is desired, lead pans instead of cast-iron ones are used. But these are easily overheated or injured.

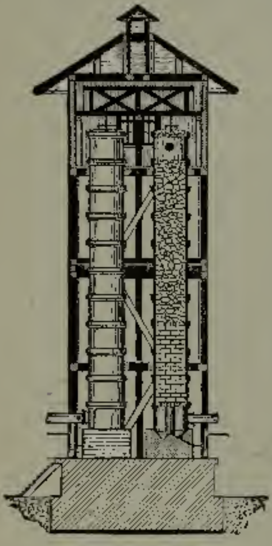
Fig. 43.

The hydrochloric acid gas is absorbed in water, by passing through tall towers (Fig. 43) † filled with coke, over which water trickles; or in a series of large earthenware Woulff bottles (*bombonnes* or *tourills*, Fig. 44 ‡), with an absorption tower at the end to catch acid gas which may pass through the bottles. These are set *en cascade* § and the side tubulatures joined so that a stream of dilute acid from the tower flows through them in opposite direction to the movement of the gas.

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* Chemische Industrie, **1881**, 253. J. Soc. Chem. Ind., **1885**, 534.

† After Lunge.

‡ Metal. Chem. Eng., **1911**, 611.

§ That is, on a series of steps, so that each stands slightly lower than the one preceding.

The standard absorber is difficult to cool externally with water and presents relatively a small liquid surface to the gas. A modified form (Fig. 45) * is claimed to be better, as it affords greater liquid surface exposure, and can be readily water-cooled.

The **Lunge-Rohrmann plate tower** (p. 77) has been tried with some success as a substitute for the coke tower and *bombonnes*, for hydrochloric acid absorption.

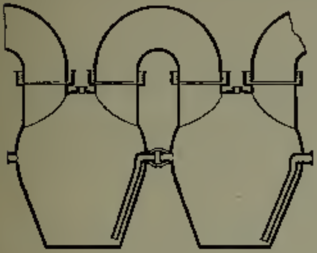

FIG. 44.

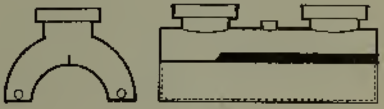

FIG. 45.

The condensation of hydrochloric acid vapors is not so simple a process as it at first appears. The gases coming from the roasters are very hot, and must be cooled before they can be absorbed to form a strong acid. Moreover, with open roasters, there is a large amount of inert gas present (nitrogen and carbon dioxide from the fire) which dilutes the acid vapors. Then, too, the vapors are not set free regularly in any roaster, there being a rapid evolution during the progress of the first reaction, and a much slower liberation during the second. This may cause a temporary rush of vapors through the apparatus, so that they cannot be properly taken up by the water.

The ordinary muriatic acid of trade is an aqueous solution of the acid vapor, having a specific gravity of about 1.20 and containing about 40 per cent by weight of dry hydrochloric acid vapor. It is impure, containing sulphuric acid, chlorine, iron chloride, arsenic, and, generally, lead and calcium chlorides. Its yellow color is partly due to organic matter, and sometimes to iron and free chlorine. To remove arsenic and sulphuric acid, the acid is diluted to 1.12 sp. gr., and barium sulphide is added; a pure hydrochloric acid vapor is then driven out by distillation and absorbed in pure water. Or a solution of stannous chloride in concentrated hydrochloric acid is added to the crude acid, which latter must have a strength of at least 1.15 sp. gr. A brown precipitate of arsenic with some tin separates and is removed by decantation.† Sulphuric acid alone is removed by

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* Metal. Chem. Eng., **1911**, 611.

† $3 SnCl_2 + 6 HCl + As_2O_3 = As_2 + 3 H_2O + 3 SnCl_4$.

$2 AsCl_3 + 3 SnCl_2 = As_2 + 3 SnCl_4$.

This leaves stannic chloride in the acid.

adding barium chloride and redistilling. To remove chlorine, the crude acid is digested with strips of copper for some hours. This precipitates arsenic, and the chlorine combines with the copper. The acid is then redistilled.

Attempts to recover hydrochloric acid from the waste liquors of the ammonia soda process (p. 122) have not proved very successful. The magnesium chloride mother-liquors from the potash salts of Stassfurt (p. 160) may be decomposed by distillation with steam, and a dilute hydrochloric acid obtained.

$$MgCl_2 + H_2O = 2\,HCl + MgO.$$

But this has not proved a commercial success.

The **Hargreaves and Robinson process** for the direct production of hydrochloric acid and sodium sulphate from salt, sulphur dioxide, water, and oxgyen is of some importance. The damp salt is pressed into blocks and dried; it is then charged into vertical cast-iron retorts, a number of which are connected in a series. These are heated from without; the temperature of the reaction is from 400° to 550° C. The sulphur dioxide, steam, and air are made to pass through all the retorts in succession, the hydrochloric acid being carried along with them. A slight excess of sulphur dioxide and steam is used to prevent the mutual reaction between the hydrochloric acid vapor and the oxygen, by which chlorine is set free. The decomposition being slow, the gases must be kept in contact with the salt for a considerable length of time; a cylinder containing 40 tons of material requiring from 15 to 20 days' continuous action to secure complete conversion.

The process is an uninterrupted one; for as soon as no more sulphur dioxide is absorbed in a given cylinder, it is cut out from the series, the sodium sulphate removed, a new charge of salt blocks introduced, and the cylinder made the final one of the series; so that newly charged salt is exposed to the most nearly exhausted sulphur fumes. The reaction representing the process appears quite simple: —

$$2\,NaCl + SO_2 + H_2O + O = Na_2SO_4 + 2\,HCl.$$

But the mechanical difficulties encountered in working it were great, and only recently has the process met with any marked success.

Sodium sulphate or **salt-cake** is largely used in the production of soda by the Leblanc process, for glass making, for ultramarine, in dyeing and coloring, and to some extent in medicine. For some kinds of glass the salt-cake must be free from iron, and consequently it is made in lead pans. Or the sulphate may be purified from iron and excess of acid by dissolving it in hot water, adding "milk of lime," and stirring into it a solution of bleaching powder. The iron is precipitated as hydroxide and settles on standing. By evaporation, crystals of **Glauber's salt** ($Na_2SO_4 \cdot 10\ H_2O$) are obtained. But generally the purified solution is rapidly evaporated to dryness, and the product is calcined to remove all the water.

REFERENCES

Berichte über die Entwickelung der Chemischen Industrie, u.s.w. A. W. Hofmann, Braunschweig, 1877. (Vieweg.)

Darstellung von Chlor und Salzsäure, unabhängig von der Leblanc Soda Industrie. Dr. N. Caro, Berlin, 1893. (Oppenheim.)

Sulphuric Acid and Alkali. 3d ed., Vol. II. G. Lunge, London, 1909. (Gurney and Jackson.)

Die Fabrikation von Sulfat und Salzsäure. Theo. Meyer, Halle, a. S., 1907.

THE SODA INDUSTRIES

THE LEBLANC SODA PROCESS

Nearly all the soda of trade was formerly obtained from certain natural deposits of the so-called "*sesquicarbonate*," or from the ashes of sea plants. But towards the end of the last century, the supply from these sources became insufficient to meet the increasing demands. About 1775 the French Academy of Science offered a large prize for a method of making soda from salt. Among other processes submitted was one by Nicolas Leblanc, which seemed promising, and being granted a patent in 1791, he began manufacturing on a commercial scale. But in the French Revolution his factory was seized, the patent declared public property, and no indemnity was paid to him. Having lost all his property, he finally committed suicide.

Leblanc's process was so perfect and complete that very slight changes, and those only in minor details, have been made up to the present. It has been in use for more than a century, and although seriously threatened by newer processes, it still produces a large part of the world's supply of soda. Owing to the fact that it produces hydrochloric acid and bleaching powder as by-products, it has been able to survive competition, although its condition is becoming more desperate every year. Its chief rival is the ammonia or Solvay process. Within a few years many electrolytic methods for caustic soda have appeared, and the extensive production of bleaching material by any of these processes will sweep away about the only source of profit left to the Leblanc manufacturer. It is not probable that this change will come immediately, although several electrolytic processes have proved fairly successful on a large scale; but the decline of the Leblanc process is generally regarded as inevitable, and inventors have, for the most part, abandoned further attempts to improve it.

The reactions of the Leblanc process are generally expressed as follows: —

1) $2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$

2) $Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2.$

3) $Na_2S + CaCO_3 = Na_2CO_3 + CaS.$

4) $CaCO_3 + C = CaO + 2\,CO.$

But these equations * do not represent all the reactions which take place during the process, for a number of other substances are formed. The first equation represents the preparation of sodium sulphate and hydrochloric acid (p. 88). The second and third reactions are realized in one operation. The fourth has no direct relation to the process, as the formation of carbonic oxide does not become marked until all the salt-cake has been decomposed. This serves to indicate the end of the process, and aids in the formation of a porous product.

The salt-cake should be friable and porous, containing very little free sulphuric acid, and no undecomposed chloride. The carbon is supplied in the form of powdered coal, which should contain very little ash-forming impurity. A little pyrite does no harm, but the coal should be as free as possible from nitrogen, in order to prevent the formation of cyanides and cyanates. Calcium carbonate in the form of pure limestone or chalk, crushed to the size of a small pea, is mixed with the crushed salt-cake and coal in order to carry out the third reaction. If the limestone contains magnesia or silica, there is a consequent loss as insoluble residue. Usually 100 pounds of salt-cake, 100 pounds of limestone, and 50 pounds of coal dust form a charge. This is an excess of limestone, the purpose of which is explained below.

The reactions are carried out in a "**black-ash**" or "**balling furnace**," which may be worked either by hand or mechanically. The hand-worked furnace is a long reverberatory (Fig. 46). The charge is introduced on the platform (A) nearest the flue, where the heat is not high. When well heated, it is raked on to the front platform (B), which is a few inches lower than (A). Here the tem-

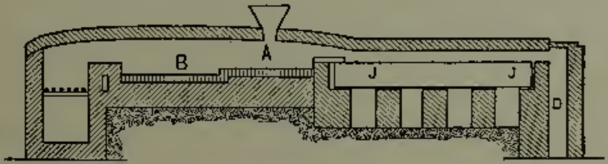

FIG. 46.

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* Lunge (Sulph. Acid and Alkali, Vol. II, 460 *et seq.*) regards the theory of Scheurer-Kestner (Comptes rendus, **57**, 1013, and **58**, 501) as correct, viz. that the reactions are: —

$$5\ Na_2SO_4 + 10\ C = 5\ Na_2S + 10\ CO_2.$$
$$5\ Na_2S + 5\ CaCO_3 = 5\ Na_2CO_3 + 5\ CaS.$$
$$2\ CaCO_3 + 2\ C = 2\ CaO + 4\ CO.$$

While these equations closely represent the net result, the first and last reactions each yield mixtures of CO_2 and CO, depending on the temperature and equilibrium conditions.

perature is high, usually about 1000° C., and the surface of the mass soon begins to fuse. It is then raked over, thoroughly exposing it to the direct heat until it becomes a thick, pasty mass, from which carbon dioxide is escaping freely. After the salt-cake is all decomposed, the charge begins to stiffen, and the evolution of carbon monoxide is shown by the appearance of jets of blue flame, known to the workmen as "candles." The charge is then raked together into a "ball," which is drawn out of the furnace into an iron barrow. The evolution of carbon monoxide continues for a few minutes after the "ball" is removed, and the bubbles escaping from the pasty mass cause it to become porous. The formation of this gas is due to the action between the coal and the excess of limestone according to reaction (4). The caustic lime formed here slakes during the lixiviation of the black-ash (p. 97), and swells, thus disintegrating the mass.

Although the heavy tools are suspended by chains, their operation is still so difficult, and the temperature is so high, that a man cannot handle much more than 300 pounds at one time. In order to work larger charges, without the expensive hand labor, revolving black-ash furnaces (Fig. 47) are much used. These are similar to the revolving furnaces described on page 21; the flame from the furnace (A) passes through the cylinder (B). The charge is introduced through the manhole (P), and the finished product discharged through the same opening, into the wagon, at the end of the operation. The cylinder is about 16 feet long by 10 feet in diameter, and is revolved by a gear (E) connected with an engine. Projections are fixed in the lining to help mix the contents. The charge is usually about two tons of salt-cake, with proportionate amounts of coal and limestone. It is customary to introduce only the limestone and a part of the coal at first, and to rotate the cylinder until some caustic lime is formed; then the remainder of the coal, together with the salt-cake, is introduced, and the rotation continued until the reactions are completed. The speed varies from one revolution in three or four minutes, at first,

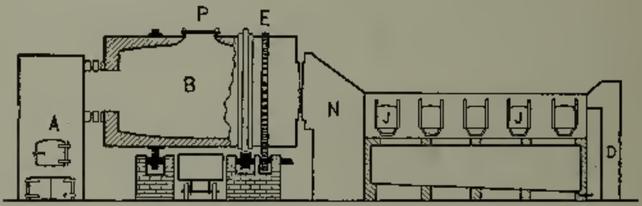

FIG. 47.

to four or five revolutions per minute during the last part of the process.

The hot gases from the black-ash furnace, whether hand-worked or mechanical, pass through the dust box (N), and then through the long flue over the pan (J, J) on their way to the chimney (D). In this shallow pan, the liquor obtained by lixiviating the black-ash is evaporated. When crystallized, the salts are removed through the small doors (J).

Black-ash is a brownish black or dark gray substance of a pumice-like texture, containing about 45 per cent sodium carbonate, 30 per cent calcium sulphide, 10 per cent caustic lime, and from 10 to 12 per cent of other impurities, — sulphate, silicate, aluminate, and chloride of sodium, calcium carbonate, coal, and iron oxide, with traces of cyanides and of sulphides of sodium.

The next stage in the process is the lixiviation of the black-ash. This presents some difficulties: if the black-ash is put directly into cold water, it often agglomerates in hard lumps, which dissolve exceedingly slowly; the free lime present forms calcium hydroxide, which reacts with the sodium carbonate solution, forming some caustic soda; the solution of sodium carbonate, especially if hot and dilute, reacts on any calcium sulphide present, forming some sodium sulphide; moreover, moist calcium sulphide oxidizes rapidly to sulphate in the air, and this reacts with the sodium carbonate. Hence the lixiviation must be done as rapidly as possible, at a low temperature, and without exposing the wet black-ash to the air.

Shank's process gives the most satisfactory results. The lixiviation is carried on in a series of tanks, each having a false bottom perforated with small holes. Because of its density, the solution of sodium carbonate sinks, and passing through these perforations, is drawn off by means of a pipe which delivers it at the top of the next tank. There must always be sufficient liquor in each tank to keep the black-ash entirely submerged. The process is continuous, sufficient fresh water being admitted to the nearly exhausted ash to give an unbroken flow of strong liquor (above 45° Tw.) from the last tank of the series. When the liquor from the last tank falls to 45° Tw., it is turned into a tank which has just been filled with new ash. The exhausted ash is washed until the wash water has a density of only 1° Tw. Then the residue of calcium sulphide and hydroxide, coal, ashes, and other insoluble matter, which constitutes the "**tank waste**," is dumped and the tank refilled with black-ash and made the last of the series, to receive the strong liquors from the preceding tank.

Since the black-ash contains caustic lime, sufficient heat is generated by its slaking during the lixiviation to warm the concentrated liquor to about 50° C., which is the best temperature for complete extraction. The temperature of the dilute lye from the first tank of the series is not allowed to rise above 38° C., in order to prevent the above-mentioned interaction between the calcium sulphide and the sodium carbonate.

Good tank liquor has approximately the following composition: —

Na_2CO_3 (+ $NaOH$)	23.60*
$NaCl$	.50
Na_2S	.13
$Na_2S_2O_3$	.30
Na_2SO_4	.23
Na_2SiO_3 $NaCN$ $NaCNS$ FeS (in solution)	Traces.

The lye obtained by the lixiviation has a specific gravity of about 1.25, and is muddy from suspended impurities. It is purified by settling and then pumped to the top of the "carbonating towers," which are filled with pebbles or coke, or have numerous chains or wire ropes suspended from the top and weighted at the lower ends. The tank liquor trickles over the porous material or chains, and comes into intimate contact with a strong current of carbon dioxide † entering at the bottom and passing up through the tower.

The carbon dioxide and oxygen which pass through the tower convert the caustic soda to carbonate, decompose the ferro-sodium sulphide (solution of ferrous sulphide in sodium sulphide), converting the sodium sulphide into bicarbonate, and precipitating the iron, together with any silica and alumina which may be present.

The reactions involved were supposed to be the following: —

1) $2\,NaOH + CO_2 = Na_2CO_3 + H_2O.$

2) $Na_2S + CO_2 + H_2O = NaHCO_3 + NaSH.$

3) $NaHCO_3 + NaSH = Na_2CO_3 + H_2S.$

Reactions (2) and (3) are incomplete, as hydrogen sulphide is of practically the same acid strength as carbonic acid; only when

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* Mohr, Analysis of Soda-ash from Stolberg (Lunge, Sulphuric Acid and Alkali, Vol. II).

† This is derived from the gases of the black-ash furnace, which also contain some oxygen. Or it is obtained from the gases from lime kilns, which are much richer in carbon dioxide and introduce less flue dust into the product.

enough CO_2 is used to convert all the carbonate to bicarbonate, or when a large excess is used at fairly high temperature, can all the sulphide be decomposed. By adding zinc hydroxide the sulphide may be precipitated: —

$$Na_2S + Zn(OH)_2 = ZnS + 2\,NaOH.$$

Or by blowing air through the tank liquor the sulphide is converted to thiosulphate: —

$$Na_2S + 2\,O_2 + H_2O = 2\,NaOH + Na_2S_2O_3.$$

Pauli's process of purifying tank liquor by adding "Weldon mud" and blowing in air and steam is more effective. Thus the sulphide is oxidized, and ferric oxide, alumina, and silica precipitate in the sludge. Assuming "Weldon mud" to be essentially manganese dioxide, the following reactions take place: —

$$2\,Na_2S + 4\,MnO_2 + 5\,H_2O = 2\,NaOH + Na_2S_2O_3 + Mn(OH)_2.$$
$$Mn(OH)_2 + 2\,O_2 = 4\,MnO_2 + 4\,H_2O.$$

The manganese oxide thus recovered is used repeatedly, until it becomes much contaminated with ferric oxide, alumina, silica, etc.

After settling, the purified and carbonated tank liquor is drawn into the evaporating pans, usually large shallow iron tanks, and heated by surface contact with the waste gases from the black-ash furnace. Sometimes deep pans, heated from below, are used, since surface evaporation gives a product contaminated with dust from the furnace. The liquor is evaporated directly to dryness, and the "black salt" (chiefly monohydrated sodium carbonate, $Na_2CO_3 \cdot H_2O$) is calcined by heating it to a red heat. Sometimes sawdust is mixed with the uncarbonated liquor before evaporation, and then on calcining, the soda-ash is carbonated by the carbonaceous matter from the wood; but the charge is liable to cake in this method. The caustic soda and sodium sulphide of the tank liquor are thus converted to sodium carbonate, and, after the sawdust is burned out, the ash becomes white or light brown.

Or the liquor is evaporated till a crystalline mass separates; then the mother-liquor ("red liquor") is drawn off, and the black salt is raked out of the pan. Much care is necessary to prevent the formation of a crust or the burning on of the precipitated carbonate.

In large works, a semi-cylindrical evaporating pan is used, provided with mechanical scrapers, to prevent the black salt from adhering to the pan. An excellent form of this apparatus is

Thêlen's pan (Fig. 48). In this, the scrapers (R, R) move the salts towards the end of the pan as they deposit, and a scoop lifts them to the draining apron. The beam (B), carrying the frame from which the scrapers are suspended, is rotated by the gear (J).

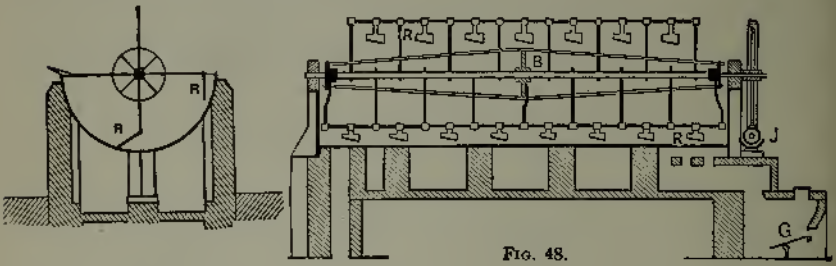

Fig. 48.

For a very light-colored product, the crude soda-ash is dissolved in water, and a little bleaching powder solution added; the precipitated iron and other impurities settle out, and the clear solution is evaporated until a thick mass of crystals separates, when the mother-liquor is drawn off to remove any soluble impurities. The monohydrated salt remaining is then calcined without the addition of carbonaceous matter, to remove its crystal water, and the product is called "white alkali" or "refined alkali." A little sodium chloride is formed by the addition of the bleaching powder, so that refined alkali is not quite so strong as soda-ash. It is chiefly used for glass making and other purposes where iron and sulphides would be detrimental. Good Leblanc soda is nearly white or pale yellow, and should contain but few black specks. It usually contains a little caustic soda, a trace of sulphides and sulphites, some chloride and sulphate, and not over 1 per cent of insoluble matter. It should be finely ground before packing.

Soda crystals or sal-soda ($Na_2CO_3 \cdot 10\,H_2O$) is made by dissolving soda-ash in warm water, allowing the hot solution to stand quietly until all sediment deposits, and drawing off the clarified liquor into crystallizing tanks, where is it cooled to the atmospheric temperature. Large crystals of sal-soda, very nearly pure, are deposited. They contain over 60 per cent of water, and are thus very bulky and not economical to ship; but they are still preferred to soda-ash for some manufacturing purposes and for household uses. They are sometimes used for making **sodium bicarbonate**, by exposing them on a grating to an atmosphere of carbon dioxide: —

$$Na_2CO_3 \cdot 10\,H_2O + CO_2 = 2\,NaHCO_3 + 9\,H_2O.$$

The water resulting from the reaction drips through, leaving the bicarbonate on the grating.

CAUSTIC SODA

Caustic soda is made from soda-ash, or from the "tank liquors" directly, by adding calcium hydroxide (milk of lime) to the solution: —

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2\ NaOH.$$

When caustic soda is the ultimate product, it is generally customary to use this lime mud ($CaCO_3$) instead of limestone, in the charge for the black-ash furnace, for the formation of caustic in the tank liquor is then of course not objectionable.

The tank liquor must not have a density of over 20° Tw. (1.10 sp. gr.), or the reaction will be incomplete.* Consequently it is diluted with the wash waters from the lime mud of a previous operation. The liquor is then heated to boiling, and run into large iron tanks, where the "milk of lime" is added, and the mixture well stirred. Air or steam is usually blown into the liquor to assist in the mixing. The air, especially when aided by the addition of "Weldon mud" (p. 118), converts the sodium sulphide to sodium thiosulphate and sulphate: —

$$2\ Na_2S + H_2O + 4\ O = 2\ NaOH + Na_2S_2O_3.$$

The thiosulphate is afterwards destroyed by oxidizing it to the sulphate.

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* This reaction may be written in the ionic form, thus: —

$$CO_3^{--} + Ca(OH)_2 \rightleftarrows 2\ OH^- + CaCO_3.$$

Equilibrium will therefore correspond to the equation, $\frac{(CO_3)^{--}}{(OH^-)_2} = \text{Const.}$, where the parenthesis indicates that the concentration of the ion enclosed is meant. It is desired to produce a high hydroxyl concentration relative to the carbonate, but this is attained only at low total concentration, since the influence of the hydroxyl ion tending to reverse the reaction is proportional to the square of its concentration while the carbonate is only in the first power. In fact in dilute solutions the reaction goes almost quantitatively to the right, but at 20° Tw. the conversion is only about 85 per cent, and at higher concentrations it is even less. These facts have been used as text-book illustration of the industrial application of the law of mass action, but it is not the incompleteness of the conversion which is the reason for the technical use of dilute solutions, since any unconverted carbonate is recovered on concentrating. It is rather the fact that the precipitated carbonate requires, in any case, large amounts of water for washing, which must be evaporated. Since this water, if used in the original batch, gives the advantage of high causticization, with no disadvantages, it is of course employed.

In large plants, the dilute caustic solution, after settling, is concentrated in multiple-effect systems to a density of 60° Tw., at which point the other salts, such as sodium carbonate or chloride, still dissolved in the liquor, begin to crystallize; the liquor is then run into cast-iron kettles (" pots "), which are heated by direct fire, and the last of the water evaporated, when caustic soda remains as a fused mass. The salts separated during the evaporation are raked out. Some nitre may be added, or air blown in, to complete the oxidation of any thiosulphate to normal sulphate, which remains in the caustic, reducing its strength. In small works the dilute liquor is evaporated directly in the iron pots. For strong caustic zinc oxide is often added to remove the sulphide from the tank liquors. The precipitated zinc sulphide is removed by settling and calcined to reconvert it into oxide.

The fused caustic soda is run directly into the sheet-iron drums in which it is sold. These are sealed as soon as cold, to prevent the absorption of moisture by the caustic.

Loewig's process * for caustic soda depends on the formation of sodium ferrate ($Na_2Fe_2O_4$), which is then decomposed with water. The soda liquors are mixed with ferric oxide, and the mass evaporated to dryness and calcined at a bright red heat, usually in a revolving furnace. By the calcination, a reaction between the sodium carbonate and the iron oxide is brought about, carbon dioxide escaping and sodium ferrate remaining in the furnace. The mass is washed with cold water until all soluble matter is removed; then water at 90° C. is run over the sodium ferrate, by which it is decomposed, caustic soda formed, and iron oxide regenerated; the last is returned to the calcining process. The ferric oxide used is a natural iron ore, very clean and free from silica or other impurities; that made by calcining a precipitated ferric hydroxide is not well adapted to the process, as it gives a product difficult to lixiviate. The density of the resulting solution of caustic is about 62° Tw. (1.31 sp. gr.), and so less evaporation is necessary than in the lime process, where the density is only 15° or 20° Tw. Moreover, there are no other salts present, such as sulphate, thiosulphate, sulphide, or chloride, and the product is purer than that yielded by the lime process. But Loewig's process is not so well adapted to use with the Leblanc soda-ash, because the tank liquors must be evaporated to dryness before calcining the ferric oxide and sodium carbonate mixture, and the sodium carbonate must be

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* German Patent, No. 1650, Dec. 21, 1877. J. Soc. Chem. Ind., **1887**, 438. Konrad W. Jurisch, Die Fabrikation von Schwefelsaurer Thonerde, p. 13.

pure. The process may be advantageously used with ammonia soda-ash, since this is obtained directly as a solid and no evaporation is necessary.

Caustic soda of better quality can be made by Loewig's method, but it cannot be made so cheaply as by the use of lime with the tank liquor of the Leblanc process, especially in small works where the output is irregular and uncertain. For although there is no expense for lime, and less fuel is used for evaporation in the former method, yet an extensive and somewhat costly plant, designed to reduce labor to the minimum, is required, and considerable fuel is needed for the calcination.

For the preparation of caustic soda by electrolysis of brine, see p. 124.

TREATMENT OF TANK WASTE

In the Leblanc process nearly all the sulphur of the salt-cake remains in the "tank waste" or residue from the lixiviation of the black-ash. The average composition of this waste is shown in the following tables: —

COMPOSITION OF TANK WASTE

FRESH*

	REVOLVER	HAND FURNACE	HAND FURNACE
Water	29.20	29.96	30.40
Na_2CO_3	3.16	1.97	1.63
$CaCO_3$	21.19	36.92	38.81
$Ca(OH)_2$	Trace	8.85	9.53
CaS	56.89	37.90	35.12
CaS_2O_3	1.07	0.68	1.49
$CaSO_3$	Trace	——	——
$CaSO_4$	Trace	0.20	——
$CaSiO_3$	3.53	1.34	1.21
Coal	7.20	7.04	6.27
Al_2O_3	1.02	0.37	0.13
FeS	1.65	2.44	2.76
Sand	2.82	1.79	2.61

* Chance, J. Soc. Chem. Ind., **1882**, p. 266.

COMPOSITION OF WEATHERED TANK WASTE

60 YEARS OLD*

	19 INCHES BELOW THE SURFACE	5 FEET BELOW THE SURFACE
$CaCO_3$	53.14	52.77
$CaSO_4$	17.87	11.11
$CaSO_3$	0.65	3.10
CaS_2O_3	0.80	2.89
CaS	——	0.04
Insoluble in HCl	10.10	10.91
Al_2O_3, Fe_2O_3, etc.	7.18	11.04
Water	10.26	8.14

When fresh waste is thrown on the dump, the changes produced by weathering cause great nuisance. The air is contaminated by the hydrogen sulphide and sulphur dioxide liberated, and the soluble polysulphides of calcium and sodium formed are dissolved by rain-water, making the objectionable "**yellow liquors**," which run into streams and sewers.

In fresh waste the sulphur is chiefly in the form of sulphide and thiosulphate of calcium, but in weathered material these have been converted by oxidation into sulphate and sulphite, which in themselves cause no trouble except by their bulk.

The simplest method of disposing of waste is to send it out to sea and dump it, if the works are so situated that this is convenient; or, if this is impossible, to spread it evenly and beat it down hard to prevent as far as possible the infiltration of rain. But since the sulphur thus lost every year represents an enormous money value, many attempts have been made to recover it in an available form. Of the numerous processes proposed only three need be considered here.

In **Mond's process** the waste was treated directly in the lixiviating tanks by blowing air or chimney gases through the wet mass. This oxidized the waste according to the following reactions: —

1) $CaS + 2 H_2O = Ca(SH)_2 + Ca(OH)_2$.

2) $Ca(SH)_2 + 4 O = CaS_2O_3 + H_2O$.

But the hydration and oxidation processes were slow, and after a time it was necessary to lixiviate the mass, blow in air, and again lixiviate. By several lixiviations the calcium sulphydrate and thiosulphate were dissolved, forming "yellow

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* Lunge, Sulphuric Acid and Alkali, 2d ed., Vol. II, p. 815.

liquors." To recover the sulphur these were treated while still hot with dilute hydrochloric acid, the following reactions * taking place : —

3) $CaS_2O_3 + 2\ HCl = CaCl_2 + H_2O + SO_2 + S.$

4) $Ca(SH)_2 + 2\ HCl = CaCl_2 + 2\ H_2S.$

In the presence of the calcium chloride solution the two gases, sulphur dioxide and hydrogen sulphide, react upon each other, forming water and free sulphur : —

5) $2\ H_2S + SO_2 = 2\ H_2O + 3\ S.$

The hydration and oxidation process was so controlled that the proportion of thiosulphate to sulphydrate yielded one molecule of sulphur dioxide to two molecules of hydrogen sulphide. When properly worked very little escape of hydrogen sulphide occurred. The precipitated sulphur was filtered from the solution of calcium chloride which went to waste. The sulphur was then refined.

This process recovered about 60 per cent of the total sulphur, but it consumed a great deal of hydrochloric acid, which now has considerable value, and some sulphur was lost, owing to the formation of sulphate and sulphite of calcium, which, being insoluble, were left in the residue after lixiviation. The process is not now in use.

Schaffner and **Helbig's** † process depends upon the reaction between magnesium chloride and calcium sulphide in a boiling solution : —

1) $CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S.$

2) $MgO + CaCl_2 + CO_2 = CaCO_3 + MgCl_2.$

The second reaction was employed to recover the magnesium chloride, but the calcium carbonate formed was too impure for use in the black-ash furnace. The hydrogen sulphide set free was pure, and could be utilized by burning it with air, and conveying the resulting sulphur dioxide into the lead chambers of the sulphuric acid plant ; or the sulphide could be decomposed with sulphur dioxide, according to the method given above, reaction (5). Lime-kiln gases were used for the carbon dioxide in reaction (2). This process was not a commercial success.

The **Chance-Claus process** ‡ appears to be the only successful method of recovering sulphur on a large scale, and even this has not fully realized the original expectations of its promoters. The reactions of the process were proposed by Gossage in 1837, but although he worked on the idea for thirty years, and spent a large fortune in experimenting, he failed to make it a success.

The following are the reactions involved : —

1) $2\ CaS + H_2O + CO_2 = CaCO_3 + Ca(SH)_2.$

2) $Ca(SH)_2 + H_2O + CO_2 = CaCO_3 + 2\ H_2S.$

3) $CaS + H_2S = Ca(SH)_2.$

A carbon dioxide containing at least 30 per cent CO_2 is necessary and is obtained in a special form of lime kiln. The tank waste is

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* Mactear proposed to use the same reactions for the treatment of the drainage from old waste heaps, which were creating a nuisance.

† J. Soc. Chem. Ind., **1882**, 264.

‡ *Ibid.*, **1888**, 162.

diluted with water and treated by counter-current system, with the carbon dioxide gas, in a series of seven cast-iron cylinders, so arranged that one may be emptied and recharged while the others are in uninterrupted operation. Since hydrogen sulphide and carbon dioxide are acids nearly equal in strength, no hydrogen sulphide is set free till the calcium sulphide is converted to a mixture of calcium sulphydrate and bicarbonate. The gas entering a freshly filled tank is largely hydrogen sulphide and nitrogen; the former is absorbed as shown in reaction (3), while nitrogen escapes, until the calcium sulphide is nearly all converted to sulphydrate. Reaction (2) then progresses and the content of hydrogen sulphide in the gas leaving the tank rises rapidly and it is collected in a gasometer. As the treatment proceeds, the hydrogen sulphide content of the gas falls off while the percentage of CO_2 rises correspondingly. When the hydrogen sulphide is below 30 per cent, the gases are diverted to a freshly filled tank, where reaction (3) takes place.

The hydrogen sulphide collected in the gasometer, together with air, is passed through the **Claus sulphur kiln** (Fig. 49), in which the reaction

$$H_2S + O = H_2O + S$$

takes place. On the grate (A) is a layer of broken fire-brick covered with about 12 inches of ferric oxide to serve as a catalyzer of the reaction. The mixture of hydrogen sulphide and air is led into the kiln at (B), and made to pass through the ferric oxide (previously heated to a dull red); this causes the reaction to take place, and at the same time the heat generated by the reaction is sufficient to keep the iron oxide at the proper temperature, after being once well started. Sulphur, nitrogen, and water vapor escape from the kiln. The sulphur vapor condenses in the chamber (D) as liquid sulphur, and in (E) as flowers of sulphur, while the steam and nitrogen, together with a small quantity of sulphur dioxide, pass on to a condensing tower, where they are brought into contact with limestone over which water is dripping, to retain the sulphur dioxide. When working well, this

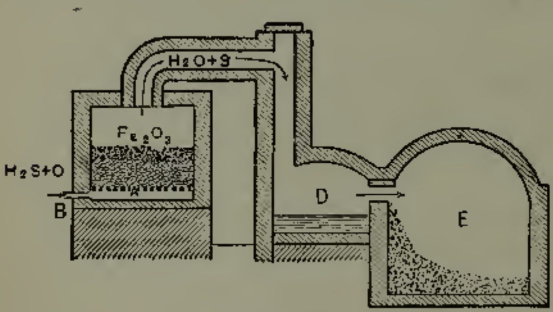

FIG. 49.

process recovers about 85 per cent of the sulphur. According to Lunge, the form of the kiln has been recently modified, but the principle of the process is unchanged. The water in the storage gasometer is usually covered with a layer of petroleum oil, to prevent the absorption of the hydrogen sulphide by the water.

The process is not very lucrative when the price of sulphur is low, but since it reduces the nuisance created by the alkali waste, and yields very pure sulphur, a number of English firms employ it. In 1893, over 30 plants were in operation in England, and more than 35,000 tons of sulphur recovered.

For the Parnell and Simpson * process for utilizing alkali waste, see p. 111.

THE AMMONIA SODA PROCESS

The reactions involved in the ammonia soda process were discovered by H. G. Dyar and J. Hemming, about 1838, but owing to the mechanical difficulties, its practical success was not thoroughly established until 1873. In 1863, Ernest Solvay, a Belgian, constructed an apparatus which has led to an enormous development of the industry, by which one-half of the world's supply of soda is now made. Its advantages lie in the strength and purity of its products and the absence of troublesome by-products, such as "tank waste." But it does not yield chlorine nor hydrochloric acid, all the former going to waste as calcium chloride.

The ammonia soda process depends upon the fact that sodium bicarbonate is but slightly soluble in a cold ammoniacal solution of common salt. The technical success of the process depends chiefly on the *proper regulation of the temperature* during the precipitation, and on the capacity of the works to handle large quantities of gases and liquids. As far as possible, manual labor must be avoided, and the products moved and treated in solution or in suspension. The reactions are as follows: —

1) $NaCl + NH_3 + H_2O + CO_2 = NH_4Cl + NaHCO_3.$

2) $2\ NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\ H_2O + 2\ NH_3.$

The first equation is the chief one; the second represents the recovery of the ammonia, and is essential to the commercial success of the process.

The salt is used as a very concentrated brine, which has been

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* J. Soc. Chem. Ind., **1889**, 11.

purified from iron, silica, magnesia, etc.; it is then saturated with ammonia gas, obtained from gas liquors, or by the recovery process according to equation (2). The carbon dioxide is obtained partly from lime kilns and partly from the calcination of the bicarbonate to form the normal carbonate (p. 110). It must contain at least 30 per cent of CO_2, and is prepared in special forms of continuous lime kilns. The lime resulting is used in the recovery of the ammonia (reaction 2), and for making caustic soda; the lime-kiln gases are cooled, and the sulphur dioxide removed, by washing in water before they pass into the carbonating towers (see below).

The brine is contained in a tank, under the perforated bottom of which the ammonia gas is introduced, and rising through the liquor, is rapidly absorbed. The heat evolved by the absorption is taken up by cold water circulating in coils. When saturated, the ammoniacal brine is pumped into a receiving and settling tank, from which it is delivered to the "**carbonating tower**" (Fig. 50).[*] This is from 50 to 65 feet high, built of cast-iron rings or segments (A, A), each about 3.5 feet high and 6 feet in diameter. At the bottom of each segment is a flat plate having a large hole in the centre. Above each plate is a dome-shaped diaphragm (D) perforated with a great number of small holes. In modern works a system of pipes passes through each segment, as shown at (B, B); in these, cold water is kept flowing, thus counteracting the heat generated by the chemical action. The ammoniacal brine is forced under pressure through the pipe (P), entering a little above the middle of the tower, which is nearly filled with brine. By this arrangement, any free ammonia in the brine, which would be swept away by the stream of

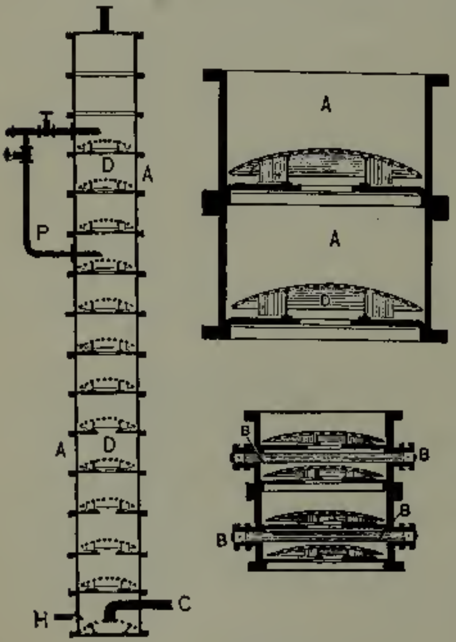

FIG. 50.

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[*] After Lunge.

gases passing up through the tower, is taken up by the carbon dioxide in the upper part of the tower. The carbon dioxide, having been previously well cooled, is forced through the pipe (C), entering under the lowest dome, and rising in small bubbles through the perforations in each dome, comes into intimate contact with the ammoniacal brine. The bicarbonate of sodium thus precipitated gradually works its way down through the tower. A thick, milky liquid, containing the bicarbonate in suspension, and ammonium chloride and common salt in solution, is drawn off through (H) at the bottom.

After a tower has been in use for some days, the holes in the domes become clogged with a deposit of bicarbonate crystals, which prevent the free passage of the gases. Consequently, every ten days or two weeks the liquid must be drawn out and the crystals dissolved by filling the tower with hot water or steam. The tower must be cooled before starting the process anew. As a rule, several towers are employed, so that one may be cleaned and cooled without interrupting the operation.

The gases escaping from the top of the tower, consisting principally of nitrogen, carbon dioxide, and some ammonia, are passed through scrubbers (p. 319), one of which contains brine, which afterwards goes to the ammonia saturating tank; in the other is dilute sulphuric acid, to absorb the small amount of ammonia which would otherwise be lost. The carbon dioxide and nitrogen are allowed to escape. The towers are run with the view to the utilization of all the ammonia possible, even though there is considerable loss of salt and carbon dioxide; usually about one-fourth of the salt remains undecomposed.

It is now customary to place a smaller carbonating tower in connection with the large one; in the former the brine is first treated with carbon dioxide and the ammonia converted to neutral carbonate $(NH_4)_2CO_3$; then the brine is pumped into the large carbonating tower, where it meets more carbon dioxide, and the bicarbonate is formed, causing the precipitation of the sodium bicarbonate. More heat is liberated in the formation of the neutral carbonate of ammonia than in its conversion to the bicarbonate, hence the temperature of the precipitation is more easily controlled when two towers are used, and less free ammonia escapes with the waste gases.

A temperature of about 35° C. is most favorable to the formation of a granular or crystalline precipitate of bicarbonate, and also to the most complete utilization of the ammonia. At higher temperatures, too much bicarbonate remains dissolved in the liquor; at lower temperatures, there is a tendency to the crystallization of ammonium acid carbonate and ammonium chloride, while the bicarbonate separates as a very fine precipitate, which is difficult to filter from the liquor.

The milky liquor from the bottom of the tower, containing the sodium bicarbonate in suspension, is filtered on sand filters (p. 19) connected with a vacuum pump; or better, it is run into centrifugal machines (p. 18), which afford more rapid and complete separation of the mother-liquor. The bicarbonate is then washed with water, to remove as much of the sodium and ammonium chlorides as possible. The mother-liquors and wash waters go to the ammonia recovery process.

The sodium bicarbonate is then calcined in large covered cast-iron pans or ovens; this converts the acid salt into soda-ash, and drives out any ammonia or moisture still in the mass. The following is the reaction: —

$$2\,NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The fumes are passed through coolers and scrubbers to remove ammonia; the concentrated carbon dioxide remaining is pumped into the carbonating towers. The ammonia liquors go to the ammonia stills.

A modification of the **Thêlen pan** (Fig. 48, p. 100) is sometimes used for this calcining. A gas-tight cover is placed over the pan, and the scrapers pass back and forth over the pan bottom, being moved by a connecting rod and crank. The gases and steam pass off through a pipe set in the cover. In practice, it has been found best to leave the mass in this pan only until all the ammonia and about 75 per cent of the carbon dioxide of the bicarbonate have been expelled; the calcination is completed in a reverberatory furnace.

The product of the calcination is called **soda-ash**; it is often very pure, containing only a trace of salt and a little bicarbonate, and is free from caustic soda, sulphide, and sulphate. But its density is only 0.8, while that of the Leblanc product is 1.2. This is disadvantageous, owing to the larger packages needed for a given weight and to the mechanical loss incurred in operations where the soda-ash is exposed to a strong draught of air. In order to increase the density, it is sometimes subjected to a second heating in a reverberatory (revolving) furnace.

The second reaction, on p. 107, is that on which the recovery of the ammonia depends. The liquid in which the bicarbonate of soda was suspended contains undecomposed salt, ammonium chloride, and ammonium carbonate. It is passed through an ammonia still, usually a tall column or dephlegmator (p. 11). Steam is admitted at the bottom of the apparatus, and bubbling up through the liquid, decomposes the ammonium carbonate into ammonia, carbon dioxide, and water; the ammonium chloride passes down into the lower part of the tower, or the still proper, where it is decomposed by "milk of lime." The ammonia set free is cooled and used to saturate the brine. The calcium chloride formed remains in solution, and together with the excess of salt, goes to waste. Some calcium chloride is recovered and finds use as a dust-layer and binder, on macadam and dirt roads. (For various proposals to utilize the waste calcium chloride for the production of hydrochloric acid and chlorine, see p. 122.)

The damp bicarbonate is dried in an atmosphere of carbon dioxide, at a temperature of about 90° C.; this prevents decomposition of the sodium bicarbonate, while the ammonium bicarbonate is decomposed, the vapors passing to the scrubbers, where the ammonia is recovered. A considerable quantity of the bicarbonate of soda is sold directly to the manufacturers of baking powder and the poorer grades to the soda-water makers.

Caustic soda can be made stronger and purer from ammonia soda-ash than from Leblanc ash, and the process is not essentially different, except that no treatment to remove sulphur is necessary; but it cannot be made so cheaply as from the "red liquors" or the "tank liquors" of the Leblanc process. If pure lime is used for causticizing ammonia soda-ash, the product is better than in the case of the Leblanc ash, as it is free from sulphur, alumina, etc.

Loewig's process (p. 102) appears especially suited for causticizing ammonia soda-ash, since it requires an ash free from silica.

H. A. Frasch devised a method for caustic soda in which nickel hydroxide acts upon sodium chloride in the presence of an excess of ammonia. A double nickel-ammonium chloride $[Ni(NH_3)_2Cl_2 + 4\ NH_3]$ separates as a violet crystalline mass, leaving caustic soda in the solution. This double salt is hygroscopic, dissolves with a blue color, and evolves some ammonia. The nickel and ammonia may be recovered by treating the salt with milk of lime.

The **Parnell and Simpson process** * was expected to solve the problem of the Leblanc "alkali waste," but it has not fulfilled the hopes of its promoters. It was proposed to work the two leading soda processes in combination. The alkali waste of the Leblanc

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* J. Soc. Chem. Ind., **1889**, 11.

process is boiled in the ammonium chloride liquor from the ammonia process, and the vapors of ammonia gas and of ammonium sulphide liberated are led directly into a brine solution in the saturating tank. The calcium chloride liquor goes to waste. The ammoniacal solution of brine and ammonium sulphide produced is sent to a carbonating tower, similar to that described on p. 108, and treated with carbon dioxide, as in the ammonia-soda process. Sodium bicarbonate is precipitated and hydrogen sulphide set free, which may be treated in a Claus kiln (p. 106), or burned to sulphur dioxide to use for sulphuric acid. The reactions involved are as follows: —

1) $CaS + 2\,NH_4Cl = (NH_4)_2S + CaCl_2$.*
2) $(NH_4)_2S + CO_2 + H_2O = NH_4HCO_3 + NH_4HS$.
3) $NH_4HS + CO_2 + H_2O = NH_4HCO_3 + H_2S$.
4) $NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl$.

The last three reactions take place † simultaneously in the carbonating tower; the hydrogen sulphide generated goes to the sulphur recovery and the ammonium chloride solution carrying sodium bicarbonate in suspension is drawn out and filtered. The ammonium chloride liquor is returned to the process.

The conversion of salt into sodium carbonate by any method involves an endothermic reaction in some part of the process. Thus energy must be expended, necessitating the use of fuel. In the Leblanc process, the fuel expenditure is large in carrying out the reactions in the salt-cake and the black-ash furnaces. But much of the expended energy reappears in the hydrochloric acid, the principal by-product.

In the ammonia process the principal reactions are exothermic, but some fuel is consumed by the calcination of the precipitated bicarbonate and in the preparation of the quicklime used in the ammonia

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* Equation (1) does not exactly represent the facts, as some polysulphides are present in the tank waste.

† According to Lunge, Sulphuric Acid and Alkali, 3d ed., Vol. III, p. 204, the sodium bicarbonate is formed by agitating the brine with crystallized ammonium bicarbonate, the latter being obtained by saturating the ammonium sulphide solution with carbon dioxide. The carbon dioxide, which must be very pure and concentrated, is made by heating ammonium bicarbonate crystals to 74° C., in a retort, CO_2, steam, and NH_3 passing off. By scrubbing (p. 319), the carbon dioxide is obtained pure.

Ammonium bicarbonate is also prepared by passing lime-kiln gases into a solution of ammonia or neutral ammonium carbonate, and then cooling it to crystallize the bicarbonate.

recovery and for generating carbon dioxide. Although less fuel is used than in the Leblanc process, the practical economy of the ammonia process is not so great as would at first appear; for all the chlorine is lost, together with much of the original salt used. As a method for soda-ash it is far superior to the Leblanc, but until a practical process for the cheap production of chlorine is discovered, the latter will continue to be an extensive industry.

THE CRYOLITE SODA PROCESS

Cryolite is a double fluoride of sodium and aluminum, found as a mineral in southern Greenland. As no other important deposit has been found, the supply is limited, and only two or three manufactories using this process were established, — one of them in this country. The reactions involved are as follows: —

1) $AlF_3 \cdot 3\,NaF + 3\,CaCO_3 = NaAlO_2 + Na_2O + 3\,CaF_2 + 3\,CO_2$.
2) $NaAlO_2 + Na_2O = Na_3AlO_3$.
3) $2\,Na_3AlO_3 + 3\,H_2O + 3\,CO_2 = 3\,Na_2CO_3 + 2\,Al(OH)_3$.

The ground cryolite is mixed with powdered limestone, and calcined at a red heat. Carbon dioxide escapes, and a mixture of calcium fluoride, sodium oxide, and sodium aluminate remains. On lixiviating this mixture with water, another sodium aluminate is formed and goes into solution, leaving the calcium fluoride as an insoluble residue. The solution of sodium aluminate is then decomposed according to the third reaction, by passing into it purified lime-kiln gases, or the furnace gases of the calcining operation. Hydrated alumina is precipitated, while sodium carbonate remains in solution. Sal-soda may be made by evaporating the solution, and was formerly the chief source of bicarbonate for culinary and medicinal purposes. If carried to complete dryness and calcined, a high grade of soda-ash is obtained. By causticizing, it yields a very excellent caustic.

The by-products aluminum hydroxide and calcium fluoride are used in the alum and glass industries respectively.

Many other processes for the manufacture of soda from salt have been proposed, but none of them are now of any commercial importance. A small amount of soda is still made from **kelp** or **varec**, which is the ash of seaweeds.

A new process for making soda has been proposed,* which is interesting, but has not as yet been placed on a practical basis. Salt-

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* J. Soc. Chem. Ind., **1895**, 933.

cake is made from salt by the Hargreaves process (p. 92); then in the same cylinder and at the same temperature, it is treated with water gas. This reduces the salt-cake to sodium sulphide, while water, carbon monoxide, and hydrogen escape. These vapors are cooled, the water condensed, and the mixture of gases burned, the products of combustion, carbon dioxide and water, passing into the cylinders containing the sodium sulphide. Hydrogen sulphide and sodium carbonate are formed, and as the temperature is much above 100° C., no water can combine with the carbonate. The hydrogen sulphide is burned to sulphur dioxide, and the latter returned to the Hargreaves process. The reactions involved are as follows: —

1) $2\,NaCl + SO_2 + H_2O + O = Na_2SO\ + 2\,HCl.$

2) $Na_2SO\ + 5\,CO + 5\,H_2 = Na_2S + 4\,H_2O + 5\,CO + H_2.$

3) $CO + H_2 + O_2 = CO_2 + H_2O.$

4) $Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S.$

5) $H_2S + 3\,O = H_2O + SO_2.$

This process seems to offer several advantages, viz.: —

1. Cheap materials.

2. Small outlay for labor, — the materials not being handled from the time the salt is charged into the cylinders until the soda-ash is raked out.

3. No waste products nor nuisance.

4. The temperature constantly decreases, being highest when the furnace is charged and lowest when the soda-ash is finished.

5. The process yields hydrochloric acid which can be utilized.

For the methods of producing caustic soda and chlorine by electrolysis of brine, see Chlorine, p. 124.

REFERENCES

Berichte ueber die Entwickelung der chemischen Industrie. A. W. Hoffmann, Vol. I, 418. (1875.)
History, Products, and Processes of the Alkali Trade. Charles T. Kingzett, London, 1877. (Longmans.)
Manual of Alkali Trade. John Lomas, London. (Crosby, Lockwood Co.)
Die Fabrikation der Soda nach dem Ammoniak-Verfahren. H. Schreib, Berlin, 1905.
Sulphuric Acid and Alkali. G. Lunge, 3d ed., Vols. II, 1909, III, 1911. (D. Van Nostrand Co., New York.)
J. Soc. Chem. Ind: —
1883, 405, Walter Weldon. **1885**, 527, Ludwig Mond. **1886**, 412, E. K. Muspratt.
1887, 416, Watson Smith. **1888**, 162, Alexander Chance. **1889**, 11, E. Parnell.

CHLORINE INDUSTRY

Chlorine is extensively used in the arts as a bleaching and oxidizing agent. It is chiefly employed in the form of a solution of "bleaching powder" or "chloride of lime," which contains calcium hypochlorite, and as chlorates or hypochlorites of the alkali metals. Liquid chlorine, compressed in steel cylinders, has recently become an article of commerce, and this form of shipment may be extended in the future.

Practically all the chlorine used in the arts must be derived from the chlorides of sodium, potassium, or magnesium, which are found more or less abundantly in nature. A large part of the hydrochloric acid made from salt (p. 88) is used for making chlorine. Since this acid is the chief by-product of the Leblanc process, a plant for making bleaching powder is always a part of those works.

The important methods of making chlorine from the acid may be considered under two heads: those using manganese oxides for decomposing the acid, and those not using manganese for this purpose.

The function of manganese is to oxidize the hydrogen of the acid, forming water and liberating the chlorine. At the same time, the manganese is converted into chloride, and being expensive, its recovery in a form that permits of its return to the process is essential.

The oxides of manganese are found in nature as pyrolusite (MnO_2), braunite (Mn_2O_3), manganite ($Mn_2O_3 \cdot H_2O$), hausmannite (Mn_3O_4), wad, and psilomelane, the last two of indefinite composition. The reactions occurring when manganese oxides are treated with hydrochloric acid are as follows: —

1) $MnO + 2\,HCl = MnCl_2 + H_2O$.

2) $MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + 2\,Cl$.

3) $Mn_2O_3 + 6\,HCl = 2\,MnCl_2 + 3\,H_2O + 2\,Cl$.

4) $Mn_3O_4 + 8\,HCl = 3\,MnCl_2 + 4\,H_2O + 2\,Cl$.

Thus it is readily seen that with pyrolusite, less acid is necessary for a given yield of chlorine, and a smaller quantity of manganous chloride must be treated to recover the manganese. This ore is purchased according to its content of MnO_2, which is estimated by determining the "available" oxygen. The presence of iron oxides, silica, calcium carbonate, etc., is disadvantageous.

In small works, especially where no attempt is made to recover the manganese, the process is carried on in simple stills of earthen-

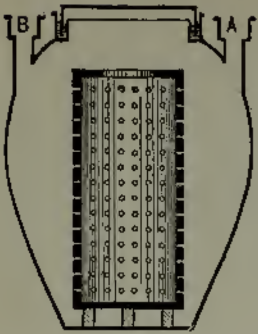

Fig. 51.

ware or sandstone. The earthenware stills (Fig. 51) * are cheap, but of limited capacity. They are heated by blowing free steam into the wooden casing in which they are set. The pyrolusite is put into the central perforated cylinder, and the acid runs through the pipe (A), chlorine escaping at (B). Sandstone stills (Fig. 52) * are made from single blocks of sandstone, or built up of slabs, the joints being made tight by a rubber packing, or by a lute of clay and linseed oil. The pyrolusite rests on a false bottom (A), and the acid is run in through (B), while steam is blown in through the sandstone pipe (C). Chlorine escapes through (D). These stills are larger than the earthenware ones, but do not utilize the acid so completely.

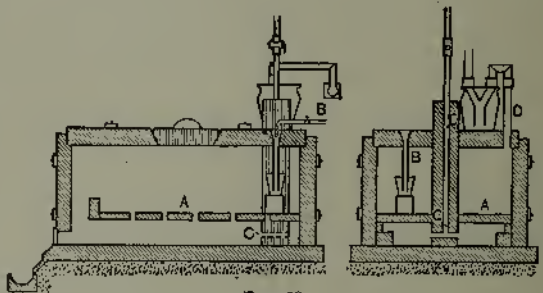

Fig. 52.

The chlorine is conducted through pipes of lead or earthenware, or tubes coated with bakelite enamel. Since valves in these pipes are rapidly corroded, a device shown in Fig. 53 * is used to shut off the flow of gas. A U-shaped bend is made in the pipe, and a small flexible tube attached at the lowest point of the U, connecting it with the vessel (A), filled with water. By raising (A), the water flows into and fills the U-pipe to the line (CD), cutting off the flow of gas. By lowering (A) to (A′), the water runs out of the U, and the flow of gas is uninterrupted.

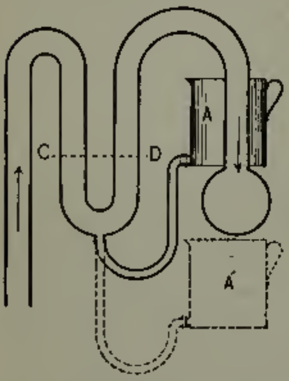

Fig. 53.

The liquor remaining in the still contains much free acid, manganous chloride, ferric chloride, etc. It continues to evolve some chlorine for a long time, and is a

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* After Lunge.

very offensive and troublesome material to dispose of, since it pollutes the air, or the streams, into which it passes.

Of the many attempts to recover the manganese, the two following are the most important: —

By **Dunlop's method**, the "still liquor" is neutralized cold, with powdered limestone, until all free acid is removed and the iron precipitated. The clear solution of manganous and calcium chlorides is then mixed with a carefully determined quantity of powdered limestone or chalk, and heated *under pressure* by steam. This precipitates the manganese as carbonate, which is settled, and the solution of calcium chloride drawn off. The manganous carbonate is washed and then calcined at about 300° C. in a retort, while water spray and a current of air are introduced. This produces a mixture of MnO_2, MnO, Mn_2O_3, etc., containing about 70 per cent of the dioxide. The process requires an expensive plant and consumes much fuel.

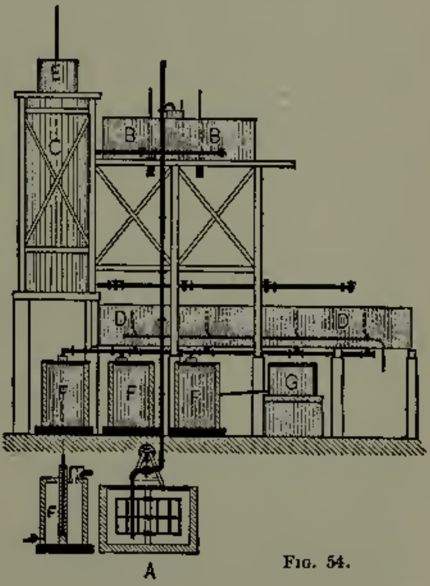

Fig. 54.

The **Weldon process** * for manganese recovery is the most successful, and is in use in many large works, since it furnishes a continuous process for chlorine making and manganese recovery. The "still liquors" are neutralized with just sufficient powdered limestone or chalk to remove free acid and precipitate the iron. This is done in the tank (A) (Fig. 54), † provided with a stirrer. The mixture is then pumped into settling tanks (B, B), where the precipitate deposits. The clear solution of manganous and calcium chlorides is then drawn into the "oxidizers" (C), where steam is blown in to heat it to 55° C. Milk of lime made from pure lime, especially free from magnesia, is added from (E) until tests show that the manganese is all precipitated; meanwhile air is slowly forced into (C). The quantity of "milk" used is noted, and then from one-half to one-

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* J. Soc. Chem. Ind., **1885**, 525.

† After Lunge.

quarter more is added, and the air blast turned on at full strength. This addition of an excess of lime is necessary to hasten and complete the conversion of manganous hydroxide into the peroxide, and to prevent the formation of Mn_3O_4 (" red batch "). The total quantity of lime used should be such that the precipitate formed during the blowing contains approximately two molecules of manganese peroxide to one of calcium oxide. This is the so-called " acid calcium manganite " $(CaO \cdot MnO_2) + (MnO \cdot MnO_2)$, a mixture of manganites of calcium and manganese. It forms a thin, slimy, black mass, and is called "**Weldon mud.**" By adding a little more neutralized " still liquors " during the " blowing," some of the calcium oxide in the calcium manganite can be replaced by manganese from the manganous chloride of these liquors.

The calcium chloride liquor, in which the mud is suspended, is run into settling tanks (D, D), from which the supernatant solution is drawn off as waste. The Weldon mud is then run into the chlorine stills (F, F) as a thin paste; if of good quality, it contains about 80 per cent of its manganese as MnO_2, and owing to its fine state of division, is readily decomposed by dilute hydrochloric acid.

A small loss of manganese occurs in the precipitate from the first neutralization with marble or chalk dust; this loss is made up by decomposing some pyrolusite with hydrochloric acid in a small still (G), and adding this liquor to that from the stills (F, F).

The Weldon process works continuously and almost automatically, the materials being handled by pumps as liquids or slimes. It is also very rapid, producing large amounts of chlorine, with but slight loss (2 to 3 per cent) of manganese oxide. But even at its best, only about one-third of the chlorine of the hydrochloric acid is obtained as gas, the remainder going to waste as calcium chloride in the liquor from the oxidizers.

Deacon's process * is the most successful chemical method of producing chlorine without the use of manganese. It depends on the oxidation of hydrochloric acid gas by the oxygen of the air. This is done in the presence of certain metallic salts, which may act as " contact " substances, or as carriers of oxygen from the air to the acid, the apparent reaction being: —

$$4\,HCl + O_2 = 2\,H_2O + 2\,Cl_2.$$

The most satisfactory " contact " or " catalytic " substance for this purpose is copper chloride. When cupric chloride is heated to 400°

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* Chemical News **22 (1870)**, 157.

C., it dissociates into cuprous chloride and free chlorine. Then, on exposing the cuprous chloride to oxygen, cupric oxide is formed and more chlorine set free. But the cupric oxide, reacting with hydrochloric acid gas, forms water and cupric chloride. The following are the reactions involved: —

1) $2\ CuCl_2 = Cu_2Cl_2 + Cl_2.$

2) $Cu_2Cl_2 + O_2 = 2\ CuO + Cl_2.$

3) $2\ CuO + 4\ HCl = 2\ CuCl_2 + 2\ H_2O.$

Thus the catalytic substance is regenerated and the cycle of changes begins anew.

During the dissociation of cupric chloride 32 Calories is absorbed, but in the other reactions 60.4 Calories is evolved. Hence there is a gain of 28.4 Calories, and *theoretically* the process once under way no addition of heat is needed. But, in fact, owing to losses by radiation, convection, and conduction, some heat must be supplied, and the mixture of air and hydrochloric acid gas is heated to 400° C. before admitting it to the "decomposers." Since the reaction between the hydrochloric acid and the oxygen is reversible, an equilibrium is established, and so all of the chlorine is not recovered.

The plant for the process (Fig. 55) * is quite extensive. The gases from the salt-cake pan (A),† together with air, are passed through cooling pipes and drying tower (B) to condense moisture; then they go through the "superheater" (C), where the temperature is raised to 400° C. The hot gases then pass into the "decomposer" (D), a tall cast-iron cylinder, containing bits of brick or other porous material which have been soaked in a solution of cupric chloride. Here the above reactions take place, and the resulting mixture of chlorine, hydrochloric acid, nitrogen, steam, and oxygen, passes through a condensing appa-

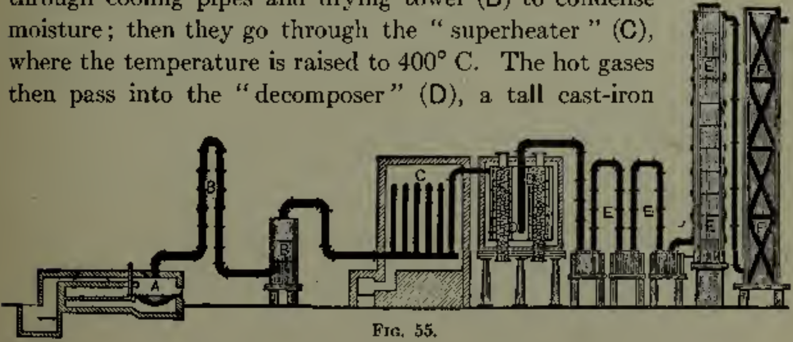

Fig. 55.

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* After Lunge.

† Roaster gas is too dilute and impure.

ratus (E, E) to remove the hydrochloric acid, and then through a coke tower (F, F) sprinkled with concentrated sulphuric acid to remove all the moisture; finally, the dry chlorine gas (with the nitrogen and oxygen) goes to the chambers where bleaching powder is made (p. 132).

The catalytic substance in the decomposer becomes inactive after a time (it seldom lasts more than four months) and must be replaced by fresh material. To accomplish this without interrupting the process the decomposers are built in separate compartments, each holding about six tons of broken brick; every two weeks one compartment is emptied and recharged without discontinuing the flow of gas through the others. This loss of activity in the catalytic substance is attributed * to the presence of sulphuric acid in the gases from the salt-cake furnace. To overcome this difficulty, Hasenclever devised a method † by which an aqueous solution of impure hydrochloric acid, made in the *bombonnes* and coke towers, is run into hot, concentrated sulphuric acid (1.42° Tw.) while a blast of air is forced through the mixture. The sulphuric acid absorbs the water and generates *pure HCl gas,* which mixes with the air in proper proportion for use in the decomposer of Deacon's process. By this method, 84 per cent of the hydrochloric acid gas is decomposed according to the reaction: —

$$4\ HCl + O_2 = 2\ H_2O + 2\ Cl_2.$$

The diluted sulphuric acid is concentrated and returned to the process. The dilute hydrochloric acid which passes through the apparatus is recovered by washing the chlorine gas, and is mixed with the strong acid from the roasters.

Owing to the admixture of nitrogen with the chlorine, the latter is weaker than that furnished by the Weldon process and for making bleaching powder a special form of absorption chamber must be used.

When the hydrochloric acid gas is taken directly from the salt-cake pan or from the muffle furnace, there is apt to be some difficulty in working Deacon's process, owing to the variation in the rate of liberation of the gas. Much care in the regulation of the air supply is necessary.

The hydrochloric acid gas from the Hargreaves process (p. 92) is too dilute for direct use in the Deacon apparatus.

Arsenic in the sulphuric acid used in the salt-cake pan, or for drying the chlorine gas, causes a loss, — in the first case by rendering the

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* Berichte d. chem. Gesellschaft, IX, 1070.

† Lunge, Sulphuric Acid and Alkali, II, 417.

copper salt inactive, and in the second, by forming hydrochloric acid, thus: —

$$As_2O_3 + 4\ Cl + 2\ H_2O = As_2O_5 + 4\ HCl.$$

Part of this hydrochloric acid combines with the As_2O_5 to form a solution which condenses in the pipes between the drying tower and the bleaching powder chambers. But some of the acid is left in the chlorine and attacks the bleaching powder, causing it to be "weak."

The cost of a Deacon plant is rather more than of a Weldon plant of the same capacity; and while it is theoretically a superior process and requires less labor, it is not yet in general use.

Several processes for the preparation of chlorine by the use of nitric and sulphuric acids have been proposed.

Schloesing's process * for chlorine by the use of nitric and hydrochloric acids and manganese oxides depends upon the following reactions: —

$$2\ HCl + 2\ HNO_3 + 4\ MnO_2 = Mn(NO_3)_2 + 2\ H_2O + Cl_2.$$

The reaction is carried out by heating the mixture of acids and manganese peroxide to 125° C., using an excess of nitric acid. By heating the manganous nitrate to 180° to 190° C., it is decomposed, and nitric acid may be regenerated from the vapors by treating them with air and steam, while manganese peroxide is recovered: —

$$Mn(NO_3)_2 = MnO_2 + N_2O_4;$$
$$N_2O_4 + H_2O + O = 2\ HNO_3.$$

Wischin, Just, and Alsberge have each patented modifications of the above process. Alsberge proposes to apply the method to the recovery of chlorine from the ammonium chloride liquors of the ammonia soda process, by employing the following equations: —

1) $2\ NH_4Cl + MgO + MnO_2 = MgCl_2 + MnO_2 + H_2O + 2\ NH_3.$
2) $MgCl_2 + MnO_2 + 4\ HNO_3 = Mg(NO_3)_2 + Mn(NO_3)_2 + 2\ H_2O + Cl_2.$

By evaporating to dryness and calcining the residue, the nitrates are decomposed thus: —

$$Mg(NO_3)_2 + Mn(NO_3)_2 = MgO + MnO_2 + 2\ N_2O_4 + O.$$

The peroxide of nitrogen is converted to nitric acid by treatment with steam and air: —

$$N_2O_4 + H_2O + O = 2\ HNO_3.$$

Dunlop's nitric acid-chlorine process depends † upon one or the other of the following equations: —

$$2\ NaCl + 2\ NaNO_3 + 4\ H_2SO_4 = 4\ NaHSO_4 + N_2O_4 + Cl_2 + 2\ H_2O.$$
$$4\ NaCl + 2\ NaNO_3 + 6\ H_2SO_4 = 6\ NaHSO_4 + N_2O_3 + 2\ Cl_2 + 3\ H_2O.$$

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* Zeit. angew. Chemie, **1893**, 99, Lunge and Pret. Wagner's Jahresbericht, **1862**, 235.

† Lunge, Sulphuric Acid and Alkali, III, 508.

The mixture of salt, sodium nitrate, and sulphuric acid is heated in an iron cylinder which is surrounded by the flames of the fire. The vapors leaving the retort are passed through concentrated sulphuric acid which retains the nitrogen oxides, and the chlorine is then washed with water to remove any traces of hydrochloric acid.

The nitrous vitriol obtained may be used in the sulphuric acid manufacture. The process was worked on a large scale at St. Rollox, England, but has been abandoned.

Donald's process * consists in passing the hydrochloric acid vapor from a salt-cake furnace through sulphuric acid to dry it, and then through a mixture of nitric and sulphuric acids kept at 0° C., when the following reactions take place: —

$$2\ HCl + 2\ HNO_3 = 2\ H_2O + N_2O_4 + Cl_2.$$

The gas mixture thus formed is led through dilute nitric acid, when the following takes place: —

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

By passing through concentrated sulphuric acid, the nitrous acid and nitrogen oxides are absorbed, while the chlorine is sent to the bleaching powder chambers.

Many attempts have been made to recover the chlorine from the waste liquors of the ammonia soda process, but no one of them has yet proved a commercial success. Several of them are, however, interesting, and deserve a few words.

Solvay conducted elaborate experiments in which he tried to realize the reaction: —

$$CaCl_2 + SiO_2 + O = CaSiO_3 + Cl_2.$$

But calcium chloride is very stable, and its decomposition in this way is incomplete, and requires enormous expenditure of heat, besides that used in evaporating the solution of calcium chloride to dryness.

Magnesium chloride is more easily decomposed than calcium chloride, and several processes have been devised, based on the use of this salt. It is proposed to use magnesium oxide or hydroxide instead of lime for decomposing the ammonium chloride solution of the ammonia process; by this, magnesium chloride is formed and the ammonia gas set free. Both Solvay and Weldon, within a few days of each other, patented methods for carrying out this idea. But the reaction between ammonium chloride and magnesia is not complete, and the solution of magnesium chloride obtained is dilute. Viewed as a method for chlorine, more promising results were obtained by using the concentrated magnesium chloride mother-liquors from the Stassfurt industries (p. 161), or from other manufacturing operations. The magnesium chloride solution is evaporated to dry-

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* Lunge, Sulphuric Acid and Alkali, III, 514.

ness at a very low temperature, and the dried chloride is decomposed by passing air or steam over it while heated to a red heat. The reactions are as follows: —

$$1)\ MgCl_2 + O = MgO + Cl_2.$$

$$2)\ MgCl_2 + H_2O = MgO + 2\ HCl.$$

The hydrochloric acid obtained is used in the Weldon or Deacon process.

The **Weldon-Pechiney**[*] **process** was the most successful of the magnesia methods, though none of them can be said to be profitable. In this, magnesium chloride solution (made by dissolving the oxide in hydrochloric acid, or obtained from waste liquors) is concentrated until it contains six molecules of water for each molecule of magnesium chloride; then 1¼ equivalents of magnesium oxide are stirred into the solution. The pasty mass heats and soon hardens to a solid cake of magnesium oxychloride, which is broken into lumps about the size of a butternut, and screened to remove the dust. The presence of dust causes the mass to cake badly during the subsequent drying. The lumps are dried at a temperature not exceeding 300° C., by passing a current of hot air over them while spread in a thin layer on gratings. Too high temperature causes a loss of chlorine as such. If not thoroughly dried, chlorine is lost as hydrochloric acid. The dried oxychloride is quickly decomposed in a special form of retort, which has been heated by producer gas to a temperature of 1000° C. before the charge is introduced. Air is passed into the retort to assist in the decomposition, which must be rapid, or the yield of chlorine is reduced. Magnesium oxide is left in the retort, while a mixture of chlorine, hydrochloric acid, and nitrogen escapes. The hydrochloric acid is recovered by washing the gases with water, and is used to dissolve part of the oxide from the retort. The chlorine, mixed with nitrogen, is used for bleaching powder, or for other purposes. The residue of magnesium oxide is returned to the first stage of the process.

The yield, including the hydrochloric acid recovered, is about 88 per cent of the whole amount of chlorine in the magnesium chloride. About 40 per cent is obtained as free chlorine, and 48.5 per cent is returned to the process as $MgCl_2$ and HCl.

Of the several methods that have been devised for the direct production of chlorine from the ammonium chloride formed in the ammonia soda industry, **Mond's process**,[†] which provides for the recovery of the ammonia, has been most carefully developed, but its practical success is as yet problematical. It is based on the dissociation of ammonium chloride into ammonia and hydrochloric acid, at a temperature of 350°–360° C.; the hydrochloric acid being then combined with some metallic oxide, to form a non-volatile chloride, to be later decomposed with libera-

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[*] J. Soc. Chem. Ind., **1887**, 775.

[†] Chemische Industrie, **1892**, 466. J. Soc. Chem. Ind., **1887**, 140, 216, 217, 440; **1888**, 626, 845.

tion of the chlorine. Oxide of nickel was used at first, but was later abandoned in favor of magnesium oxide. The reactions are: —

1) $MgO + (2\,NH_3 + 2\,HCl) = MgCl_2 + H_2O + 2\,NH_3.$
2) $MgCl_2 + O = MgO + Cl_2.$

Since an excess of magnesia is present, it is probable that considerable magnesium oxychloride is also formed, according to the reaction: —

$$2\,MgO + 2\,HCl = MgO \cdot MgCl_2 + H_2O.$$

Then this is decomposed by the air (reaction 2), thus: —

$$MgO \cdot MgCl_2 + O = 2\,MgO + Cl_2.$$

The liberated ammonia passes from the apparatus to the scrubbers of the ammonia recovery process. The complete recovery of this ammonia is the first essential to the success of this method.

The ammonium chloride is crystallized from the liquors of the Solvay carbonating towers (p. 108), by cooling them to about 0° C. The dry crystals are then vaporized by introducing them into melted zinc chloride, contained in an iron vessel lined with an antimony alloy.

The magnesium oxide, mixed with some potassium chloride, china clay, and lime, is made into balls ("pills"), about one-half inch in diameter, and baked. The decomposer is then filled with the "pills" and heated to 360° C., when vapors of ammonium chloride are passed through the apparatus. The reaction between the ammonium chloride and magnesia raises the temperature in the decomposer above 400° C. Next, inert gases, such as those from lime kilns, heated to 550° C., are passed into the apparatus to drive out the ammonia and water vapors; these also heat the charge above 500° C. Air, heated to 800° C., is then admitted to break up the magnesium chloride (reaction 2) and regenerate the oxide; it also sweeps out the chlorine formed. After cooling to 360° C. ammonium chloride vapors are again introduced and the cycle of operations is repeated. To secure uninterrupted working, there are usually four decomposers in each plant.

ELECTROLYTIC PROCESSES FOR CHLORINE AND CAUSTIC SODA

By passing a current of electricity through a sodium chloride solution the salt is decomposed into chlorine at the anode and sodium at the cathode. But the latter at once decomposes a molecule of water of the solution, forming caustic soda and setting free hydrogen. Hence the products of electrolysis are chlorine, caustic soda, and hydrogen, of which the last mentioned is of slight value at present.

While electrolysis appears very simple and direct at first glance, there are, in fact, serious difficulties encountered in all electrolytic processes for decomposing salt. The migration velocity of hydroxyl ions is so much greater than that of chlorine ions, that the former carry a large part of the current, which tends to an accumulation of the hydroxyl ions in the anode compartment, where various reactions take place, resulting in the liberation of some oxygen, which mixes with the free chlorine, or attacks the carbon anodes, forming carbon dioxide in the gas. This deposition of hydroxyl ions also represents a serious waste of energy. The chlorine diffuses somewhat, through the electrolyte, and coming in contact with the caustic from the cathode, increases the tendency to secondary reactions.

To prevent this migration and diffusion, various devices have been proposed, and the great number of cells devised to overcome these difficulties may be brought under four general classes: —

I. Those in which the products of the electrolysis are kept apart by use of a porous diaphragm or partition, in the cell.

II. Those employing a moving mercury cathode to remove the alkali metal from the immediate field of decomposition.

III. Those depending upon the specific gravity of the alkali solution produced, to keep it away from the action of the chlorine.

IV. Those using fused salt as electrolyte, thus avoiding secondary reactions by eliminating the hydroxyl ion from the bath.

Porous diaphragms between the anode and cathode seem simple, but no material is available which offers no resistance to the passage of electricity, yet prevents the migration and diffusion. Furthermore very few substances can be used for the diaphragms, because of the destructive action of the chlorine. Then, magnesia, silica, etc., from impurities in the salt, deposit in the pores of the diaphragm, and with continued working of the cell cause a considerable increase of the resistance. The nascent chlorine is also very destructive to the anode, and only platinum, or fused magnetite (Fe_3O_4) or iron oxide, which are expensive and fragile, or Acheson graphite have proved efficient in withstanding its action.

If the hydrogen liberated at the cathode is permitted to escape through the solution, it stirs the liquid, aiding the diffusion of the chlorine, and the consequent formation of chlorates and hypochlorites, thus: —

1) $NaCl = Na + Cl.$
2) $Na + H_2O = NaOH + H.$
3) $2\ NaOH + 2\ Cl = NaClO + NaCl + H_2O.$
4) $3\ NaClO = NaClO_3 + 2\ NaCl.$
5) $NaClO + 2\ H = NaCl + H_2O.$

Reactions (3), (4), and (5) cause loss, since they regenerate salt.

Le Sueur's process,* one of the earliest of the diaphragm methods, has undergone several modifications. The diaphragm is asbestos cloth which rests against the iron gauze cathode. The anodes, 60 in each cell, are platinum wire gauze. Diffusion of the sodium hydroxide through the diaphragm is hindered by feeding salt solution slowly into the anode chamber, thus keeping the level of liquid in that space slightly higher than in the cathode compartment. Each cell takes 1000 ampères, at 6½ volts, and the chlorine efficiency is claimed to be 88 per cent or higher; but the caustic production is less efficient.

In **Carmichael's apparatus** † the asbestos diaphragm, impregnated with Portland cement, rests on the horizontal or slanted cathode at the bottom of the cell; above it is a bell to collect the hydrogen given off. The anode, suspended in the top of the cell, is a grating of copper rods, covered with hard rubber, through which numerous platinum points project into the brine. The brine is fed in at the top of the cell in a rapid stream of drops, so regulated that the caustic formed at the cathode is drawn off before it has time to diffuse through the liquid. The cathode liquor produced contains about 20 per cent caustic soda, and about 75 per cent of the salt is decomposed. The reaction is conducted at about 80° C., in the top of the cell, near the anode, while the region around the cathode is kept as cool as possible.

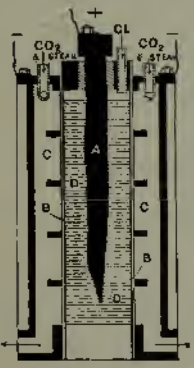

Fig. 56.

The **Hargreaves-Bird cell** ‡ Fig. (56) consists of a tall, narrow, vertical cell, having two upright diaphragms (B, B) composed of Portland cement with asbestos, supported on the vertical cathodes of iron wire gauze. The cell is 8 feet long by 6 feet high and about 14 inches thick, and is enclosed in a cast-iron box, which also supports the cathodes. The anode space (D, D) between the diaphragms is filled with strong brine, and the weakened brine leaves the compartment through an overflow pipe near the top of the cell. By admitting steam to the cathode space (C, C), between the outside case and the diaphragms, the sodium ions passing through them are combined to form caustic soda, which washes down to the outlet pipe.

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* J. Soc. Chem. Ind., **1892**, 963; **1894**, 453.
J. Am. Chem. Soc., **1898**, 868. U. S. Pat. No. 723,398.

† Zeitschr. f. angew. Chemie, **1896**, 537.

‡ J. Soc. Chem. Ind., **1894**, 250, 256; **1895**, 166, 1011.
Eng. Min. J., **1898** (**65**), 611; **1902** (**73**), 471.

If carbon dioxide or furnace gases are admitted to the cathode space, sodium carbonate solution is formed; this improves the efficiency, since the rate of migration of the carbonate ion is less than that of the hydroxyl ion. The anodes (A) are graphitized carbon blocks, connected by copper rods, and buried in cement so that only the ends of the carbons are exposed to the brine. Eight anodes are placed in each cell.

The **Townsend cell** * (Fig. 57) also has vertical diaphragms (D) of asbestos cloth, the pores of which are filled with a mixture of iron oxide, asbestos fibre, and precipitated amorphous iron hydroxide. This is supported on the perforated iron plate cathodes (S, S), and forms a chamber filled with brine surrounding the graphitized carbon anodes (G). The cathode compartment is filled with kerosene oil (K), and the drops of caustic liquor percolating through the diaphragm, on meeting the oil, assume the spherical shape and fall to the bottom of the cathode space, under the oil; the caustic liquor then escapes by a trap (A). The brine (T) is continuously added to the anode space. These cells take from 2500 to 5000 ampères at an average of 4.7 volts. The caustic liquor averages 150 grams sodium hydroxide and 200 grams of salt, per litre.

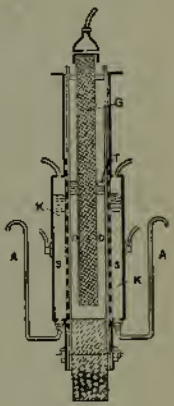

Fig. 57.

The **Griesheim-Elektron process** † (Fig. 58) employs porous cement diaphragms forming the walls of the anode compartment; the anodes (A) are cast from fused iron oxide. From six to twelve of these small cells are placed in an iron vat (K) constituting the cathode bath, and provided with a run-off pipe for the caustic liquor. Salt solution is introduced into the anode chamber through a pipe (Z).

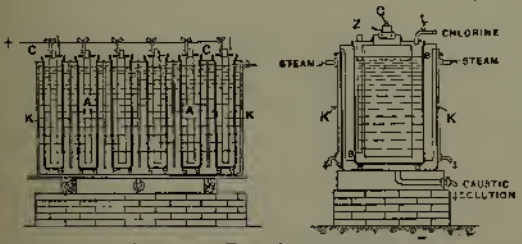

Fig. 58.

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* Electro-chem. Met. Ind., **1907**, 209. J. Soc. Chem. Ind., **1907**, 746. 7th Internat. Cong. Appd. Chem. **1909**, Sec. X, p. **36**.

† Ber. **1909** (**42**), 2897.

Elektrochemie wässriger Lösungen. F. Förster, Leipzig, 1905.

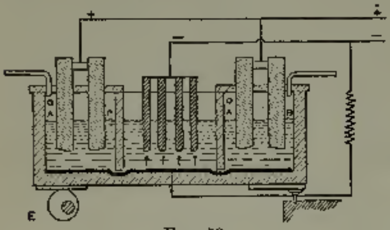

FIG. 59.

The **Castner process** * was the first successful method employing a moving mercury cathode. The cell (Fig. 59) is divided into three compartments and is given a slight rocking motion by the cam (E). The two outside compartments contain the iron cathodes, and the centre chamber contains the carbon anodes. The mercury lies about one-eighth inch deep on the bottom of the cell, and flows alternately from each anode compartment into the cathode chamber, where it is deprived of its sodium content by the water therein, forming caustic liquor. Brine is fed into the anode compartment, and the sodium set free is taken up by the mercury, forming amalgam, which flows into the cathode compartment. Owing to a slight reaction between the sodium and chlorine in the anode chamber, the amalgam is a little deficient in sodium ions in the cathode chamber, and the current tends to decompose water, thus oxidizing the mercury. To avoid this, a metallic connection is made outside the cell, between the iron cathode and the mercury-amalgam layer in the caustic chamber; this accelerates the reaction between the water and the amalgam, and yet is independent of the current in the chlorine chamber. Kellner has improved on the Castner process by making the decomposing cell stationary and circulating the mercury through the anode chamber by means of an Archimedian screw, or wheel pump. The anodes of platinum gauze weigh about 1 gram each, and 525 are placed in each cell. The cells take 4000 to 10,000 ampères at 4.3 volts, thus reducing the size of plant as compared with the original cells.

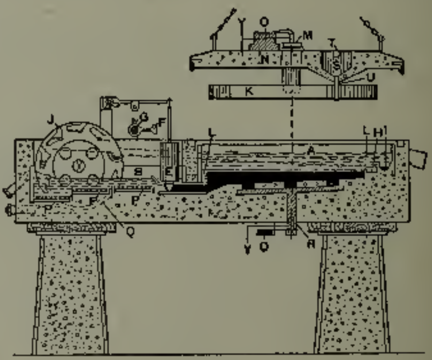

FIG. 60.

The **Whiting cell** † (Fig. 60) operates intermittently, the mercury remaining stationary in the anode compartment until an amalgam of

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* J. Soc. Chem. Ind., **1893**, 301. Eng. Min. J., **1894** (**58**), 270.

† Trans. Am. Electrochem. Soc., **1910** (**17**), 327.

desired concentration is produced. This is then entirely removed and a new portion of mercury introduced. By placing several compartments in parallel and operating them successively, the cell becomes practically continuous in its action. The cement cell consists of a shallow box having a decomposing compartment (A) and an oxidizing space (B). The graphitized carbon anodes (K), submerged in the brine in (A), are supported from the cell cover just above the surface of the mercury on the bottom of the chamber. The oxidizing chamber has inclined channels (P, P) forming a zig-zag path, leading to the pump-pit (Q). The current flows from (K) through the brine to the mercury, and out by the iron cathode (R). The sodium set free forms amalgam, which after a short interval of time is drawn off by the valve (E) into the oxidizing chamber (B), where the sodium is removed by water during the passage down the incline (P) to the pump-pit. The mercury, free from sodium, is elevated by a wheel pump (J) and returned to (A). The cycle of operations occupies about two minutes in each compartment. The cells are six feet square and take about 1400 ampères, with voltage approximately four. Chlorine of 98 per cent purity, with 2 per cent hydrogen, and pure caustic solution of any desired strength up to 40 per cent sodium hydroxide, is claimed.

In **Bell's apparatus** * the mercury is moved into the electrolysis chamber by the pressure exerted by the hydrogen evolved in the caustic compartment.

In **Rhodin's apparatus** † the mercury is moved by the centrifugal action of the rotating earthenware bell which serves as the cover of the anode chamber. Neither the Bell nor the Rhodin cells have been commercially successful.

The disadvantages of using mercury are the tendency of other metals, especially magnesium, derived from impurities in the brine, to accumulate in the amalgam and reduce its fluidity; the high voltages (four or over) necessary; the cost of the mercury itself, and of the installation in general.

The "**gravity**" or "**bell process**" ‡ (Fig. 61) employs a cell without diaphragm or mercury. An earthenware bell (B) is suspended in a tank containing brine. The anode (A) is near the top of the

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* Electrochem. Ind., **1903** (I), 505.

† J. Soc. Chem. Ind., **1897**, 745; **1900**, 418; **1902**, 449. Electrician, XL, 8. U. S. Pat. No. 608,300 (**1898**).

‡ J. Soc. Chem. Ind., **1898**, 1147; **1904**, 545. Zeitschr. Elektrochem., **1901** (**7**), 581; **1904** (**10**), 317. Ber. **1908** (**41**), 1789; **1909** (**42**), 2904.

liquid inside of the bell, and the cathode (K) is outside. New brine is constantly fed in by the pipe (C, C) and the caustic liquor overflows at (F), chlorine passing out at (D). The relatively large distance separating the electrodes raises the resistance to four volts. The cell is of small size, however, and an extensive plant is necessary for a commercial enterprise.

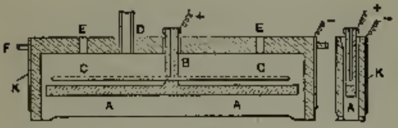

Fig. 61.

Electrolysis in fused baths is represented by the patents of Vautin, Heulin, and Acker. The **Acker process** * (Fig. 62) employs a bath of melted lead for the cathode, on which the fused salt rests; a sodium-lead alloy forms and is decomposed by steam in a special chamber (C), producing anhydrous fused caustic directly. The cell is divided into three compartments; in one (A), the salt fused at about 850° C. is decomposed and the melted lead on the floor unites with the sodium.

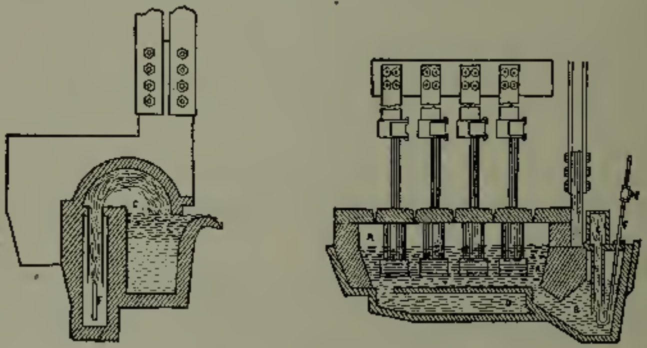

Fig. 62.

The melted alloy flows into (B) and is ejected into (C) by a steam-jet from (F). The melted lead and fused sodium hydroxide separate by gravity in (C), the lead flowing back to (A), and the caustic is drawn off. Each cell takes 8000 ampères at 6 to 7 volts. Much energy is consumed in fusing the salt, and by losses through radiation, conduction, and resistance at the connections, and the up-keep expense is heavy. The only commercial trial of these cells was at Niagara Falls but the plant was destroyed by fire in 1907.

The destructive action of caustic and chlorine on the diaphragms and other parts of the electrolytic apparatus, and the large size of the plant needed for a comparatively small output, are serious dis-

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* Trans. Am. Electrochem. Soc., I (**1902**), 165. U. S. Pat. No. 649,565.

advantages of electrolysis; then, except in a few places where water-power is cheap, the electricity is generated with steam-engine and dynamo, a method of low efficiency, considering the fuel consumption.

The electromotive force necessary to decompose salt is 2.3 volts; but the resistance of the bath and polarization increase this to 3.5 or 4 volts. One ampère of current yields, theoretically, 0.00292 pound of chlorine and 0.0033 pound of caustic soda per hour. If the efficiency is 80 per cent, one ampère yields 28.56 grams NaOH and 25.2 grams Cl in 24 hours;* or, to make one kilo of NaOH in 24 hours, the current must be 35 ampères. If a theoretical yield were obtained, the chlorine evolved would make about 100 pounds of bleaching powder for each 40 pounds of caustic produced. But the latter, which is in much greater demand than bleaching powder, can be made cheaply from ammonia soda; this would seem to limit the electrolytic processes to supplying bleach and chlorates, while the caustic must be considered as a by-product.

The caustic liquors produced by wet electrolysis in diaphragm processes are contaminated with salt and are dilute, requiring much evaporation. As the concentration of caustic in the electrolyte increases, there is increased carrying of current by the OH ions, with liberation of oxygen and formation of water. This causes such serious loss in strong solutions that the practical limit of concentration is about 12 or 15 per cent of NaOH. When mercury is used as cathode, strong, pure caustic is produced, with less consumption of fuel.

HYPOCHLORITES

By passing chlorine into a cold solution of sodium or potassium carbonate, a mixture of the chloride and hypochlorite of the alkali metal is formed. But if any excess of chlorine is introduced, the hypochlorite is decomposed into chloride and free hypochlorous acid (HOCl): —

1) $K_2CO_3 + H_2O + 2\ Cl = KCl + KOCl + H_2O + CO_2$.

2) $K_2CO_3 + H_2O + 4\ Cl = 2\ KCl + CO_2 + 2\ HOCl$.

This solution of hypochlorous acid is a powerful bleaching and oxidizing agent. It was first made about 1789, and brought into trade in France as a "**bleach liquor**" under the name of *eau de Javelle,* or *eau de Labarraque.* In 1798 or 1799 Charles Tennant took out a patent in England for a "bleach liquor" made by passing chlorine

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* Zeitschr. f. Elektrochem., **1895**, 21.

into "milk of lime," by which a solution of calcium chloride and hypochlorite was formed: —

$$2\ \mathrm{Ca(OH)_2} + 4\ \mathrm{Cl} = \mathrm{CaCl_2} + \mathrm{Ca(OCl)_2} + 2\ \mathrm{H_2O}.$$

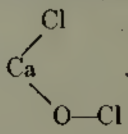
This bleach liquor is cheaper, stronger, and more convenient to use than bleaching powder (see below), but since it is unstable, evolving oxygen even when kept in a closed vessel in the dark, it is usually made only for immediate use.

The tanks in which the milk of lime is treated with chlorine are provided with stirring apparatus; the temperature must not rise much above 30° C., or chlorates are formed. A dilute chlorine may be used. The density of the solution obtained is about 8° Tw.

Calcium carbonate suspended in water may also be employed for preparing bleach liquor: —

$$\mathrm{CaCO_3} + \mathrm{H_2O} + 4\ \mathrm{Cl} = \mathrm{CaCl_2} + \mathrm{CO_2} + 2\ \mathrm{HOCl}.$$

These liquors are chiefly used for bleaching vegetable fibres and for disinfectants.

The absorption of chlorine in milk of lime soon led to trials of dry, slaked lime or calcium hydroxide for the same purpose. A dry bleaching powder, fairly stable and constant in strength, resulted; but its composition is not the same as that of the bleach liquor made from milk of lime. It was at first supposed that a direct combination took place between the lime and chlorine, and that the powder was simply calcium hypochlorite [$\mathrm{Ca(OCl)_2}$], so the name "chloride of lime" was given to it. Other investigations led to the view that it contained a mixture of calcium chloride and hypochlorite. But this was disproved by Lunge[*] and his students, who demonstrated the correctness of Odling's[†] formula  $\mathrm{Ca}\begin{smallmatrix}\diagup \mathrm{Cl}\\ \diagdown \mathrm{O{-}Cl}\end{smallmatrix}$. Hence it is an oxychloride of calcium. When dissolved in water, this forms hypochlorite and chloride of calcium.

For making bleaching powder, a pure, fat lime is desirable. It is slaked carefully, so that the resulting hydroxide contains about 24.5 to 25.5 per cent of water, *i.e.* there should be a slight excess of water over that necessary to form calcium hydroxide.

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[*] Chemische Industrie, **1881**, 289. Dingl. J., **237**, 63. Annalen der Chemie, **219**, 129. Berichte d. deutsch, chem. Gesellschaft, **1887**, 1474. Zeit. f. anorg. Chemie, II, 311.

[†] Odling, Handbuch der Chemie, I, p. 59.

The absorption chambers are brick, cast-iron, or lead, and are usually 6.5 feet high, and have about 200 square feet of floor area per ton of bleach made per week. Brick chambers are tarred inside to make them gas tight and to protect them from the chlorine; large ones are usually made from lead, much like the vitriol chambers (p. 70), and may have a floor area of 30 by 100 feet. The slaked lime is sifted through screens with from 20 to 25 meshes per linear inch, as only the fine powder is suitable. This is spread three or four inches deep on the floor, and is furrowed with a special rake in order to assist the absorption by increasing the surface. The chlorine is introduced at the top of the chamber, and settling to the bottom because of its density, is at first rapidly absorbed by the lime.

After a time the process goes on more slowly, and finally the gas enters under some pressure. Usually there are three or more chambers in a series, the strongest chlorine entering that containing the most nearly finished bleach, and passing out through that containing the fresh lime. The degree of absorption of chlorine is judged by the color of the gases seen through the glass "sights" in the chamber walls. The powder is turned over once or twice, and the treatment ("gassing") continued until tests show that it contains from 36 to 37 per cent of "available chlorine." If under strength ("weak"), after the third "gassing," it should be packed and sold for what it will bring, for further exposure will cause the formation of chlorate and chloride with loss of strength.

During the absorption considerable heat is generated; for strong powder the temperature should not exceed 40° to 46° C.* The chlorine should be admitted in a very slow stream, and should be concentrated, dry, and free from hydrochloric or carbonic acids. When dilute (as from Deacon's apparatus), a large, special chamber provided with numerous shelves, on which the slaked lime is spread to secure a greater absorbing surface, is employed; or the apparatus shown in Fig. 63 is used. The yield from 100 pounds of good lime is about 150 pounds.

Mechanical apparatus (Fig. 63) for the absorption of the chlorine is much used. Several horizontal cast-iron cylinders (A), set one above the other, each contains a rotating shaft carrying blades which act as conveyers; the shafts in the several cylinders are all driven at the same speed by a system of gears (B). Slaked lime is fed continuously in a small stream to the upper cylinder through (H), and is carried by the blades to the opposite end of the cylinder, where

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* Lunge and Schäppi, Dingl. J., **237**, 63.

it drops through the opening (D) into the next, and so on to the bottom. Chlorine enters the lowest cylinder at (C), passes over the surface of the lime, ascends through (D) to the next higher cylinder, and thence up through each in succession, the unabsorbed gas finally escaping at the top through (E). The bleaching powder thus formed collects in (F), from which it is dropped directly into the casks for packing.

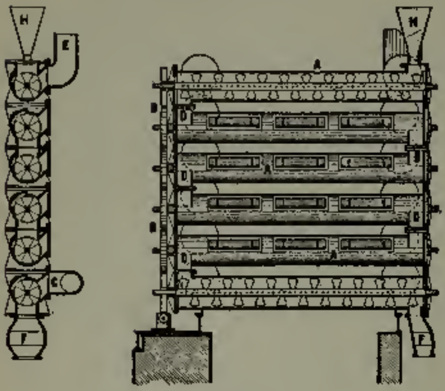

Fig. 63.

Bleaching powder is a yellowish white substance, which should be perfectly dry and free from lumps. On exposure to the air, it absorbs moisture and carbon dioxide, giving off hypochlorous acid, the evolution of which gives bleach its peculiar odor. Good samples contain about 36 per cent "available chlorine." Its chief use is for bleaching vegetable fibres for the textile and paper industries.

In order to liberate the chlorine for bleaching purposes, the powder is usually decomposed by a mineral acid, thus: the fibre, having been saturated with the bleaching powder solution, is passed into a dilute acid bath, where the hypochlorite is decomposed and the chlorine set free. The nascent chlorine combines with the hydrogen of the water, liberating nascent oxygen, which, in turn, destroys the organic coloring matter in the fibre.

Bleaching powder, obtained from a cheaper base and giving higher chlorine efficiency, has replaced hypochlorites made from alkali carbonates and chlorine (p. 131). Free hypochlorous acid oxidizes hypochlorites to chlorates ($NaClO + 2\ HClO = NaClO_3 + 2\ HCl$), but in alkaline solution, where no free acid exists, they are relatively stable. The action of chlorine on carbonates liberates hypochlorous acid, which thus destroys hypochlorite. The use of alkali hydroxides avoids this loss ($2\ OH^- + Cl_2 = Cl^- + ClO^- + H_2O$). As liquid chlorine is now a commercial article, hypochlorite solutions made by absorbing the gas in caustic liquor are much used; this has the advantage over lime that it is easily washed from the goods and forms no insoluble soaps.

Hypochlorites in dilute solution are strong oxidizing agents on organic matter; chlorates do not have this action, hence only the hypochlorite of the solution is "available" for bleaching purposes, and it is only the oxygen of the hypochlorite which is active. The chlorine equivalent of this hypochlorite oxygen is called the "*available chlorine.*"

CHLORATES

The **chlorates** are stable salts and are always made by decomposition of hypochlorites in hot solution (see above). Formerly chemical chlorine was run into calcium or magnesium hydroxide (Liebig's process). From the reactions it is seen that five times as much chloride is formed as chlorate. The chlorate solution was double decomposed with potassium salts, with precipitation of **potassium chlorate**, it being less soluble in the calcium or magnesium chloride solution. A large part of the product was lost, however, in the mother-liquors.

These methods are now entirely superseded by the production of the chlorine and alkali by electrolysis of alkali chloride solutions, no diaphragm being used, thus allowing anode and cathode products to interact. The chloride regenerated by the above reactions is re-electrolyzed, thus enabling the conversion of all the chloride to chlorate. Since the hypochlorite is subject to reduction by the nascent hydrogen at the cathode forming water according to the reaction,

$$2\,H + ClO^- = Cl^- + H_2O,$$

and to deposition at the anode with loss of oxygen, all representing lost efficiency, the conversion to chlorate is made as rapid as possible by keeping the solution hot and slightly acid. The current efficiency can be made from 85 to 90 per cent. The voltage required for the deposition of chlorate ion is much higher than that for chlorine or hydroxyl ion, hence, so long as chloride remains in the bath, no chlorate deposits, but when all chloride is oxidized, chlorate deposits, best at high-current densities, with formation of perchlorate, $ClO_3^- + O = ClO_4^-$, the oxygen coming from anodic deposition of chlorate. **Perchlorates**, especially those of potassium and ammonium, are now made in this way, and are largely used for explosives which possess great stability against shock.

The crude chlorate is purified by recrystallizing from water, and the crystals are drained and washed in a centrifugal machine, and may be sold as coarse crystals; or they are ground to fine powder in buhrstone mills, care being taken that no organic matter, dirt, or metal (iron, etc.) gets into the mill, lest an explosion result. No fire should be permitted in the building, and heating should be by steam, and lighting by electricity. The grinding mill should be at a distance from the main works.

Sodium chlorate is much more soluble and is more difficult to crystallize than potassium chlorate, but it is, however, made in large quantity.

Persulphates of potassium and ammonium are made by electrolyzing at very low temperatures strong solutions of the acid sulphates or acid carbonates with high current densities on smooth platinum anodes. The anions KSO^-_4 and KCO^-_3 combine to form persulphate ($K_2S_2O_8$) or percarbonate ($K_2C_2O_6$), which crystallize as moderately stable salts. In solution they are active oxidizing agents, and are used to a limited extent for bleaching and oxidizing purposes.

REFERENCES

Die Fabrication von chlorsäurem Kali und anderen Chloraten. Dr. Conrad W. Jurisch, Berlin, 1888. (R. Gaertner.)
Die Darstellung von Chlor u. Salzsäure, unabhängig von der LeBlanc Soda Industrie. Dr. N. Caro, Berlin, 1893. (R. Oppenheimer.)
Sulphuric Acid and Alkali. G. Lunge, 3d ed., Vol. III, New York, 1911. (Van Nostrand Co.)
J. Soc. Chem. Ind.: — **1883**, 103, Ferdinand Hurter.
1885, 525, W. Weldon. **1887**, 248, C. Longuet Higgins.
1887, 775, James Dewar. **1896**, 713, Ludwig Mond.
Electro-Chemistry. M. Leblanc, translated by W. R. Whitney and J. W. Brown, New York, 1907. (Macmillan & Co.)
Elements of Electro-Chemistry. Lupke.
Die Fabrikation der Bleichmaterialien. V. Hölbling, Berlin, 1902. (Springer.)
Grundriss der reinen und angewandten Elektrochemie. P. Ferchland, Halle a. S., 1903. (W. Knapp.)
Elektrochemie wässriger Lösungen. F. Förster, Leipzig, 1905.
Applied Electrochemistry. By M. deKay Thompson, New York, 1911. (Macmillian Co.)

NITRIC ACID

The manufacture of nitric acid is often carried on in conjunction with sulphuric acid making, especially in those plants where the liquid acid is used in the lead chamber process. Large quantities, however, are produced for general manufacturing purposes.

Practically all nitric acid is made by treating sodium nitrate (p. 145) with sulphuric acid in cast-iron retorts. The reactions are as follows: —

1) $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$.
2) $2\ NaNO_3 + H_2SO_4 = Na_2SO_4 + 2\ HNO_3$.

But it is now thought that a sodium acid sulphate* is formed and reacts with some of the sodium nitrate,

3) $NaNO_3 + 2\ H_2SO_4 = NaH_3(SO_4)_2 + HNO_3$.
4) $NaH_3(SO_4)_2 + NaNO_3 = 2\ NaHSO_4 + HNO_3$.

In practice the quantities of material used do not correspond with either of these equations, but the charge is so regulated that a mixture of acid and neutral sulphates of sodium, which remains liquid at the temperature employed, is left in the retort. If reaction (1) were followed, too much sulphuric acid would be used for profitable working, except in soda works, where the resulting acid sulphate is used in the salt-cake furnace. If reaction (2) is carried out, the temperature must be high, and the nitric acid is partly decomposed by the heat, before it can escape from the retort, causing smaller yield and a product discolored by the nitrogen oxides produced.

The sulphuric acid employed is usually that from the lead pan evaporation (sp. gr. 1.70), but for strong nitric acid the sulphuric acid should be of 92 per cent strength, and the temperature kept as low as possible during the distillation. The sodium nitrate used is purified Chili saltpetre having 96 to 99 per cent $NaNO_3$ when dry. Chlorides should not be present because of the decomposition resulting (p. 141). The size of charge ranges from 500 to 1200 pounds or more of nitrate, and 60° Bé. sulphuric acid, amounting to 20 or 30 per cent excess over the theoretical quantity.

The apparatus (Fig. 64) commonly used consists of a horizontal cast-iron cylinder or retort (A) about six feet long by four or five feet

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* J. Am. Chem. Soc., **1901** (**23**), 489.

diameter, set in a furnace in such a way that the flame plays over its entire surface, heating all parts equally hot. Cast-iron is but little attacked by concentrated nitric acid or its vapors, and it is important that the retort be hot enough in all parts to prevent any condensation of acid. Retorts having exposed ends made of sand-stone slabs, or vitrified brick laid in cement, are sometimes used. The charge of nitre is introduced by a door in the end, or side, of the retort, and the sulphuric acid is run in by a pipe (E). After the reaction the fused residue is run off by (D) and on cooling forms the so-called "**nitre cake.**"

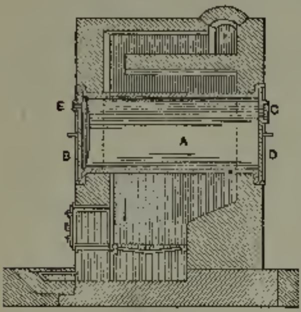

Fig. 64.

The acid vapors escaping from the retort are condensed in earthenware pipes or worms, surrounded by water, or in a series of Woulfe bottles (*bombonnes*) (Fig. 44) with an absorbing tower at the end to catch the fumes escaping from the bottles. The dilute acid from the tower may or may not flow through the series of bottles in a direction opposite to the movement of the acid vapors.

The most concentrated acid condenses in the first two or three bottles but is contaminated with sulphuric acid; the last of the series contains dilute acid, which is contaminated with chlorine; in the middle bottles is pure acid of moderate strength. Owing to more or less reduction of the nitric acid in the retort, the condensed acid has a yellow or red color, due to absorbed nitrous vapors. For a commercial acid, these must be removed by "bleaching"; the acid is heated to about 90° C., and air blown in which carries away the nitrogen oxides to an absorbing tower for recovery.

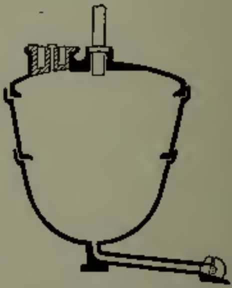

Fig. 65.

Guttmann's apparatus* is much used. The large cast-iron retort (Fig. 65) is made in three pieces and is entirely surrounded by the flames from the grate. The retort gases pass into a system (Fig. 66) of vertical earthenware pipes (A, A) having very thin walls and joined at the top by bends, while they open at the bottom into a nearly horizontal collecting pipe (B, B) which is divided into sections by diaphragms. The sections are connected by U-tubes passing under the partitions. The diaphragms

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* J. Soc. Chem. Ind., **1893**, 203.

force the acid vapors to pass up one pipe and down the next, in order to go through the system. The thin walls (8 mm.) of the vertical pipes allow efficient and rapid cooling by the cold water in the tank, and the vapors are quickly condensed. Air at 80° C. is injected from (F) into the outlet pipe (D), where it converts some of the nitrous vapors into nitric acid, increasing the yield. The uncondensed nitrous vapors pass into the Lunge-Rohrmann plate tower (E), where they are absorbed in sulphuric acid or water. If the vapors remain in the retort too long, part of the acid is decomposed and nitrogen peroxide is formed and absorbed by the condensed acid, to which it imparts a red color. Since there is good draught in this apparatus, the vapors are drawn out of the retort soon after they are evolved, and are at once condensed; very little peroxide is formed, and a light-colored, concentrated acid is obtained. It is claimed that 40° Bé. acid, requiring no "bleaching," is made, and with water-cooled pipes, 98 per cent of the theoretical yield is obtained as concentrated acid, while 2 per cent condenses in the plate tower.

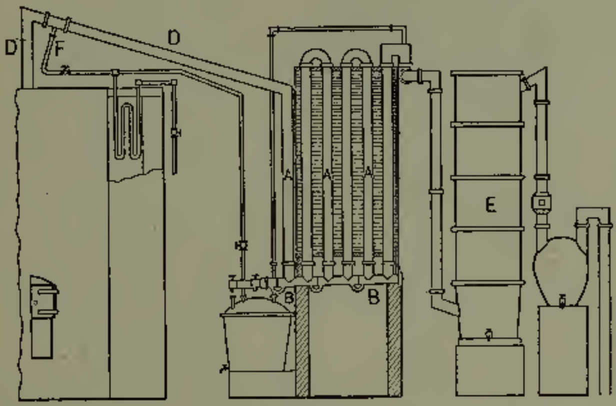

FIG. 66.

Hart's tube condenser[*] (Fig. 67) for nitric acid is made of glass and earthenware tubes, and is placed above the brick arch over the retort, thus occupying but little floor space. The vapor from the retort (A) passes into the pot (B) and thence through the vertical earthenware tube (C). From (C) to (D) extend a number of glass tubes, inclined slightly towards (C), and cooled by jets of water from the perforated pipe (E, E). From (D) the uncondensed vapors pass

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[*] J. Soc. Chem. Ind., **1894**, 1197. J. Am. Chem. Soc., **1895** (**17**), 576.

to a plate tower. The acid condensed in the glass tubes flows back into (C), and then into (B), thus coming into contact with the hot vapors from the retort. This heats the acid so hot that the nitrous vapors are driven out and the light-colored acid is run off by the U-tube (F). In this apparatus the acid is condensed very quickly and little peroxide is formed. Frothing in the retort gives no trouble, as any overflow is caught in (B) and is easily removed. The water flow from (E) can be so regulated that nearly all of it is evaporated on the surface of the glass tubes, giving great cooling effect with small consumption of water; any excess of condenser water is caught in (G). The chief repairs are of broken tubes, which are cheaply and easily replaced.

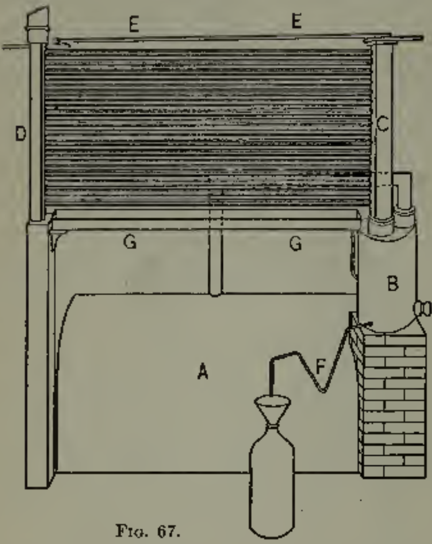

Fig. 67.

Valentiner's process * consists in distilling the mixture of sulphuric acid and nitre in a vacuum of from 60 to 65 cm. of mercury, the temperature being about 85° C., but finally rising to 160° C. There is very little decomposition of the nitric acid, and a large yield of concentrated, light-colored acid is obtained. The charge is about 1000 kg. of Chili nitre, with the requisite amount of 60° Bé. sulphuric acid, and provision is made for frothing. The acid gases are condensed in an earthenware worm, cooled with water. The uncondensed vapors pass through milk of lime, and then to a bronze vacuum pump. The yield of acid is claimed to reach 98 per cent of the theoretical.

The **Rhenania process** † is based upon the reactions between fused sodium bisulphate and sulphuric acid, forming the so-called polysulphate, which in turn reacts with the sodium nitrate:

1) $NaHSO_4 + H_2SO_4 = NaH_3(SO_4)_2$.
2) $NaH_3(SO_4)_2 + NaNO_3 = 2\ NaHSO_4 + HNO_3$.

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* J. Soc. Chem. Ind., **1893**, 155; **1896**, 36; **1899**, 492, 1122; **1901**, 544. Zeit. angew. Chem., **1899**, 269, 1003. Chem. Zeit., **1895**, 118; **1897**, 511.

† Chem. Ind., **1901**, 189, 544, 896, 1189. J. Soc. Chem. Ind., **1902**, 173. J. Am. Chem. Soc., **1901** (**23**) 489.

The apparatus (Fig. 68) consists of three iron retorts; two (A) heated to 200° C. by the waste heat from the third (B) at 300° C. Sodium nitrate and fused polysulphate are introduced into (A), where reaction (2) runs for a considerable time, and is then completed by drawing the charge into the hotter retort (B), containing some fused bisulphate from the previous operation. Here reaction (2) is completed and the last of the nitric acid driven out. Most of the bisulphate is then drawn from (B) and part of it heated with 60° Bé. sulphuric acid in a pan (C) to form polysulphate for the next charge. Since the reaction in (A) is slow, while the final one in (B) is rapid, the two retorts (A) are connected with one retort (B), and by running alternate charges in the former to be finished in (B), the process becomes practically continuous. Retort (A) yields concentrated acid, but that from (B) is rather dilute.

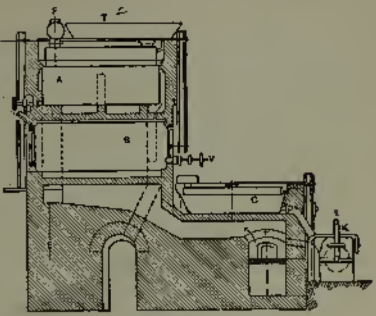

Fig. 68.

The strength of the nitric acid produced depends upon the strength of the sulphuric acid, on the temperature of the retort, and on the purity of the sodium nitrate. With sulphuric acid of 1.71 sp. gr. the nitric acid varies from 1.38 to 1.42 sp. gr. (40° to 42° Bé.). If the sodium nitrate contains chlorides, some of the nitric acid is decomposed by the hydrochloric acid produced: —

$$HNO_3 + HCl = H_2O + NO_2 + Cl.$$

For chemically pure acid, pure materials are used; but the common acid may be purified by treating with silver and barium nitrates and redistilling. Concentrated acid cannot be distilled without some decomposition, and the product must be "bleached" by heating and blowing in pure air.

Fuming nitric acid is a solution of nitrogen peroxide in concentrated nitric acid. It is red in color and has a specific gravity of 1.55 to 1.62. To make this, perfectly dry sodium nitrate and oil of vitriol (1.84 sp. gr.) are used. The reaction is carried so far that neutral sodium sulphate is formed: —

$$2\,NaNO_3 + 2\,NaHSO_4 = 2\,Na_2SO_4 + 2\,NO_2 + H_2O + O.$$

The nitrogen peroxide dissolves in the nitric acid to form the fuming acid. A little starch may be added to assist in the reduction. An impure fuming acid is made by distilling a mixture of concentrated nitric and sulphuric acids.

Priestley and Cavendish observed that nitric acid is formed by the action of electric sparks on damp air. This results from the direct union of oxygen and nitrogen at high temperature, to form nitric oxide: $N + O \rightleftarrows NO$. The reaction is endothermic and is accelerated by high temperatures, with larger yields of nitric oxide. But for each temperature, an equilibrium is reached, corresponding to a definite percentage of nitric oxide, and the yield is not increased by longer heating at that temperature. With air at 2000° C., this equilibrium is reached almost instantly, but at 1500° C. the reaction is slow. According to Nernst * only 0.1 per cent by volume of nitric oxide is produced at 1500°; 0.37 per cent at 1811°, and 0.97 per cent at 2195°. At higher temperatures larger percentages are produced, until at 3327° about 5 per cent of nitric oxide should be formed. But as the reaction is reversible, there is much decomposition of the product during its cooling, so the yield is decreased. Below 1500° C., decomposition of the product is slight, so very rapid cooling to this temperature is essential. As the electric arc is the most feasible method of attaining high temperatures, this method of producing nitric acid direct from the air has attracted considerable attention.†

The first technical attempt at the electrical fixation of atmospheric nitrogen was the **Bradley and Lovejoy process.** ‡ A spark at about 10,000 volts is jumped a short distance through the air, and the arc formed is immediately broken. The machine makes about 414,000 arcs per minute, and the nitrogen oxides in the air leaving the apparatus are condensed in towers to form nitric and nitrous acids. The process failed industrially.

The **Birkeland and Eyde process** § has been more successful, although mainly as applied to making nitrates rather than the acid. It is based on the fact that in a magnetic field the electric arc is deflected to one side. The furnace (Fig. 69) is a narrow, disk-shaped vertical box with fire-brick lining. Two copper electrodes (E), internally cooled by water, project horizontally into the furnace opposite to each other, and one-third of an inch apart. Around the elec-

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* Zeitschr. anorg. Chem., **1905** (**45**), 126; **1906** (**49**), 213.

† J. Soc. Chem. Ind., **1906**, 567; **1915**, 113.

‡ J. Soc. Chem. Ind., **1902**, 1138. Electrician, **1902**, 684. U. S. Pat. Nos. 709,867, and 709,868.

§ Zeitschr. angew. Chem., **1905**, 217. Chem., Ind., **1905**, 699; **1915**, 114. Electrochem. Met. Ind., **1904**, 399; **1906**, 126.

trodes are the coils of an electromagnet, by which the arc is deflected until it breaks and a new arc forms, to go through the same cycle. The speed of formation, deflection, and breaking of the arc is so rapid that about 700 arcs per second are formed, and a "disk of flame" is produced. Air enters the oven by narrow channels (A), and encounters the arcs in (B), leaving the furnace by the flues (C) mixed with about 2 per cent of nitric oxide. The nitric oxide is oxidized rapidly to peroxide and the gases go to quartz-packed absorbing towers, fed with water on the counter-current principle. Nitric acid of 50 per cent strength is obtained, which is mostly used to make calcium nitrate for fertilizer. Furnaces of 1000 to 3000 kilowatts capacity are used, and a yield of 500 to 600 kilograms of anhydrous nitric acid per kilowatt-year is claimed.

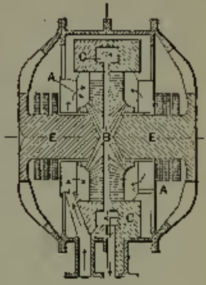

Fig. 69.

The **Schoenherr process** * exploited by the Badische Anilin u. Sodafabrik uses the apparatus shown in Fig. 70. The arc is sprung inside of a long narrow iron tube, having in the lower end an insulated iron electrode (E), which is pushed forward as needed through a copper water-jacket. The air enters at (A), passes through concentric pipes surrounding the reaction tube, and enters the latter near the electrode (E) by means of the tangential inlets in the movable sleeve (S). The air is thus given a spiral, rotary motion through the tube. The upper end of the reaction tube is water-jacketed for one-third its length and the tube itself forms the other electrode. The arc is started by moving the bar (Z) to short-circuit from the electrode (E) to the reaction tube; the arc thus starting in the centre of the whirling current of air, one end of it is

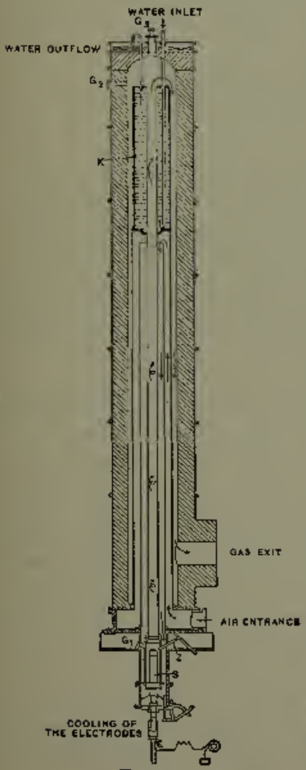

Fig. 70.

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* Zeitschr. angew. Chem., **1908**, 1633. J. Soc. Chem. Ind., **1915**, 115. Met. Chem. Engineering, **1909**, 245.

driven along the tube wall until it reaches the water-cooled section, where it again strikes the tube wall. The arc is thus extended to 5 or 7 metres length, and the air surrounding it is in contact with it for relatively long time. The hot gases pass out of the cooled end of the reaction tube and enter an annular space surrounding the inlet pipe, to which they impart some of their heat, for pre-heating the incoming air. Furnaces taking 1000 H. P. are in use and yields of 140 grams HNO_3 per kilowatt-hour are claimed.* Only 3 per cent of the total energy supplied is used for the production of nitric oxide, which is oxidized to peroxide by the excess air present, when cooled below 600° C. The absorption of the mixed nitric oxide and peroxide gases from the furnace is troublesome, since the reaction

$$3\ NO_2 + H_2O = 2\ HNO_3 + NO$$

regenerates much nitric oxide. If this, with air, is led into hot soda-liquor, sodium nitrite is obtained: —

$$2\ NO + O = NO + NO_2.$$
$$2\ NaOH + NO + NO_2 = 2\ NaNO_2 + H_2O, \text{ or}$$
$$2\ NaOH + 4\ NO = N_2O + 2\ NaNO_2 + H_2O.$$

This method for nitrite has replaced the old reduction process from sodium nitrate by metallic lead. Milk of lime yields calcium nitrite, which is used as a fertilizer under the name "air-saltpetre." When the dilute nitric acid from the water absorption is mixed with the calcium nitrite liquor and evaporated to dryness, some nitrous acid escapes and calcium nitrate is obtained, which is sold as "Norway saltpetre," for fertilizer.

The **Pauling process** † uses an apparatus shown in diagram by Fig. 71. The arc formed between the diverging electrodes (A, A) is elongated to about one metre, into the fan-shaped space between (A, A) by a blast of air from the nozzle (E). Each furnace is said to take 400 kilowatts at 4000 volts for treating 600 cubic metres of air. The gases after oxidation to peroxide are absorbed in water to produce nitric acid. The yield is said to be 60 grams of anhydrous acid per kilowatt-hour.

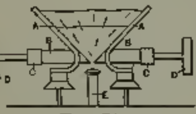

FIG. 71.

Nitric acid is largely used in making explosives; for parting gold and silver; in the manufacture of coal-tar dyes and other products;

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* Zeitschr. angew. Chem., **1909**, 1174.

† J. Soc. Chem. Ind. **1907**, 1204; **1909**, 1317; **1915**, 115.
J. Ind. Eng. Chem., **1914**, 68.

as a "pickling liquor" for cleaning metal; for various etching processes; and in making metallic nitrates. The pure acid is a colorless liquid, boiling at 86° C., but with decomposition. It also decomposes on exposure to strong light and becomes yellow (NO_2). Ordinary commercial acid (1.42 sp. gr.) distils at 123° C., contains 68 to 69 per cent HNO_3, and concentrated acid of 1.50 sp. gr. contains about 94 per cent HNO_3.

NITRATES

The most important nitrates are those of sodium and potassium, but ammonium, lead, iron, silver, strontium, and barium nitrates are used to some extent in the arts.

Sodium nitrate,* also called **Chili saltpetre**, is found in natural deposits in desert regions along the west coast of South America, especially near the boundary lines between Peru, Chili, and Bolivia, in latitude 20° to 26° S. The territory is now chiefly owned by Chili. The deposits extend about 220 miles in length, and average about 2 miles in width.

The crude nitrate, called "*caliche*," varies from yellowish white to brown or gray, and contains from 20 to 55 per cent $NaNO_3$; it forms beds about 5 feet thick, lying near the surface, but usually covered by a conglomerate of rock débris, cemented together by salt and gypsum. The region is rainless, and water and fuel, being very scarce, are used as economically as possible in refining the crude ore. The *caliche* is crushed and boiled with water in tanks heated by steam coils, until the liquor reaches a density of 110° Tw., when it is run off to crystallize. The mother-liquor retains most of the chloride, iodide, and iodate of sodium and magnesium, together with about 20 per cent of the nitrate. Hence the liquors are diluted with the wash water from the residue, and used again to lixiviate another portion of *caliche*. But after two or three repetitions of this process the mother-liquor is too contaminated for further use. It is then run off and treated for the recovery of the iodine (p. 252) which it contains. The residue from the lixiviation contains some nitrate, and is washed with fresh water, yielding a weak solution, which is used to dilute the mother-liquors before using them for leaching. The sodium nitrate crystals are drained or "centriffed" and dried in the sun. They are then packed and shipped as crude Chili salt-

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* J. Soc. Chem. Ind., **1890**, 664; **1893**, 128.

petre, containing from 94 to 98 per cent of $NaNO_3$. For many purposes this is purified by recrystallization.

Deposits of sodium nitrate have been found recently in Upper Egypt and in the trans-Caspian region, but these have not been much developed as yet, and nearly all the world's supply comes from Chili.

The formation of these beds is attributed to the decomposition of sea-plants under such conditions of temperature and humidity that the ammonia produced was converted into nitrate by the action of the nitrifying bacillus, an organism found in the soil. The region being rainless, the sodium nitrate was not washed away.

Potassium nitrate, or saltpetre, is derived from three sources: —

1. Natural nitrate beds, formed by the decomposition of organic matter in warm, damp climates.
2. Artificial nitrate beds, prepared especially for the purpose.
3. The decomposition of sodium nitrate by potassium chloride.

In many tropical countries, especially in India, Persia, and Egypt, native deposits of potassium nitrate are found impregnating the earth in the neighborhood of large cities and towns. This formation is due to the action of the nitrifying bacteria, and is not strictly an oxidation process. The deposits are continually forming, a white efflorescence appearing on the surface of the ground. This is scraped up, lixiviated with water, and the clarified solution evaporated directly, to crystallize the nitre. But all the calcium nitrate in the mother-liquors is thus lost. By adding potash obtained from wood ashes the calcium nitrate is decomposed, and a larger yield of nitre is obtained.

The artificial production of saltpetre in beds of decaying organic matter is now of slight importance, though formerly largely practised in Sweden, Switzerland, and France when nitre was collected as a part of each farmer's tax. By this process putrefying organic matter is mixed with old mortar, or with porous earth containing calcium carbonate and wood ashes, and the pile allowed to stand for some months, being occasionally moistened with the liquid drainage from stables. The nitrifying organisms soon impregnate the mass with nitrates of calcium, potassium, and magnesium. On leaching, these go into solution; when boiled with wood ashes, the calcium and magnesium are precipitated as carbonates, while the clarified liquor yields potassium nitrate on concentrating. The solution is clarified by adding a little glue, which combines with the impurities, forming a scum, which is removed by skimming.

Potassium nitrate, made by double decomposition of sodium nitrate with potassium chloride, is now the most important from a commercial standpoint. The reaction is very simple: —

$$NaNO_3 + KCl = NaCl + KNO_3.$$

Commercial potassium chloride, containing about 80 per cent KCl, is dissolved in water in cast-iron, copper, or lead lined wood tanks holding 500 to 600 gallons. When the hot solution has a density of about 40° to 42° Tw. (1.20 to 1.21 sp. gr.), sodium nitrate containing 95 per cent $NaNO_3$ is added, and the boiling mixture well stirred for an hour. On evaporation, the common salt, being less soluble than the nitrate, precipitates, and as much as possible of it is " fished " out, the concentration being continued until the density of the solution is 100° Tw. (1.50 sp. gr.). The liquid is allowed to stand a short time to settle, and then, while still hot, is drawn from the sediment into crystallizing tanks, where it is actively stirred while cooling. This causes the separation of the nitre as " crystal meal ", which is washed with a saturated solution of potassium nitrate (or often with cold water) to remove the mother-liquor and remaining sodium chloride. The wash waters and mother-liquors are used to dissolve the next lot of potassium chloride. One or two recrystallizations free the potassium nitrate from all but a trace of chloride.

When the potassium chloride contains some magnesium chloride, it is best to precipitate the magnesium by soda-ash before adding the sodium nitrate, since traces of magnesium chloride may otherwise remain in the product. This salt, being deliquescent, may cause the nitrate to become wet on exposure.

The chief uses of potassium nitrate are for making gunpowder and explosives, in matches, in pyrotechnics, in assaying, in metallurgical and analytical operations, and for curing meat.

Ammonium nitrate is now used to a considerable extent in the manufacture of certain " flameless " explosives, and also, in a less degree, for making nitrous oxide (" laughing gas "). It is usually made by neutralizing nitric acid with ammonia. Attempts to produce it by double decomposition of sodium nitrate with ammonium salts result in incomplete reactions, and some sodium nitrate remains undecomposed.

Lead nitrate is generally made by dissolving litharge (PbO) in hot dilute nitric acid. After filtering, the solution is concentrated to a density of 100° Tw. (1.50 sp. gr.) and allowed to crystallize.

It is used in dyeing and calico printing, for the manufacture of certain orange and yellow pigments (chrome yellows), for some explosives, and in some kinds of matches. It is important in that it furnishes a moderately soluble lead salt.

Ferric nitrate (nitrate of iron) is generally made by dissolving scrap iron in nitric acid of 1.30 sp. gr. The reaction is as follows: —

$$2\,Fe + 8\,HNO_3 = 2\,Fe(NO_3)_3 + 2\,NO + 4\,H_2O.$$

By concentrating the solution, colorless crystals, containing six or nine molecules of crystal water, are obtained.

The aqueous solution will dissolve ferric hydroxide, and this basic solution is much used in textile coloring. By using an excess of iron, and permitting the reaction to continue slowly after all the acid has been acted upon, a precipitate of insoluble basic ferric nitrate ultimately forms. The solution obtained in this way is of a red-brown color and indefinite composition. It is chiefly used for blacks in silk dyeing, and for iron-buff on cotton.

Ferrous nitrate is prepared by dissolving iron in *cold* dilute nitric acid (1.10 sp. gr.). But a considerable amount of ammonium nitrate is also formed in the solution, according to the reaction: —

$$4\,Fe + 10\,HNO_3 = 4\,Fe(NO_3)_2 + NH_4NO_3 + 3\,H_2O.$$

This solution is very unstable and decomposes when heated even slightly, forming basic ferric nitrate and liberating nitric oxide.

To prepare a pure ferrous nitrate, decomposition of a ferrous sulphate solution by barium or lead nitrate is employed: —

$$FeSO_4 + Ba(NO_3)_2 = BaSO_4 + Fe(NO_3)_2.$$

The solution is filtered or decanted from the precipitated barium sulphate.

There is a preparation sold as "**nitrate of iron**" (probably so called because some nitric acid is used in making it), which is not a nitrate, but a basic ferric sulphate and sulphate-nitrate solution. A solution of ferrous sulphate (copperas) is oxidized by nitric acid, according to the following equations: —

1) $6\,FeSO_4 + 2\,HNO_3 + 2\,H_2O = 3\,Fe_2(SO_4)_2 \cdot (OH)_2 + 2\,NO.$
2) $6\,FeSO_4 + 5\,HNO_3 = 3\,Fe_2(SO_4)_2 \cdot (NO_3) \cdot (OH) + 2\,NO + H_2O.$
3) $6\,FeSO_4 + 8\,HNO_3 = 3\,Fe_2(SO_4)_2 \cdot (NO_3)_2 + 2\,NO + 4\,H_2O.$
4) $12\,FeSO_4 + 3\,H_2SO_4 + 4\,HNO_3 = 3\,Fe_4(SO_4)_5 \cdot (OH)_2 + 4\,NO + 2\,H_2O.$

Equation (4) gives the best product.

The solution of basic ferric sulphate and sulphate-nitrates is a dark brown-red liquid, and is much used in silk dyeing. It is only mentioned here because of the frequent confusion of names in the commercial article.

Silver nitrate is made by dissolving the metal in dilute nitric acid: —

$$6\ Ag + 8\ HNO_3 = 6\ AgNO_3 + 4\ H_2O + 2\ NO.$$

If the silver contains copper, the resulting solution of nitrates is evaporated to dryness and then heated cautiously to about 250° C., at which temperature the copper nitrate is decomposed into copper oxide, nitric oxide, and oxygen, while the silver salt is not altered. By extracting the residue with water, the silver nitrate is dissolved, leaving the copper oxide. The solution is then evaporated to crystallize the silver nitrate.

The salt fuses unchanged at 225° C., but decomposes if heated nearly to redness; it is cast in small sticks, and is used in medicine for a cautery, under the name of *lunar caustic*. Silver nitrate has a very corrosive action on organic matter. It is largely used in photography, and to a lesser degree in pharmacy, in the manufacture of mirrors, in preparing "indelible inks," and as a chemical reagent.

Barium nitrate is made by dissolving the native carbonate (witherite) in hot, dilute nitric acid; or it may be prepared by decomposing a concentrated solution (32° Bé.) of barium chloride, by the addition of sodium nitrate, the less soluble barium nitrate precipitating. The salt is purified by recrystallization. It is chiefly used for producing "green fire" in pyrotechnics and for making barium peroxide (BaO_2) (p. 272). It is also used as an oxidizing material in certain explosives.

Strontium nitrate is made by dissolving the native carbonate (strontianite) in hot nitric acid. Its chief use is for "red fire" in pyrotechnics.

REFERENCES

Berichte über die Entwickelung der chemischen Industrie, u. s. w. A. W. Hofmann, 1877. (Vieweg, Braunschweig.)
Sulphuric Acid and Alkali. G. Lunge. 3d ed., Vol. I, 1903. (London.)
The Manufacture of Explosives. Oscar Guttmann. (Nitric acid and nitre.)
Der Chilisalpeter und Zukunft der Salpeterindustrie. H. Polakowsky. Directorium der landwirthschaftl. Hauptgenossenschaft zu Berlin. Berlin, 1893.
Die technische Ausnützung des atmosphärischen Stickstoffes. E. Donath u. K. Frenzel, Leipzig, 1907.
Zeitschrift f. angewandte Chemie., **1893**, 37. Oscar Guttmann.
Journal American Chemical Society, **1895**, 576. Edward Hart.
J. Soc. Chem. Ind., **1893**, 128. J. Buchanan. (Sodium nitrate in Chili.) **1893**, 203. Guttmann. (Nitric acid.) **1905**, 924.
Utilization of Atmospheric Nitrogen. By Thomas H. Norton. Bull. No. 52, Special Agents Series, Department of Commerce and Labor. Bureau of Manufactures. Washington, D.C., 1912.

AMMONIA

The destructive distillation of organic matter containing nitrogen yields more or less ammonia, and the greater part of the commercial supply is obtained from the distillation of coal for coke or gas; of peat; of bituminous shales; of bones and refuse animal matter; of putrid urine and excreta; of the residues from the fermentation of beet sugar molasses for alcohol; and the waste gases from blast furnaces.

Ammonia can be prepared synthetically from the nitrogen of the air in several ways, but these processes meet severe competition from the ammonia recovered as by-product. It was early proposed * to pass air over a mixture of barium oxide and carbon, at a white heat, and then to decompose the barium cyanide formed, by passing in steam after the temperature had been lowered to 450° C.: —

$$BaO + 3\ C + 2\ N + O = Ba(CN)_2 + CO_2.$$

$$Ba(CN)_2 + 3\ H_2O = BaO + 2\ CO + 2\ NH_3.$$

The process failed commercially because of the great consumption of fuel.

The **Frank and Caro process** † is based upon the decomposition of calcium cyanamid (p. 267) by the action of superheated steam: —

$$CaCN_2 + 3\ H_2O = CaCO_3 + 2\ NH_3.$$

Yields of 96 to 97 per cent are claimed, and the ammonia is very pure.

The **Haber process** ‡ depends on the realization of the reaction: — $N_2 + 3\ H_2 = 2\ NH_3$. Since this reaction takes place with decrease in volume and with a large evolution of heat (24 Cal.), it is driven to the right by increase in pressure, but tends to reverse at higher temperatures. While the equilibrium corresponds to high percentages of ammonia at ordinary temperatures, dissociation into the elements rises very rapidly with the temperature. Moreover, at low temperatures, the reaction rate is very slow. Haber has been able to find many catalyzers, of which he uses uranium powder and carbon, but even with these the rate is too slow for commercial work below 500° C.

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* Compt rendu, L, 1100.

J. Soc. Chem. Ind., **1882**, 364; **1883**, 328.

† Zeitschr. angew. Chem., **1903** (**16**),536. J. Soc. Chem. Ind., **1903**, 809; **1908**, 1093. Met. Chem. Eng., **1915** (**13**), 213.

‡ Zeitschr. Elektrochem., **1910** (**16**) 244. J. Soc. Chem. Ind., **1910**, 485, 1453.

To get reasonable yields at this temperature, the pressure must be increased to 150 to 200 atmospheres. The reaction products, containing only a few per cent of ammonia, are cooled, the ammonia absorbed as a double compound with suitable salts, such as ammonium nitrate, and the gases returned to the reaction chamber. The ammonia is then driven off by heat, and the ammonium nitrate thus regenerated.

In **Serpek's process** * a mixture of calcined bauxite and coke is heated in nitrogen, or a producer gas containing 65 per cent of nitrogen, to 1600° or 2000° C., in a rotary furnace: —

$$Al_2O_3 + 3\ C + N_2 = 2\ AlN + 3\ CO.$$

The aluminum nitride, containing about 30 per cent nitrogen, is decomposed with water, according to the reaction

$$2\ AlN + 3\ H_2O = Al_2O_3 + 2\ NH_3.$$

The bauxite enters the upper one of two superimposed rotary kilns, and is heated by the combustion of the carbon monoxide issuing from the lower kiln; the calcined alumina passes into the lower kiln, along with the carbon, and here the main reaction takes place. The aluminum oxide produced is pure enough to meet market requirements.

The chief source of ammonia is the " gas liquor " from the coke and gas manufacture (pp. 36, 314). The nitrogen in coal yields ammonia and cyanogen compounds by destructive distillation: in the " gas liquor " are found free ammonia, with ammonium carbonate, sulphide, and sulphydrate, which are volatile with steam, and sulphate, thiosulphate, sulphite, sulphocyanide, and ferrocyanide, which are not volatile. Gas liquor is valued according to its percentage of ammonia as determined by distilling with caustic soda, absorbing the vapors in standard sulphuric acid, and titrating the excess acid.

The gas liquor contains some tar, but on standing this settles, and the clear liquor is then distilled for the ammonia. In the simplest apparatus, the liquor is heated in one still until the volatile salts are expelled, and then is drawn into another still, where " milk of lime " is added, and heated until the fixed salts are decomposed and the ammonia driven off. The ammonia and volatile salts are absorbed in acid and the hydrogen sulphide and other foul-smelling gases evolved are led into the chimney, or decomposed in a Claus kiln (p. 106).

Generally, continuous stills constructed on the principle of the

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* U. S. Pat. 867,615, 888,044, 987,408, 996,032. Met. and Chem. Ind., **9** **(1913)**, 137. J. Soc. Chem. Ind., **1913**, 1143.

Coffey still, or some special apparatus, as that of Feldmann, or of Grüneberg and Blum, are used to distil the gas liquor. **Feldmann's apparatus** (Fig. 72) is much used in this country: the gas liquor from the settling tank (F) passes into the economizer (E), a long, cylindrical shell, containing a number of narrow tubes, through which the liquor flows. In the vessel (D) is sulphuric acid, to combine with the ammonia vapors passing from the still by the pipe (G). The hydrogen sulphide and carbon dioxide liberated in (D) collect under the bell. The heat of the reaction between the acid and ammonia raises the temperature of these gases to a high degree, and they pass into the jacket or shell surrounding the tubes in the economizer, where they heat the liquor in the small tubes, so it arrives hot, at the top of the tower (AB) by the pipe (K). In the tower, the ammonia and its volatile salts are driven out by steam passing up through it. The liquor containing the fixed ammonia salts then passes to the lower part of (AB), where it is mixed with "milk of lime," while steam is blown in. The mixture then overflows through (M) into the smaller still (C) where all the ammonia set free by the lime is driven out by a steam jet from (S). This ammonia passes through (ON) into the first tower, mixes with the gas escaping from (AB), and is absorbed in (D). The waste liquor escapes through (P), and the sludge of calcium salts formed in (B) is drawn off at regular intervals through (R). The still may run for months without stopping.

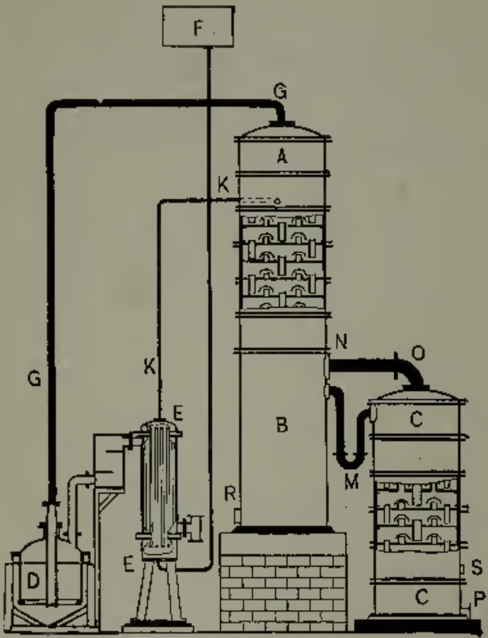

Fig. 72.

The **Grüneberg-Blum apparatus** is more complicated in details, but involves nearly the same principles as the above. All of these stills employ dephlegmation (p. 11).

Sometimes in distilling gas liquor, the vapors set free by the action of the lime are made to bubble through fresh liquor in a second vessel. Thus the volatile ammonia salts are expelled by the heat of these vapors, and pass with them to the absorption vats, while the gas liquor is drawn into the first vessel to be treated with lime. This method was used in the old apparatus of Grüneberg and of A. Mallet.

The ammonia gas set free in any of these stills is generally absorbed in sulphuric acid. If dilute acid (80° to 100° Tw.) is used, there is no separation of ammonium sulphate crystals in the saturator, and the liquor is easily clarified from tar and suspended impurities before evaporating to crystallize, and yields a light-colored product. With concentrated acid (140° Tw.) ammonium sulphate crystals separate in the saturator, and are " fished out." But they are often discolored. As the crystals are removed, fresh acid is introduced into the saturator. This is always covered with a hood, from which a pipe carries off the foul gases, consisting largely of hydrogen sulphide. These gases are often led to a Claus kiln (p. 106) to recover the sulphur, and avoid contaminating the atmosphere. The ammonia gas is led into the saturator through a pipe perforated with small holes and submerged in the acid.

Plants for distilling peat * in Mond producers (p. 43) to recover gas and ammonia are in operation abroad. The moist peat is treated with superheated steam and air at 350° to 500° C.; the yield of ammonia varies from 40 to 130 kg. of ammonium sulphate per ton of peat.

Ammonia has been made in this country by distillation of waste animal matter from slaughter houses and tanneries. † The material is dried and put into an upright iron cylinder, provided with a manhole at the top and bottom, and having a large perforated pipe running up through the centre, about three-fourths the distance to the top. Chimney gases, forced by an air compressor through a superheater (a furnace containing coils of pipe heated to a bright red heat) into the perforated pipe, come into direct contact with the refuse matter. The volatile products pass out at the top of the retort into a hydraulic main, similar to that in a gas works. The tarry matter settles in the main and the gases pass through condensers. Both the condensed liquors and the gases pass into absorption tanks containing water; the unabsorbed gases then go to a " scrubber " (p. 319) to remove the last of the ammonia, and are then burned under the retort. The liquor produced in the absorbers and scrubber is distilled in an ammonia still. Much nitrogen remains in the coke in the retort.

* Zeitschr. angew. Chem., **1906**, 1574. J. Soc. Chem. Ind. **1908**, 796; **1911**, 744.

† The process failed in practice and has been given up.

A considerable amount of liquid ammonia is prepared for use in ice machines (p. 23). This is compressed into steel cylinders, usually containing about 100 pounds of the liquid.

Ammonium sulphate, as found in commerce, has a light gray or yellowish color, or, if carefully made and washed after crystallizing, is nearly white. When prepared by direct saturation, the color may be brown or nearly black. Common acid made from pyrites yields a salt which is yellow in color, owing to the iron or arsenic present. The crystals should be washed, and dried in a lead-lined centrifugal machine. When sold in large quantities it is valued according to its content of ammonia or nitrogen. Good samples contain from 23 to 25 per cent NH_3. It is largely used as a source of nitrogen in making fertilizers, but for this purpose must be free from sulphocyanide, which is injurious to vegetation. When made by absorbing the gas in acid, little or no sulphocyanide is present, but by direct neutralization of the gas liquor the cyanide may separate with the sulphate. The salt is used as a source of other ammonium compounds, and to a slight extent in rendering fabrics, wood, and other tissues non-inflammable. By distilling with lime it yields a very pure ammonia gas, which may be absorbed directly in water for the "aqua ammonia" of trade; or the gas may be passed through towers filled with charcoal, to remove any trace of pyridine or tar, before absorption. Any sulphuretted hydrogen may be removed by passing the gas over oxide of iron.

Ammonium chloride is made by absorbing ammonia gas in dilute hydrochloric acid, or by neutralizing gas liquor with the acid directly and evaporating the solution. During the evaporation much of the tarry matter separates, and is skimmed off. Some nuisance may result from the gases escaping during the neutralizing.

Another method is to mix a saturated solution of ammonium sulphate with a strong solution of salt or potassium chloride. On evaporating somewhat, monohydrated sodium sulphate ($Na_2SO_4 \cdot H_2O$) separates from the hot liquor, leaving the ammonium chloride in solution. On cooling, the ammonium chloride crystallizes: —

$$(NH_4)_2SO_4 + 2\ NaCl = Na_2SO_4 + 2\ NH_4Cl.$$

The crystallized chloride is more or less discolored by tar, and is purified by sublimation in iron or earthenware pots or retorts. The ammonium chloride collects on the cover of the pot as a thick, fibrous cake, in which form it comes in trade under the name of *sal-ammoniac*. This generally contains iron as an impurity. It was formerly made by subliming the soot obtained by burning dried camel's dung, but is now nearly all made from gas liquor. The crystallized salt is often sold under the name of "muriate of ammonia," and is usually less pure than sal-ammoniac. Muriate of ammonia is much used in the arts for charging Leclanché electric batteries; in the process of "galvanizing" iron; in soldering liquors; for making "rust cement" for pipe joints; and in textile coloring.

Ammonium carbonate as found in commerce is not a pure salt, but is a mixture of acid ammonium carbonate ($NH_4 \cdot HCO_3$) and a salt of carbamic acid ($NH_2 \cdot CO_2 \cdot NH_4$). The commercial salt is made by heating a mixture of the sulphate and powdered calcium carbonate in iron retorts. The vapors are condensed in lead-lined chambers, and the impure product is generally sublimed in iron pots having lead caps. A little water is put into each pot along with the salt, this causing the sublimed product to be transparent instead of opaque white. The temperature of this second sublimation is not much above 70° C.

Ammonium carbonate is transparent when fresh and pure, but on exposure to the air becomes covered with a white layer of bicarbonate, owing to the loss of ammonia. It is entirely volatile when heated, and from this fact is derived its old name of *sal-volatile.* It is used considerably in wool scouring, in certain baking powders, in medicine, and for the preparation of "smelling salts," and to some extent as an analytical reagent.

Ammonium sylphocyanide (thiocyanate), p. 291.

REFERENCES

Acetic Acid, Vinegar, Ammonia, and Alum. John Gardner, F.I.C., F.C.S., London, 1885. (J. and A. Churchill.)

Chemie des Steinkohlentheers. Dr. Gustav Schultz, 2te Auf., Vol. I, Braunschweig, 1886. (Vieweg und Sohn.)

Das Ammoniak-Wasser. Albert Fehrmann, Braunschweig, 1887. (Vieweg.)

Ammoniak und Ammoniak-Praeparate. Dr. R. Arnold, Berlin, 1889.

Traitement des Eaux Ammoniacales. L. Weill-Goetz et F. Desor, Strasbourg, 1889. (G. Fischbach.)

Die technische Ausnützung des atmosphärischen Stickstoffes. E. Donath und K. Frenzel, Leipzig, 1907.

Das Ammoniak und seine Verbindungen. J. Grossmann. Halle, a. S., 1908.

Coal Tar and Ammonia. G. Lunge, 4th ed., London, 1909. (Gurney and Jackson.)

Coal Gas Residuals. Frederick H. Wagner. New York, 1914. (McGraw-Hill Co.)

POTASH INDUSTRY

Previous to the invention of the Leblanc Soda Process, the most important alkali was potassium carbonate, — potash, which was nearly all derived from wood ashes. But with the development of the soda industry, the demand for potash was greatly diminished, and at the present time, soda has replaced it for all except a few special purposes.

The chief sources of potassium salts are: —

Wood ashes.
Beet-sugar molasses and residues.
Wool scourings. (*Suint.*)
Stassfurt salts.

Land plants take up considerable quantities of potassium compounds from the soil. When the plants are burned, about 10 per cent of the weight of the ashes is potassium carbonate,* which may be obtained by lixiviation. Potash from wood ashes is now chiefly made in Russia, Sweden, and America, the woods most employed being elm, maple, and birch. Sometimes the stumps and small branches only are burned, the trunks being used for timber. The ashes are moistened slightly, put into tanks having false bottoms on which straw is spread, and then lixiviated with warm water. The lye so obtained is evaporated (sometimes by the waste heat from the burning wood) in iron pots until it solidifies on cooling. The dirty brown mass is then calcined in a reverberatory furnace until all the organic matter is destroyed. The product is known as potash or crude pearlash. It is white or gray in color, and contains about 70 per cent K_2CO_3, with some sulphate and chloride and sodium salts. By redissolving the crude potash in water, settling and concentrating the solution until the sulphates and chlorides separate as crystals, a concentrated and pure lye is obtained. When this is evaporated to dryness and the residue calcined, it yields a much purer product, known as "**refined pearlash**," and containing from 95 to 97 per cent of K_2CO_3. It is necessary that a low heat be employed in the calcination, since the charge fuses at a moderate temperature.

Often, some quicklime is put in the bottom of the tanks before the ashes are introduced. On leaching, the solution of potassium

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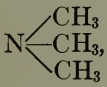
* Those plants which contain much silica or phosphoric acid — straw and grasses — yield but little potash.

salts reacts with the lime, forming insoluble calcium salts, and yielding more or less potassium hydroxide in the lye. The resulting product is then a mixture of potash and caustic potash.

In the manufacture of beet sugar, a very impure molasses remains, containing among other things a large amount of soluble potassium salts. This molasses is now generally fermented, in which process the sugary substances are converted into alcohol, which is distilled off, leaving the mineral salts in the liquid residue, called *vinasse* or *schlempe.* If this is evaporated to dryness and the mass calcined, the organic potassium salts are decomposed, leaving in the cinder about 35 per cent potassium carbonate, and a large amount of chloride and sulphate, together with sodium salts.

If the *vinasse* be evaporated to dryness and the residue destructively distilled in retorts, a distillate is obtained, containing organic compounds of which methyl alcohol, CH_3OH, ammonia, and trimethylamine,  $\mathrm{N}\begin{matrix}\diagup \mathrm{CH_3}\\ -\mathrm{CH_3}\\ \diagdown \mathrm{CH_3}\end{matrix}$, are valuable. The cinder in the retort contains potassium salts, which are obtained in solution by lixiviation, and a considerable quantity of potash is thus recovered. Very often, however, the ash is used as a fertilizer, thus returning the potash to the soil.

Wool scourings furnish some potash in countries where much wool is washed. Sheep's wool as it comes from the animal contains from 30 to 75 per cent of its weight of impurities, consisting of dirt, sand, dung, etc.; wool grease or "yolk," a fat-like substance, made up of cholesterine and compounds of it with oleic, stearic, and palmitic acids; and *suint,* which consists chiefly of potassium salts of oleic, stearic, and other organic acids, with small quantities of chlorides and sulphates and nitrogenous matter. The "*suint*" exudes from the animal in the perspiration, and is deposited on the wool by evaporation. It is soluble in cold water, and is thus removed in the scouring process. If these wash waters, containing wool grease and *suint,* are run into streams, pollution of the water results. Prevention of this nuisance, as well as the value of the potash, has necessitated disposal of the washings in some economical manner, and they are usually evaporated to dryness and calcined. If the calcination is done in closed retorts, a considerable quantity of ammonia is obtained. The cinder is lixiviated, and on evaporation, the solution yields, first, chlorides and sulphates of potassium and sodium, and finally a pure potash, which averages nearly 4 per cent of the weight of the raw wool scoured. For the recovery and treatment of wool grease, see pp. 369 and 500. This utilization of wool grease and *suint* is mainly practised in France, Belgium, and Germany, where it is done chiefly to prevent the pollution of the streams. Cheap fuel is essential to a successful working of the process. On a small scale it is not profitable, and the wash waters are often run on to the fields as fertilizer.

For potassium carbonate from potassium chloride, see p. 162.

Certain seaweeds, especially some varieties of brown algæ, which grow in rather deep water, have the power of storing potassium salts in large amount. For many years the collection of seaweed in the kelp industry (p. 252) has been practised on the coast of Scotland and France, and from the ashes of these plants potassium chloride and sulphate, and iodine have been recovered. Recently the enormous beds of these plants (locally known as *kelp*) along the coast of California and in the Puget Sound region have attracted attention * as possible source for potash salts and iodine. The potassium salts may be extracted by diffusion processes, or by burning the plants at low temperatures and lixiviation of the ash.

Reports * of large deposits of alunite (p 286) in Utah, Nevada, and Colorado have lately turned attention to the possibility of extracting potash from this basic alumino-potassium sulphate. By roasting, sulphur trioxide is evolved, the alumina rendered insoluble, and potassium sulphate may be lixiviated from the mass. The investigation of these deposits is not yet completed.

By far the most important source of potassium compounds at the present time is the great natural deposit of potassium salts found at Stassfurt and Leopoldshall, near Magdeburg, Germany. This consists of immense beds of various salts, which have been deposited from sea water. They were discovered in attempting to reach the underlying rock-salt, but because of the large proportion of potassium and magnesium chlorides, the material was at first thrown aside as worthless, the name applied to it, — "*abraumsalze*," — indicating the small value attached to it. But in 1861–4 methods were devised by which potassium chloride and sulphate could be obtained cheaply from the Stassfurt salts, and since these furnish a valuable source for nearly all other potassium salts, a rapid development of the industry followed.

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* Fertilizer Resources of the United States. Senate Document No. 190, 62d Congress. Washington, 1912.

Sea water contains about 3.5 per cent of solids, consisting of: —

Sodium chloride	76.49	per cent *
Magnesium chloride	10.20	"
Magnesium sulphate	6.51	"
Calcium sulphate	3.97	"
Potassium chloride	1.98	"
Magnesium bromide Calcium bicarbonate, etc.	0.85	"

By the evaporation of sea water under certain conditions, these salts, together with various double salts, formed by mutual inter-reactions, crystallize in the order of their relative insolubility.

The Stassfurt deposit was undoubtedly formed by the evaporation of sea water, under peculiar conditions. The mode of formation has been studied by many investigators, to whose memoirs the reader is referred for full explanations. † The deposit is nearly 3000 feet thick, and about 16 different salts have been identified in the various strata. The more important salts and their composition, are given below: —

Gypsum	$CaSO_4 \cdot 2\ H_2O$
Anhydrite	$CaSO_4$
Kainite	$K_2SO_4,\ MgSO_4,\ MgCl_2 \cdot 6\ H_2O$
Carnallite	$KCl,\ MgCl_2 \cdot 6\ H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Polyhalite	$K_2SO_4,\ MgSO_4,\ 2\ CaSO_4 \cdot 2\ H_2O$
Rock-Salt	$NaCl$
Sylvine	KCl
Tachydrite	$CaCl_2,\ 2\ MgCl_2 \cdot 12\ H_2O$
Boracite	$2\ (Mg_3B_8O_{15}) + MgCl_2$
Astrakanite	$MgSO_4,\ Na_2SO_4 \cdot 4\ H_2O$
Schoenite	$K_2SO_4,\ MgSO_4 \cdot 6\ H_2O$

The beds are not sharply defined layers of separate salts, the deposit being generally regarded as containing four principal "regions."

The rock-salt or anhydrite region is the lowest of these. This consists of thin layers of very pure rock-salt, separated by narrow strata (one-fourth of an inch thick) of anhydrite. The anhydrite is separated from the salt mechanically, and the latter is then ground for use directly. This bed is nearly 2000 feet thick in places.

The polyhalite region, about 200 feet thick, is above the rock-salt region. It is composed of 91 per cent of rock-salt, and 6½ per cent of polyhalite, with smaller quantities of other salts.

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* Regnault (Thorpe's Dictionary of Applied Chemistry, Vol. IV, 340).

† A very good account is given in Thorpe's Dictionary of Applied Chemistry, Vol. IV, pp. 340–341. Also see Pfeiffer's Handbuch der Kali-Industrie.

The kieserite region, lying next above, is about 185 feet thick, and contains 65 per cent rock-salt, 17 per cent of kieserite, 13 per cent carnallite, and 5 per cent of other salts.

The carnallite region lies nearest the surface, and is about 140 feet thick. This is the most important and contains: —

Carnallite	55–60 per cent
Rock-salt	20–25 per cent
Kieserite	16 per cent
Tachydrite Boracite	4 per cent

In parts of this region, changes have taken place through the action of water, by which considerable deposits of kainite and sylvine have been formed. The composition of raw carnallite is about as follows: —

	I	II
Potassium chloride	16.2 per cent	15.7 per cent
Magnesium chloride	24.3 "	21.3 "
Sodium chloride	18.7 "	21.5 "
Calcium chloride	0.2 "	0.3 "
Magnesium sulphate	9.7 "	13.0 "
Calcium sulphate	2.1 "	00.0 "
Water	28.8 "	26.2 "
Insoluble	00.0 "	2.0 "

The crude carnallite is often colored a deep red by the presence of iron compounds.

The present commercial supply of potassium chloride, and incidentally of other potassium compounds, is obtained from **carnallite.** The crude material is treated with the hot mother-liquor from a previous lot, in an iron kettle having a stirring apparatus and a false bottom. This mother-liquor contains about 20 per cent $MgCl_2$, which prevents the solution of the rock-salt and kieserite, but does not hinder the dissolving of the carnallite. The action of the magnesium chloride solution is continued until the hot liquor reaches a density of 1.32 sp. gr., when it is drawn off from the sludge and allowed to cool slowly. At this density, the greater part of the potassium chloride crystallizes on cooling, leaving the magnesium chloride and some potassium chloride still in solution. This liquor is then further concentrated, until it contains about 30 per cent magnesium chloride. On cooling, crystals having the composition $KCl, MgCl_2 \cdot 6 H_2O$, — artificial carnallite, — separate, leaving only the excess of magnesium chloride in solution. The artificial carnallite is decomposed with water, and the potassium chloride crystallized out, leaving the magnesium chloride in solution; a part of this liquor, diluted with the wash water from the sludge, is used to extract the next portion of raw carnallite. The potassium chloride is washed with a small portion of very cold water, to remove the common salt.

The residue from the solution of the raw carnallite consists largely of kieserite mud ($MgSO_4 \cdot H_2O$), which is insoluble in water; but on standing for some time in contact with water, it passes over into the soluble **Epsom salts** ($MgSO_4 \cdot 7\ H_2O$). At an intermediate stage of the hydration, the mud solidifies in a manner similar to plaster of Paris when mixed with water. When this solidification is about to take place, the mud is moulded into blocks, which become very hard, and in which form it is shipped. But after some time they take up moisture from the air, and fall to a powder of Epsom salt.

Glauber's salt is made at Stassfurt in the winter time as follows: Solutions of common salt and magnesium sulphate (*e.g.* from kieserite) when kept below 0° C. will react together, thus: —

$$MgSO_4 + 2\ NaCl = MgCl_2 + Na_2SO_4,$$

and at the low temperature, the sodium sulphate crystallizes to form $Na_2SO_4 \cdot 10\ H_2O$.

Kainite ($K_2SO_4, MgSO_4, MgCl_2 \cdot 6\ H_2O$) is extensively used in the crude state as a fertilizer. Some of it, however, is treated for **potassium sulphate**, by the method of H. Precht. When heated with water under pressures of four or five atmospheres, kainite decomposes into a double potassium-magnesium sulphate, magnesium chloride, and potassium chloride, thus: —

$$3(K_2SO_4, MgSO_4, MgCl_2 \cdot 6\ H_2O) = \\ 2(K_2SO_4, 2\ MgSO_4 \cdot H_2O) + 2\ MgCl_2 + 2\ KCl + 16\ H_2O.$$

The double potassium-magnesium sulphate separates in crystals, and is freed from chlorides by washing; during the washing, one molecule of the magnesium sulphate is also removed, and a salt of the composition, $K_2SO_4, MgSO_4$, remains. This is dried and calcined and sold as double potassium-magnesium sulphate; or it may be decomposed directly by treating with a solution of potassium chloride of 1.142 sp. gr.: —

$$K_2SO_4, MgSO_4 + 2\ KCl = MgCl_2 + 2\ K_2SO_4.$$

The potassium sulphate is separated from the magnesium chloride by crystallization.

Potassium sulphate, made from kainite as above, or by the action of sulphuric acid on potassium chloride, is largely used as a fertilizer and for the manufacture of potassium carbonate.

Potassium chloride, chiefly obtained from carnallite, is extensively used for preparing other potassium salts, especially the nitrate (p. 146), sulphate, and carbonate.

Potassium carbonate or **potash** is made from potassium chloride by the Leblanc process, in the same way as soda-ash from salt. But the ammonia process cannot be employed, because the acid carbonate of potassium ($KHCO_3$) is soluble in ammoniacal solutions, and does not precipitate.

Potassium carbonate is sold in trade under the name of potash or pearlash, and is used chiefly in the glass industry, for caustic potash and for chromates of potassium. A considerable quantity is bought by soap makers, and causticized, the solution being used for soft soaps (p. 373).

Caustic Potash is made in the same way as caustic soda (p. 101). The mother-liquors from the black-ash lixiviation are decomposed directly with slaked lime. Caustic potash is much more deliquescent than caustic soda, and is generally made where it is to be used.

In soap making, it was formerly customary to saponify the fat with caustic potash, and then to add common salt. An interchange between the potassium and sodium took place, and a hard sodium soap resulted. But as soda is now cheaper, and yields a hard soap directly, potash soaps are only used for special purposes.

Potassium nitrate (see p. 146).

Potassium bichromate ($K_2Cr_2O_7$) is made by roasting chromite (a native oxide of chromium and iron) with potash, lixiviating the fused mass with water, and adding enough sulphuric acid to convert the neutral potassium chromate into bichromate. The reactions involved are as follows: —

$$Cr_2O_3 + 3\ O = 2\ CrO_3.$$

$$CrO_3 + K_2CO_3 = K_2CrO_4 + CO_2.$$

$$2\ K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O.$$

The finely powdered chrome ore is mixed with lime and potash, and roasted at a bright red heat, with free access of air and frequent stirring. After several hours the chromic oxide is all oxidized to chromium trioxide (CrO_3), which combines with the lime and potash to form neutral chromates of calcium and potassium. The mass is then treated with a hot solution of potassium sulphate, which forms potassium chromate from the calcium chromate. The solution of neutral potassium chromate, when saturated, is drawn off and settled. It is then decomposed in lead-lined tanks, by the addition of sulphuric acid. Since potassium bichromate is very much less soluble in cold solution than the neutral chromate, about three-fourths of the total amount of bichromate formed precipitates. The remaining liquor, containing potassium sulphate, is used to leach a new portion of cinder. The precipitated bichromate is recrystallized from water.

The addition of lime to the furnace charge is necessary to prevent the fusion of the mass, and to keep it porous, so that the oxidation of the chrome is more complete.

Potassium bichromate is much used as a source of other chromium compounds; as an oxidizing agent in dyeing and making coal-tar dyes; as a mordant; as a bleaching agent for oils and fats; and for the preparation of leather in the chrome tannage processes.

REFERENCES

Die Industrie von Stassfurt u. Leopoldshall. G. Krause. Coethen, 1877.
Handbuch der Kali Industrie. E. Pfeiffer, 1887.
Die Salz Industrie von Stassfurt. Dr. Precht, Stassfurt, 1889. (R. Weicke.)
Die Stassfurter Kali-Industrie. G. Lierke, Wien, 1891. (Hilschmann.)
Die norddeutsche Kaliindustrie. Precht-Ehrhardt, Stassfurt, 1906.
Chemie und Industrie der Kalisalze. Erdmann, Berlin, 1907.
Die deutsche Kaliindustrie. Dr. K. Kubierschky, Halle, a. S., 1907.
Die Verwertung des Kalis. Kiersche, Halle, a. S., 1907.
Fertilizer Resources of the United States. Senate Document No. 190, 62d Congress. Washington, 1912.
J. Soc. Chem. Ind., **1883**, 146. C. N. Hake.
Chemische Zeitung, **1890**, Grief. **1891**, Heyer.
Dingler's polytechnisches Jour. Vol. **241**. Precht.

FERTILIZERS

Growing plants abstract from the soil and air certain elements, as carbon, hydrogen, potassium, calcium, sulphur, phosphorus, and nitrogen, and apply them to their nourishment. To a less degree, silicon, iron, sodium, magnesium, and chlorine are taken up also. Natural weathering of the minerals in the soil usually provides enough of the elements needed by plants, but the supply of potassium, phosphorus and nitrogen is insufficient for frequent repetitions of the same crops, and the soil becomes less productive * or barren. To supply this yearly drain on the soil, *fertilizers* are employed. The natural fertilizers, barn-yard manure, urine, and decomposing vegetable mould or muck, need little or no treatment before use, and will not be considered here.

Artificial fertilizers are manurial substances prepared from materials needing special treatment to render them fit for plant food. The chief requisites for a good artificial fertilizer are: It must contain at least one substance fit for plant food, and which is easily converted by rain or moisture into a form that plants can assimilate; it must be dry and finely pulverized, for even distribution over the surface of the ground; nothing injurious to plant life may be present.

A complete fertilizer supplies the three essentials, potassium, nitrogen, and phosphorus. Often only one or two of these elements may be afforded, the fertilizer being intended for use with certain crops or on particular soils.

Potassium is generally returned to the soil in the form of sulphate or carbonate (wood ashes), and occasionally as chloride. The preparation and use of these salts have already been considered and also the preparation of ground kainite (p. 161) for this purpose.

Nitrogen is frequently supplied as ammonium salts (p. 154), or nitrates, particularly sodium nitrate (p. 145). But many substances used for fertilizers contain nitrogen in organic compounds, which decompose readily in the soil, setting free the nitrogen.

Recently calcium cyanamid † ($CaCN_2$), made by treating calcium

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* Loss of fertility may be due to other causes then *depletion* of plant food: there is some evidence that plants leave deleterious excretions in the soil, which for a time act toxically upon the same variety of plant.

† Zeitschr. angew. Chem., **1903 (16)**, 536; **1910 (23)**, 2405.

J. Soc. Chem. Ind., **1903**, 809.

Electrochem. Met. Ind., **1907**, 77; **1908**, 341; **1910**, 539; **1915**, 213.

carbide at 1000° C. with nitrogen gas from liquid air (p. 267), has come into use as a nitrogenous fertilizer under the name "*nitrolim.*"

Phosphorus is nearly always applied to the soil in some form of calcium phosphate derived from mineral sources or from organic matter.

Fertilizers are largely made from the **waste products** of slaughter houses, such as blood, bits of waste meat and other refuse, bones, hoofs, horns, and hair. Tainted meat and animals which have died of disease are also sent to the rendering tanks.* **Blood** is dried at a moderate heat and crushed to powder between rolls. It contains about 10 per cent N, and is very uniform in composition.

Raw bones contain fatty matter which is slow to decompose; but if allowed to ferment in compost heaps with wood ashes and stable manure for a few months, they become more active and yield 3 to 4 per cent nitrogen, as well as 20 to 25 per cent phosphate. As a rule bones are extracted with superheated steam to remove the fat and gelatine, and then ground to yield "**bone meal,**" carrying about 27 to 28 per cent of phosphoric acid. This is much more active as a fertilizer than the crushed raw bones. Steaming reduces the nitrogen to about 1 to 2 per cent, and makes the bone more easily decomposed in the soil. If treated with sulphuric acid, the nitrogen and phosphoric acid are rendered more available and the product is called "**dissolved bone.**"

Bones are often subjected to destructive distillation in retorts, by which nearly all the nitrogen is driven out as ammonia, ammonium carbonate, pyridine, and other nitrogenous organic compounds, while the residue left in the retort, known as "**bone-char**" or "**bone-black,**" contains calcium phosphates and other salts, mixed with carbon. This bone-char is extensively used as a decolorizing agent in the purification of sugar, glucose, oils, and other liquids; when it can no longer be employed for this purpose (see p. 311), it is burned with free access of air to form "**white-ash,**" which contains a high percentage of phosphorus. This bone-ash may be used directly as a fertilizer, but is usually treated with sulphuric acid to form "superphosphate" (p. 169), which is more soluble than the tricalcium phosphate of the bone.

A process for extracting the mineral phosphate from bones by digesting with hydrochloric acid has been practised to some extent.

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* "Rendering" consists in extracting all the fats, oils, and gelatinous matter from the carcasses by treating with benzine or steam under pressure. The fat extracted is used for soap stock. The dried residue, called "tankage," is ground fine for fertilizer, and furnishes both nitrogen and phosphoric acid.

The solution of phosphoric acid thus obtained is neutralized with milk of lime, by which the calcium phosphate is precipitated, chiefly as dicalcium phosphate ($Ca_2H_2P_2O_8$). This is sometimes sold as "precipitated phosphate," but the method is more commonly applied to low grades of mineral phosphates (p. 171) than to bones.

Garbage containing fatty matter is now collected in many cities and subjected to a rendering process. It is put into steel digesters and subjected to the action of steam at 50 pounds pressure for eight or ten hours, when the mass is reduced to a soft pulp which is put into presses and the oily matter pressed out. The press-cake is broken up and dried in revolving steam-heated drums, after which it is powdered, sifted, and used for "filler" in fertilizers, under the name "**tankage**."* It contains nitrogen, phosphoric acid, and a little potash. On cooling, the oily matter forms a soft grease, which is used for soap and candle stock. The water which is pressed out of the tankage with the grease contains a large amount of ammonium salts and some potash; it is evaporated to dryness and the residue mixed with the tankage, thus increasing the nitrogen and potash in the latter.

Other **nitrogenous wastes** from various industries — leather scrap, wool waste, and dust from shoddy and felt mills — are used to some extent; but these, though very rich in nitrogen, are very slow in decomposing, and are so light when powdered that they are easily blown away.

The **press-cakes** from various oil industries (*e.g.* the manufacture of cotton-seed, rape, and castor oils) are often ground for fertilizer. Sometimes the cake is burned for fuel and the ashes used for fertilizing, but in this case the nitrogen is lost, only the potassium and phosphorus being returned to the soil. In the manufacture of fish oils there is a considerable amount of residue from which the oil has been pressed (p. 363). This is known as "**fish scrap**," and consists of the scales, bones, fins, and meat of the fish. It contains about 7 per cent of nitrogen and nearly 16 per cent of phosphorus pentoxide (P_2O_5). Dried (usually by exposure to the sun) and crushed to a rather coarse powder, it is a valuable fertilizer, decaying rapidly in the soil.

Peruvian guano, formerly of great importance as a fertilizer, but the beds now nearly exhausted, consists of dried excrement, feathers, and carcasses of sea fowl, and is rich in nitrogen and phosphoric acid. It is found in certain islands near the coast of Peru and Chili,

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* This term is also applied to the dried residues of various rendering processes.

and also on the mainland at the base of the Andes, near the sodium nitrate beds (p. 145). The region is dry and hot, and the guano has been preserved with a high percentage of nitrogen, largely as uric acid and its salts. It needs no preliminary treatment before spreading on the soil. **Fresh guano**, from various islands in the South Pacific, is damp, and contains much ammonium carbonate; this must be "fixed" by mixing with sulphuric acid, to prevent loss of the nitrogen.

Fossil guanos, consisting of fossil excrement and remains of birds and reptiles, are found in the West Indies, Bolivia, Chili, and the South Pacific islands. Since more or less rain falls in these climates, the soluble ammonium salts and nitrates have been washed out, leaving only the calcium phosphate. Some of these guanos have entered into combination with the rocks on which they were deposited, thus altering their original character considerably; *e.g.* some of them contain a large amount of calcium sulphate. Fossil guanos are prepared in the same way as phosphate rock (see below).

Phosphoric acid is chiefly supplied by phosphate rocks, such as *apatite*, or *phosphorite*, found in large deposits in Belgium, Germany, France, Spain, Algiers, Canada, South Carolina, Florida, Tennessee. Arkansas, Montana, Wyoming, Idaho, Utah, the West Indies, and certain islands in the Pacific and Indian oceans. At present the United States deposits are the most important.

Apatite [$3\,Ca_3P_2O_8 + CaF_2 \cdot (CaCl_2)$] is a crystalline mineral, occurring in large deposits in Canada and Spain. The former are very extensive, and are found in Ontario, between the St. Lawrence and Ottawa rivers, and in Quebec Province, along the Gatineau and du Lièvre rivers. The mineral sometimes occurs in veins and pockets (bonanzas) of nearly pure, massive apatite; and in other cases as distinct, hexagonal crystals or nodules, disseminated in calcite or pyroxene. The material is sold on a guarantee of 75 or 80 per cent of calcium phosphate, and to secure this degree of purity, "cobbing" * and hand-picking must be employed. The ore being exceedingly brittle and the gangue rock hard, there is much loss in the "fines," from which it is not profitable to separate the phosphate rock.

Apatite varies in character from a moderately hard rock to a soft and friable mass, called "sugar." The color varies much, but is generally blue-green or red-brown. The tricalcium phosphate being quite insoluble, the mineral must be treated with sulphuric acid to

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* Breaking the large lumps with hammers by hand.

form "superphosphate." But since more or less calcium fluoride and chloride are present, considerable acid is uselessly consumed, and a special condensing apparatus is necessary to retain the vapors of hydrofluoric and hydrochloric acids set free, or a nuisance is created. Apatite also requires a rather strong acid (1.78 sp. gr.) for its decomposition, while the calcite and other minerals connected with it, being acted upon, cause considerable loss of acid.

These objections do not apply to the phosphorites of the United States and Europe, and the cost of mining is not so great. As a result the use of apatite for fertilizer making has ceased.

Phosphorites are amorphous rocks of varying composition, but all containing a large percentage of tricalcium phosphate, and sometimes iron and aluminum phosphates. The mode of formation of these rocks has been a much-disputed question, but they are now generally regarded as of organic, and probably animal origin. The beds are filled with fossil remains of land and marine animals and fishes. A nodular variety found in England was erroneously supposed to be fossil reptilian excrement, and was called "Coprolites."

Some phosphorites are compact and hard to grind, as is the Spanish variety, but the American rock is softer and porous. In the United States there are two varieties, "land rock" and "river rock."

Land rock occurs in beds averaging from 10 to 12 inches in thickness, and from 2 to 40 feet below the surface of the ground. These beds are sometimes composed of loose pebbles or gravel, but frequently these have been compacted into solid layers having a laminated structure; or they may form great boulders or conglomerate masses. The beds are often continuous over a large area, but "pockets" or isolated beds are frequently found. Good rock will average from 75 to 80 per cent of tricalcium phosphate ($Ca_3P_2O_8$). In some cases the land rock is hard, dense, and nearly pure (hard phosphate), while in others it is soft, resembling clay in its consistency, and usually containing rather a large proportion of iron and aluminum.

Land rock is mined by stripping off the overlying earth, and digging out the phosphate rock with pick and shovel. It has been found practical to use steam shovels and dredges for "soft phosphate" and "pebble" deposits. In compact rock, blasting is necessary. The work is done in open pits, tunnelling not having proved successful. The depth of overburden which may be profitably removed depends upon the thickness and purity of the deposit, but about 20 feet is the limit, except in the case of very thick beds of high-grade ore. For ordinary rock, the limit is about 10 or 12 feet. In a few cases hydraulic mining has been employed to wash away the overburden.

After mining, the rock is put through a "breaker," and reduced to lumps about 4 inches in diameter. These go to the "washer," which consists of a long, semicircular trough, set at a slight incline, in which there is a revolving shaft, carrying teeth or blades about 9 inches long, and arranged around it in the form of a spiral screw, having a pitch of about 1 in 6. The trough is set in a tank of water, or a large stream of water enters at the upper end. The lumps of rock are fed into the trough at the lower end, and being caught by the teeth, are forced along and *up* the trough, against the water. The rubbing against each other and the action of the water wash away the sand and clay, and at the upper end the clean rock falls on screens, which separate the several sizes of lumps. It is usually dried by piling it on racks of cord wood, which are then fired and allowed to burn out; or it may be piled over cast-iron pipes having numerous apertures through which hot air from a furnace is forced. The rock is then shipped to the makers of "superphosphate."

River rock is dredged or dug from the beds of rivers and streams, especially Peace River and its tributaries in Florida, and from the streams near Charleston and Beaufort, S.C. When the deposit is in the form of loose nodules and gravel, steam dredges or centrifugal pumps are used to raise it; but when it is compact rock, special forms of grips and dredges are necessary. In most cases, river mining is not carried on in water more than 30 feet deep.

River rock is very similar in composition to land rock, but is darker in color, even black, and contains more animal remains and fossils. It is preferred by foreign superphosphate makers and is generally shipped abroad.

"**Superphosphate**" is the name given to a soluble phosphate, prepared by treating insoluble rock or bone* phosphate, with sulphuric acid. By the action of the acid, the insoluble tricalcium phosphate is converted into monocalcium phosphate ($CaH_4P_2O_8$), while in many cases some free phosphoric acid is also formed.

The reactions involved are as follows: —

1) $Ca_3P_2O_8 + 2\ H_2SO_4 + 4\ H_2O = CaH_4P_2O_8 + 2\ (CaSO_4 \cdot 2\ H_2O)$.
2) $Ca_3P_2O_8 + 3\ H_2SO_4 + 6\ H_2O = 2\ H_3PO_4 + 3\ (CaSO_4 \cdot 2\ H_2O)$.
3) $Ca_3P_2O_8 + H_2SO_4 + 4\ H_2O = (Ca_2H_2P_2O_8 \cdot 2\ H_2O) + (CaSO_4 \cdot 2\ H_2O)$.

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* Superphosphate made from bones contains some nitrogen as well as phosphoric acid.

Reactions (1) and (2) are the ones desired in fertilizer making, but if too little acid is used, reaction (3) takes place to a greater or less extent, forming dicalcium phosphate, which is also insoluble. If too much acid is used, reaction (2) takes place to an undesirable extent, and the product contains an excess of free phosphoric acid, which attracts moisture from the air, making the fertilizer moist and lumpy. A small excess of acid over the theoretical quantity needed is generally used to prevent "reversion" (below) as far as possible. The proper regulation of the amount of acid requires great care, and must be controlled by analysis of the material. The acid employed is "chamber acid" of 1.54 to 1.60 sp. gr. Concentrated acid is not used, because water is necessary in order that a hydrated calcium sulphate may be formed. The formation of the gypsum ($CaSO_4 \cdot 2\,H_2O$) aids in the subsequent drying of the product.

Hydrochloric acid is unsuitable for fertilizer making, because of its expense, and the formation of calcium chloride in the product. The raw phosphate should be as free as possible from impurities, such as carbonates, iron oxide, and alumina. About 3 per cent of $Fe_2O_3 + Al_2O_3$ is the limit now allowed.

The phosphate rock, ground in Griffin, Kent, or ball mills (p. 188) to pass a 60- or 80-mesh sieve, is put, with the required amount of acid, into a cast-iron mixer, provided with a stirring device. The mixing is complete in two to five minutes, when the slimy mass is at once run into a brick-lined "pit" or "den," where the reactions take place. The temperature rises to 100° or 110° C., and much fume (HF, SiF_4, CO_2) escapes. As the reactions progress, the charge stiffens and finally solidifies into a porous dry mass. Successive charges from the mixer are dumped into the "den" until it is filled; then the whole is left quiet for some days or weeks, for the reactions to end. The product is then dug out of the pit, pulverized in a disintegrator, where nitrogenous or potash materials may be added if desired, and packed in bags for market.

If the phosphate rock contains much iron or aluminum oxide, or if the decomposition by acid has been incomplete, a series of secondary reactions ensues when the superphosphate is stored. By these, a part or all of the monocalcium phosphate ($CaH_4P_2O_8$) and the free phosphoric acid may be converted into the insoluble dicalcium phosphate, or into insoluble phosphates of iron or aluminum. This constitutes "**reversion**," and the insoluble calcium or iron phosphates so formed are called "reverted phosphate." Since fertilizer is valued according to its percentage of soluble phosphate, reversion is a serious matter for manufacturer and buyer. Reverted phosphate is recognized as having value for fertilizer purposes, but less than superphosphate.

When due to incomplete decomposition of the rock, reversion takes place according to the following reaction: —

$$CaH_4P_2O_8 + Ca_3P_2O_8 = 2\ Ca_2H_2P_2O_8.$$

When the rock contains iron or alumina, the temperature of the reaction in the pit is kept as low as possible, to prevent combination between these oxides and the free phosphoric acid formed. It is customary in this case to remove the superphosphate from the pit as soon as it solidifies, and to cool it by exposure to the air.

A "**double superphosphate**" is also made, in Europe, and contains more soluble phosphoric acid than the ordinary superphosphate. A quantity of bones or phosphate rock is decomposed with sufficient dilute sulphuric acid to set free all the phosphoric acid and precipitate all the calcium as hydrated calcium sulphate. The precipitate is removed by the filter press (p. 15), and the clear solution of phosphoric acid is concentrated by surface heating in lead pans, to a density of 45° Bé., at which strength the solution contains nearly 45 per cent P_2O_5. During concentration, the iron and aluminum phosphates separate and are removed. The strong solution of phosphoric acid is then treated with ground phosphate rock, in proper quantity to form monocalcium phosphate, which is dried and disintegrated. The reactions are as follows: —

1) $Ca_3P_2O_8 + 3\ H_2SO_4 + 6\ H_2O = 3(CaSO_4 \cdot 2\ H_2O) + 2\ H_3PO_4.$

2) $Ca_3P_2O_8 + 4\ H_3PO_4 = 3\ CaH_4P_2O_8.$

By this process, a very concentrated fertilizer, containing no gypsum or other sulphate, is obtained. Moreover, a low-grade phosphate rock, which would not furnish a strong fertilizer with sulphuric acid, can be used for making the phosphoric acid.

Phosphate rock is also used directly for fertilizer, without other preparation than fine grinding. But tricalcium phosphate, being insoluble, is only slowly assimilated by plants, and its action is not very marked. Several years are necessary for its complete decomposition.

Phosphatic slag is now used to a considerable extent as a fertilizer, especially in Europe. In the process of making Bessemer steel by the Thomas and Gilchrist method, pig iron from ores containing phosphorus is treated with an excess of lime in a Bessemer converter, lined with lime, while a blast of air is forced into the liquid mass. At the high temperature of the melted iron, the phosphorus is oxidized to pentoxide, which combines with the lime. The silica, alumnia, lime, and magnesia unite to form a slag, into which the calcium phosphate produced also goes. By proper regulation of the charge, a slag containing about 17 per cent of pentoxide (P_2O_5) is obtained. The phosphate in the slag is supposed to be a tetracalcic phosphate ($Ca_4P_2O_9$), which is insoluble in water, but is much less stable than tricalcium phosphate. When exposed to the weather in the soil, it decomposes, though somewhat slowly, and the phosphorus passes into a form which plants can assimilate. In order that this decomposition may take place, the slag must be ground very fine, so that 90 per cent of it will pass through a sieve with 100 meshes to the linear inch. The grinding is best done in a **ball mill** (p. 187).

Slag fertilizer needs no further treatment than very fine grinding, but it is slow in decomposing, and its full effect is not obtained for two or three years. It decomposes more rapidly than ground phosphate rock, however, and is cheap.

There has been considerable controversy among agricultural chemists as to the relative value of soluble and insoluble phosphates. Some hold that the soluble phosphate is at once converted into the insoluble form when it comes into contact with the lime, alumina, and iron in the soil; and that this insoluble phosphate is dissolved or absorbed by the sap in the plant roots, the sap presumably having an acid nature. Other chemists claim that only the soluble phosphate, as such, can be taken up by the plant. It appears from observed facts that both soluble and insoluble phosphates are taken up by the plant, but the nature of the soil is an important factor. On a soil *poor in lime,* and containing some organic matter, insoluble phosphates produce their best results; but if the soil contains much lime, then the superphosphate appears to have the advantage.

The soluble character of the superphosphate permits its diffusion through the soil by rain, so that it is brought immediately to the roots of the plants. But the insoluble phosphate must be turned under the soil, and the roots grow to it; then, too, when not finely ground, it possesses but little value, owing to the slow decomposition; but when in a very fine powder, it is taken up in some way by the roots of the plant with fair rapidity.

The manufacture and sale of artificial fertilizers are, to a certain extent, under legal restriction in nearly all the states. To prevent fraud, manufacturers are required to take out a license, and to submit samples for analysis by state chemists; frequently a guarantee of the stated composition is required.

The methods of analyses of fertilizers are set forth in detail in the bulletins of the several state agricultural experiment stations and of the United States Department of Agriculture.* In general the matter determined by the analysis may be summed up as: —

(*a*) Water, both hygroscopic and combined.
(*b*) Total phosphoric acid.
(*c*) Soluble phosphoric acid.
(*d*) Reverted phosphoric acid.
(*e*) Total nitrogen.
(*f*) Potash.

Another substance frequently sold as fertilizer is pulverized gypsum ($CaSO_4 \cdot 2\,H_2O$), which, when crushed to a fine powder, is brought into commerce under the name of "plaster." As a fertilizer it is of little value, except in soils poor in lime or those containing "black alkali" (sodium carbonate). But it is also claimed to have a beneficial action in retaining nitrogen in the soil. The calcium sulphate is supposed to be decomposed by the ammonia and carbonic acid from the air and rain, forming ammonium sulphate and calcium carbonate. Ammonium sulphate furnishes nitrogen in a form which plants can assimilate.

Much attention has been devoted, especially in Germany, to methods of recovering fertilizing material from the sewage of cities. But when closets are flushed with water, the effluent is generally too dilute to be worth recovering. It is, however, used to some extent, in irrigating lands, generally those owned by the municipality. Sewage is often precipitated with lime or other substance, but this generally renders the sludge useless for fertilizing. The contents of dry vaults or cesspools are collected at regular intervals and used for fertilizing.

But sewage treatment of any kind is usually practised to prevent pollution and unsanitary conditions in the streams and water supplies, rather than for the utilization of the fertilizing materials to be obtained.

REFERENCES

Lehrbuch der Düngerfabrication. Paul Wagner. Braunschweig, 1877.
Report of the Commissioner of Agriculture of South Carolina, for the year 1880. Chas. U. Shepard.
Bulletin de la Société Chimique, 1884, 219. E. Dreyfus.
Die künstlichen Düngermittel. Dr. S. Pick, Leipzig, 1887. (Hartleben.)

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* Bull. No. 28, U. S. Dept. Agriculture; Division of Chemistry.

The Nature and Origin of Deposits of Phosphate of Lime. R. A. F. Penrose, Bull. 46, U. S. Geological Survey, Washington, 1888.

A Treatise on Manures. A. B. Griffiths, London, 1889. (Bell and Sons.)

The Phosphates of America. Francis Wyatt, New York, 1891.

Florida, South Carolina, and Canadian Phosphates. C. C. Hoyer Millar, London, 1892. (Fischer and Co.)

Les Phosphates de Chaux naturels. Paul Hubert, Paris, 1893.

The Phosphate Industry of the United States. Carroll D. Wright, Washington, 1893. (Sixth Special Report of the U. S. Commissioner of Labor.)

J. Amer. Chem. Soc., **1893**, 321. C. U. Shepard. **1895**, 47. W. E. Garrigues.

J. Soc. Chem. Ind., **1888**, 79. W. T. MacAdam. **1894**, 842. Kalmann and Meissels.

Agricultural Analysis. H. W. Wiley, 2d ed., Vol. II, Fertilizers, 1908.

Die Superphosphatfabrikation. Dr. Ritter von Grueber, Halle, 1907.

The Manufacture of Chemical Manures. J. Fritsch, New York, 1911.

Fertilizer Resources of the United States. Senate Document No. 190, 62d Congress. Washington, 1912.

LIME, CEMENT, AND PLASTER OF PARIS

Good lime is nearly pure calcium oxide; it is one of the most important substances used in chemical industry, and is prepared in enormous quantities by calcining calcium carbonate (limestone, chalk, or the shells of mollusks) at a bright red heat. If the carbonate used contains much silica, iron, alumina, or other impurity, the lime does not slake freely with water, and is said to be "poor" or "lean"; with but small quantities of these impurities present, a fair lime is produced, when properly burned. Such impure carbonates are difficult to burn, as slight overheating causes semi-fusion of the lumps, and the lime combines with water slowly and incompletely, and is said to be "burned to death." A pure lime, which combines readily with water to form a fine white powder, free from grit, and which makes a smooth stiff paste with an excess of water, is called a "fat" lime.

Calcium carbonate begins to decompose below a red heat into calcium oxide and carbon dioxide, but the decomposition is not complete until a bright red heat (800° or 900° C.) is reached. The temperature should not rise much above 1000° to 1200° C., as there is danger of overheating the lime. It is essential that the gases escape freely from the kiln, the draught usually being sufficient to remove them as they form. This escape may be accelerated by blowing steam or air into the kiln during the burning, or even by wetting the carbonate as it is introduced. If the gases are retained, they cause pressure in the kiln and thus hinder the decomposition; and on cooling, the carbonic acid recombines with the lime.

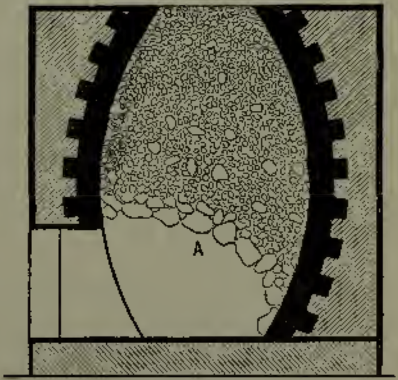

Fig. 73.

Limekilns are of two classes, **periodic** and **continuous** (see p. 22). In this country, long-flame, periodic kilns are sometimes used, though they are uneconomical of fuel and time: but they are employed because of simplicity and cheapness of building. They are made of brick or large stone blocks, an arch (A, Fig. 73) being turned two or three feet from the ground, with numerous openings left for the flames to pass into the kiln. The fire burns under the arch, on top of which the limestone is piled, the lumps varying from the size of a cocoanut just above the arch, to that of a goose egg at the top of the kiln. In starting the kiln the temperature is slowly raised during six or eight hours, to prevent the limestone arch from crumbling; then a full red heat is held for two days or more, when the fire is allowed to burn out and the kiln cools. During the time of cooling, discharging, and recharging, the kiln stands idle, thus losing much time. Moreover, a large amount of fuel is required to heat the walls of the kiln after each recharging.

Continuous kilns are preferred where fuel is expensive, and where a large, regular output is desired. They are tall furnaces (shaft kilns), built of brick or of iron plates, and usually from 40 to 50 feet high, by 6 to 10 feet diameter. The limestone is fed in at the top and the lime taken out at the bottom without interrupting the process. Vertical shaft kilns for mixed feed of fuel and limestone, or separate combustion of the fuel, are frequently used. The mixed feed kiln is cheaper to build and operate, but yields a product somewhat unevenly burned and discolored. The separate combustion type is commonly used at the larger plants, and while of lower fuel efficiency, it yields clean, high-grade lime. Such a kiln (Fig. 74)* consists of a steel shell, lined with fire-brick (B) forming a shaft $6\frac{1}{2}$ feet inside diameter and 48 feet high. There are four furnaces (A), the flames from which enter the shaft at (D) and pass up through the limestone in the shaft. From the cooling cone (C), the lime is dropped at intervals through the draw-gate into the car below.

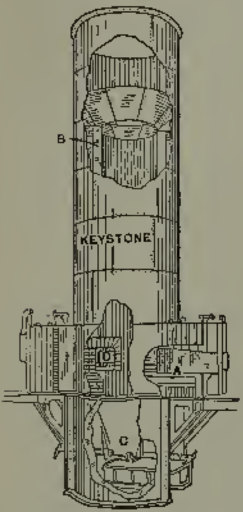

FIG. 74.

The separate combustion type of kiln works best with a long-flame combustible, such as wood, soft coal, oil, or gas. Otherwise the only heat supply for the reaction is from the hot gases from the grate, from which the heat absorption is slow. A volatile combustible may be burned in immediate contact with the charge, even within the pores of the lime itself, evolving its heat exactly where needed. A

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* Courtesy of Steacy-Schmidt Manufacturing Company, of York, Pa.

recent improvement* in kiln construction (Doherty-Eldred Kiln, Fig. 75),† is the use of induced draft by a fan drawing the gases from the top of the kiln, diverting a part of them into the air supply under the grate. There the carbon dioxide is reduced to carbon monoxide by the coal, and is later reoxidized by excess air in the kiln itself. This secures a long-flame action of the combustion, producing uniform heating, with less destruction of the furnace lining and less overburned lime.

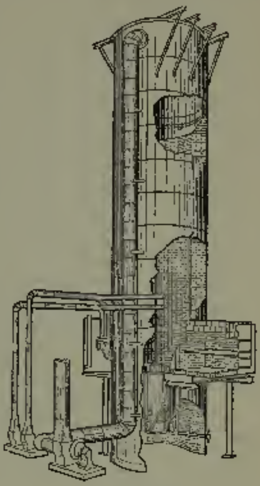

FIG. 75.

The best fuel for lime burning is wood, since it gives a long flame of only moderate heat intensity; but owing to its cost, other fuels, as coal, coke, oil, and natural and producer gas, are used. Oil and gas firing yields very clean lime, burned at a constant temperature. To calcine one kilo of calcium carbonate requires 425 Cal.: thus taking the thermal value of carbon as 8140 Cal., it appears that each 100 kilos of limestone, or each 56 kilos lime produced, will require $\frac{425 \times 100}{8140} = 5.2$ kilos of carbon as fuel. This takes no account of the fuel needed to heat the limestone to the temperature of dissociation, nor of losses by radiation and conduction in the burning. In practice, for each 100 kilos of lime produced, the kilns consume from 16 to 20 kilos of good coal, and with periodic kilns this may be nearly doubled.

Excepting the limekilns in the ammonia-soda works, no attempt, as a rule, is made to save the carbonic acid gas which escapes from the top of the kiln. But in Europe the gas is often collected and used for technical purposes.

Freshly burned lime is called "caustic" lime, or "quicklime," because of its corrosive action on organic matter. When pure, it is white and amorphous, but iron gives it a yellow tint. The crystalline limestones and pure marble yield the best lime. Owing to the loss of water, organic matter, and carbon dioxide during the burning, there is great reduction in the weight of the charge, but only a slight decrease in its volume. As a rule, 100 pounds of good lime-

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* This is an application of the Eldred combustion process. Eng. Pat. 17,197 of **1901**. Jour. Soc. Chem. Ind., **1902**, 696.

† Catalogue of the Improved Equipment Co., of New York.

stone yield about 56 pounds of lime, but the shrinkage in bulk is not over 10 to 20 per cent of the original volume of the stone. The hardness decreases and the lime is much more porous than the limestone, absorbing considerable water before slaking. Lime has great affinity for water, and when wet the lumps expand and fall to powder of calcium hydroxide (slaked lime), with the evolution of much heat, especially in the case of "fat lime." When exposed to the air, lime absorbs carbon dioxide and moisture, and soon falls to a powder called "air-slaked lime," consisting of a mixture of calcium carbonate and hydroxide. Lime for mortar and other purposes is generally slaked immediately before use. Pure lime is infusible at the temperature of the oxyhydrogen flame (hence its use in the "calcium light"), but if silica, iron, alumina, or other impurity is present, the lime combines with it to form a slag or glass. Lime is a powerful *base* and combines with acids to form calcium salts.

Magnesium carbonate is a common associate of limestone, but if there is not more than 5 per cent of magnesia present, the burned product is called a high-calcium lime; if 30 per cent or more magnesia is present, the lime is "high-magnesium" lime. Dolomite ($CaCO_3 \cdot MgCO_3$) and high-magnesian limestones generally appear to dissociate at lower temperatures * than do the pure limestones. Magnesian limes slake slowly and with less heat evolution than pure lime, and they make a stiffer mortar paste.

Certain siliceous or argillaceous limestones yield a product, upon burning, which slakes and falls to powder when treated with water; but after a time the pulverized mass becomes hard and rocklike through further action of the water upon the calcium silicates or aluminates, produced during the burning. Such lime is called "**hydraulic lime**" and forms an intermediate link between the common limes and the true cements. The calcination is conducted at medium temperature but high enough to cause combination between some of the calcium oxide with nearly all of the silica and alumina, and still leave enough free lime to slake the clinkered material. Limestone suitable for hydraulic lime usually contains from 70 to 80 per cent of calcium carbonate, with 12 to 17 per cent of silica, and less than 3 per cent of alumina and iron together. Hydraulic limes are chiefly employed in mortar and cement mixtures.

Since much heat is liberated in the slaking of lime, the storage and shipment are attended with some danger. If water comes into contact with the lime in presence of combustible material, fire is very apt to ensue.

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* Probably about 600 to 700° C. (Eckel).

Hydrated lime, slaked with just the proper quantity of water to yield a dry fine powder, is prepared commercially. The crushed lime is slaked in mechanical hydrators, sometimes of a form similar to the chlorine absorber (Fig. 63). The water and lime enter the top cylinder in measured amounts, and the hydration proceeds to completion. Batch hydrators, consisting of a revolving pan with ploughs to mix the charge of lime and water, are also used. After hydration the slaked lime is screened and ground to fine powder, and then packed for market. Hydrated lime does not deteriorate so rapidly in storage and the fire risk is greatly reduced. It can be mixed with cement and other materials, where quicklime is not suitable.

The following are a few of the important uses of lime in the arts: in mortar and cement mixing; in bleaching powder; in the alkali manufacture; for purifying illuminating gas; in the preparation and purification of many chemicals, such as acetic, citric, oxalic, and tartaric acids, caustic soda and potash, etc.; for purifying sugar solutions; in bleaching cotton; in tanning; in glass making; in metallurgical operations; for disinfecting, etc.

Mortar is an aqueous pasty mixture of slaked lime, sand, and other materials, which dries without excessive shrinkage and becomes hard on exposure to the air, owing to absorption of carbon dioxide and formation of carbonate of lime. It will not harden while it remains very wet, and this is one of the chief differences between mortar and cement. The hardening of the two substances is due, in part at least, to different causes.

If a paste of freshly slaked lime is allowed to dry by exposure to the air, it shrinks considerably, and if in thick masses, numerous cracks are formed. The admixture of three or four volumes of sharp sand prevents this shrinkage by separating the lime paste into very thin layers, which fill the spaces between the grains of sand. The sand also gives the mortar a porous structure, which facilitates the penetration of the carbon dioxide during the hardening period. The interlacing crystals of calcium carbonate enclose the sand grains and join them together, thus increasing the hardness and strength of the mortar. This addition of sand also cheapens the mortar by increasing the mass obtained from a given amount of lime. "Fat lime" requires a much larger proportion, which is replaced in part by the impurities in "poor" lime.

For a good mortar it is necessary that the lime be thoroughly slaked, in the proper quantity of water added all at once, or the product is apt to be granular and lumpy. The mass is covered with a layer of sand, or with boards or canvas, to retain the heat and moisture, and is not stirred while slaking, but is allowed to swell and fall to powder without disturbance. Water is then added, and the paste allowed to stand for several days, or even weeks, well protected from the air, before being stirred up with more water for use in mortar.

The first change noticeable in a mortar is the "set," which is a solidification of the mass, due to the loss of its water through evaporation or absorption by the bricks, etc. But it is not until the mass becomes nearly dry that the real hardening begins. This is very slow, since it progresses from without towards the interior of the mass; and the surface layer of calcium carbonate first formed is but slowly penetrated by carbon dioxide from the air. The interior of thick walls will often show an alkaline reaction after the lapse of a century or two, but after twenty-five years the change is very slight under ordinary conditions. After several hundred years there appears to be a certain amount of combination between the silica of the sand and the calcium carbonate to form a hydrated silicate of calcium. This secondary reaction does not increase the hardness of the mortar. Hardening is a true chemical change, and should not be too rapid for the best results. In order to hasten the hardening of mortar and plastering in new houses, builders sometimes build coke or charcoal fires in open grates or baskets. But this is liable to cause uneven drying and excessive shrinkage, resulting in cracks or scaled places. In certain mortars hair or other fibrous material is added to increase the toughness, especially while wet.

Since mortar does not harden until dry, it should never be used in damp places, such as foundations and cellars, nor in very thick walls. Sometimes it is mixed with some cement, increasing its strength and usefulness. When thoroughly hardened, good mortar is about as hard as limestone, and adheres firmly to the bricks or stones of the wall.

Sand-lime bricks * made by mixing sand with about 8 per cent of slaked lime, moulding the mixture in a brick mould and subjecting the product to the action of steam at pressures of 130 to 150 lbs. per square inch, for four or five hours, have come into general use for building purposes, especially for inside work. It is claimed that under the action of the steam at high pressure, the lime and sand combine to form calcium silicates, possibly similar to Portland cement. But this seems doubtful, as the temperature is not comparable with

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* Trans. Am. Ceramic Soc., **1903**; **1911**, 648. Jour. Soc. Chem. Ind., **1899**, 48; **1902**, 1183; **1903**, 421.

that required for cement making. Possibly the bonding substance is a mixture of the three calcium silicates, but chiefly the meta-silicate ($CaSiO_3 \cdot H_2O$).

CEMENT

Cement consists of certain anhydrous double silicates of calcium and aluminum, which are capable of combining chemically with water, to form a hard mass. It differs from lime mortar in that it hardens while wet, does not require the presence of carbon dioxide for hardening, and is very insoluble in water. It is well adapted for use in moist places, or even under water, and since its hardening is simultaneous throughout the whole mass, and is quite rapid in most varieties, it finds extensive use in building operations.

There are three general classes of cement: —

1. Those formed from certain volcanic tufas, or from artificial mixtures resembling these. Such cements generally need the addition of lime before they display hydraulic properties, *i.e.* form insoluble silicates when treated with water. In this group are the natural volcanic tufas, Pozzuolan, *trass*, and Santorin earth, together with blast furnace slags and certain coal ashes, which are occasionally used.

2. Those which contain a large proportion of free lime, having been made by burning natural argillaceous limestones at a temperature sufficiently high to drive off all the carbon dioxide, but not to fuse the product. These include "hydraulic limes" (p. 178) and Roman cements.

3. Those prepared by burning an intimate mixture of clay or other alumino-siliceous material and powdered calcium carbonate, at a very high temperature, so that incipient fusion takes place in the mass. These constitute the Portland cements.

Pozzuolanic cements are chiefly derived from volcanic tufas, found in Italy, near Naples (Pozzuoli), in the islands of the Grecian archipelago, and in Germany near Andernach on the Rhine. These tufas consisting of easily decomposable silicates have resulted from the action of volcanic fires, and need no further treatment than fine grinding and mixing with lime. Such cements are slow in hardening, but have considerable ultimate strength. Pozzuolan has been used since the time of the Romans, who were well acquainted with its properties.

Blast furnace slag, high in alumina and silica, is now much used for Portland cement, limestone being the other ingredient. The melted slag is chilled and granulated by running into water and the sandy material is dried, ground fine, and mixed with the ground limestone. The dry mixture is then calcined to produce a clinker, which, after fine grinding, yields an excellent cement; but it may be rather high (3 to 4 per cent) in calcium sulphide.

Hydraulic limes have already been mentioned (p. 178). The free lime which they contain is sometimes slaked with *just sufficient water* to hydrate the quicklime before the material is sold; but not enough water should be added to set the cement.

Roman cement is made by burning argillaceous limestone in kilns. It was first made in England by J. Parker, who patented a process for preparing it from the *septaria nodules,* consisting of clay and chalk found in the bed and along the banks of the Thames River. Later, the beds of clay limestones were used, but as there was much irregularity in the composition of these rocks, the product did not give satisfaction. But by careful selection of the material and proper mixing of different kinds of stone, the quality of cement produced has been improved. These rocks are also found in France, Holland, and Germany, and in the United States. There are several deposits that are very pure and vary but little in the different parts of the bed. Nearly all these rocks contain a large percentage of magnesia, but this does not appear to injure the cement made from them. Roman cement was first made in this country in New York state, from a rock found on the banks of Rondout Creek and near the Hudson River, and is called "Rosendale," from the chief town in the district; it still constitutes a large part of the natural cement made in this country. Another important region is on the Ohio River, near Louisville, the cements made there being known by the latter name. Pennsylvania, Illinois, Wisconsin, and Colorado also supply natural cement.

The rock is broken into lumps about the size of a goose egg, in order to secure evenness in burning. The burning is done in continuous kilns, as a rule, and the temperature must be carefully regulated, high enough to drive out the carbon dioxide, but not to fuse the rock. Then the rock is carefully ground and sifted. The finer the grinding, the better the product. In order to secure supposed uniformity in the product, it is often customary to mix rock from several beds, in the same kiln, but this is of doubtful benefit.

The color of Roman cement varies greatly, from pale yellow to red-brown, and is due chiefly to the amount of iron and manganese oxides present. But there should not be great variations in the color of the products made from the same rock, as this indicates inequality in burning.

Roman cement is generally quick-setting, and hence is preferred by many engineers for work under water. It weighs from 50 to 56 pounds per cubic foot. Its strength is inferior to Portland cement.

The following analyses* are of typical cement rock: —

	N. Y., Ulster County, Rosendale	Illinois, Utica	Wisconsin, Milwaukee	Pennsylvania, Coplay
$CaCO_3$	45.91	42.25	45.54	67.14
$MgCO_3$	26.14	31.98	32.46	2.90
SiO_2	15.37	21.12	17.56	18.34
Fe_2O_3	11.38	1.12	3.03	7.49
Al_2O_3			1.41	
Na_2O	—	—	—	0.19
K_2O	—	—	—	
H_2O	1.20	1.07	—	3.94
Undetermined		2.46	—	

Analyses of natural cements: —

	Rosendale	Utica	Louisville, Ky.	Lehigh Valley
SiO_2	22.75	35.43	21.10	18.28
Al_2O_3	16.70	9.92	7.51	7.43
Fe_2O_3				
CaO	36.70	33.67	44.40	51.53
MgO	16.65	20.98	7.00	2.07
K_2O	—	—	0.80	1.50
Na_2O	—	—		
CO_2	5.00	—	11.18	16.20
$CaSO_4$	1.30	—	6.85	—
H_2O		—	1.16	—
Undetermined		—	—	2.93

Portland cement is entirely an artificial product, but represents the most important branch of the cement industry. The first patent was taken out in England, in 1824, but the process extended in a few years to France and Germany. In the United States the manufacture of this cement was begun in 1878, at Coplay, Penn., and the industry has become enormous.

The materials used are calcium carbonate and clay rich in silica. Limestone and shale, or marl and clay, are used in this country and

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* W. A. Smith, Mineral Industry, Vol. I, 1892.

Europe, and chalk and clay mud from the estuaries of the Thames and Medway rivers are preferred in England. But in any case the proportion of calcium carbonate to aluminum silicate must be controlled between tolerably narrow limits.

The average composition of raw materials is shown in the following table: —

	CLAY	MARL	LIMESTONE	SHALE
SiO_2	42.20	0.50	3.0	15
Al_2O_3	12.30	0.20	1.5	7
Fe_2O_3	4.60	0.10		
$CaCO_3$	23.90	94.50	96.0	71
$MgCO_3$	16.05	2.25	3.0	4
Alkalies, moisture, etc.	0.95	2.45	—	—

A most thorough mixing of the ingredients is very essential. This is done in two ways: the "dry process" is used when the materials are hard (limestone and shale); and the "wet process" for soft materials containing much water (marl, chalk, and clay).

The **dry process** is simple and cheap, but requires excessively fine grinding for uniformity of the product. The proper proportions (by weight) of shale and limestone are crushed together, and often lightly calcined to drive off moisture, and then ground in the Griffin mill or ball-mill so that 80 per cent passes through a 200-mesh sieve. This powder is usually fed directly to the rotary kiln, or may be pressed into bricks and burned in a shaft kiln or ring furnace.

The **wet process** is carried out in various ways, according to the economic conditions prevailing in each locality. Usually the clay and chalk or marl are ground in edge-runners with heavy rolls, and water is added till enough is present (40 to 50 per cent) to make a slime or "slurry" which will flow or can be pumped. Sometimes a wash-mill, consisting of flat stones sliding over a smooth bed of stones or iron, propelled by a rotary shaft with arms, is used for this preliminary mixing and grinding; or a disintegrator mill may be employed.

The wet slurry is then pumped or run to buhrstones or tube-mills (p. 188) and given a very thorough grinding. Often an intermediate mixing is given in tanks having rotary arms, or compressed air agitators.

The next treatment of the slurry varies in different mills; it may be settled or filtered and the excess water run away; the mud may then be pressed in a brick machine, or dried on floors heated by waste heat from the kilns. The bricks or lumps are then sent to the kilns. In this country the slurry is generally run directly into the rotary kilns, the water evaporating in the upper third of the kiln, and the dried mass forming little balls or gravel-like lumps, which are thoroughly burned while passing through the rest of the kiln.

Various kinds of kilns are used for Portland cement burning, the old periodic dome-shaped or shaft kilns being still in use in some places, although costly as to fuel and output. Continuous shaft kilns are more common, especially where labor is cheap and fuel high; in America they have been displaced by the rotary kilns, which have much greater capacity. In shaft kilns, owing to the high temperature, the charge tends to stick to the furnace walls, unless careful attention is given during the burning. With rotary kilns, the amount of powdered coal consumed varies from 25 to 40 per cent of the weight of the cement produced.

The **Dietzsch** two-storied kiln (*Etageofen*) (Fig. 76) is much used abroad for Portland cement. The charge, introduced at (A), fills the vertical shaft or pre-heating chamber, and absorbs the heat of the escaping combustion gases as it descends into the combustion chamber (B). The fuel, either coke or coal, is introduced through (D), while the material from (B) is raked down into the chamber (C), mixing with the fuel, and attaining there the highest temperature of the calcination. The burned material, mixed with the fuel ash, is withdrawn at (E). Air enters at (E), and passing through the hot clinker, arrives in (C) at a very high temperature, where it supports the combustion of the fuel. The hot gases passing off through (B) and (A) serve to heat the charge before it arrives in (C). These kilns now are often worked with forced draught, and produce about 7 tons of clinker per ton of coal.

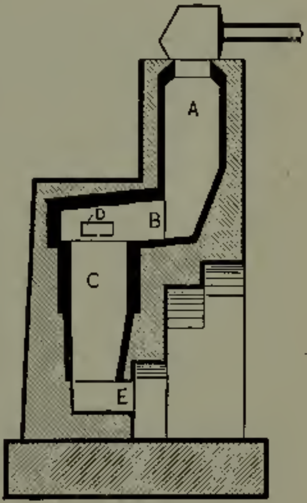

FIG. 76.

Hoffmann's ring furnace (Fig. 77) is also much used in cement burning. This consists of an elliptical gallery built around a central chimney (A). The gallery is divided into 15 or 20 compartments (B, B) each having a door (C) opening outside, a flue (D) leading to the chimney (A), and a wide opening (D) into the next compartment. Each flue has a damper, by which connection with the chimney (A) may be opened or closed. The openings (E) between the compartments may be closed with a sheet-iron or heavy paper diaphragm, as will be explained below. If the door of the compartment on one side of the diaphragm be opened, and the damper of the flue (D) leading from the compartment on the other side of the diaphragm is also opened, while all the other doors and flues are closed, the draught of the chimney (A) will cause air to enter the open door and pass around the entire gallery, through each compartment in succession, and finally out through the open flue (D) to the chimney. In the roof over the gallery are charging holes (G), several being in each compartment, through which fuel is introduced. The furnace is run as follows: Assume that there are 14 compartments, as shown. Twelve compartments contain cement bricks, and their doors and chimney flues are closed. Suppose that No. 1 is being emptied, while No. 14 is being filled. The paper diaphragm closes the opening between No. 13 and No. 14, and the flue (D) of No. 13 is open to the chimney. Compartment No. 7 is at the height of combustion, while Nos. 6, 5, 4, 3, 2 contain bricks which have been burned. In Nos. 8, 9, 10, 11, 12 are bricks to be burned. Cold air is drawn in through the open door of No. 1, and passing in order through Nos. 2, 3, 4, 5, 6 becomes heated by contact with the hot bricks in these compartments until, after passing through No. 6, which is still red hot, it arrives in No. 7 at a very high temperature. In No. 7 the fuel is burning at a white heat, and the hot gases pass on through Nos. 8, 9, 10, 11, 12, 13, from which they escape to the chimney. By this passage of the hot gases through the compartments, the unburned bricks are heated, those in No. 8 being nearly red hot; but as no fuel has been introduced into these chambers, combustion and white heat are confined to No. 7. When No. 14 is filled with green bricks, its doors are closed, and also the chimney damper of No. 13, while that of No. 14 is opened, and the diaphragm transferred to the opening between No. 14 and No. 1. Fuel is now introduced into No. 8, which becomes the combustion chamber, and the door of No. 2 is opened. The burned bricks in No. 2, having been cooled by the passage of cold air, are taken out, while No. 1 is being refilled. Thus the cycle of operations

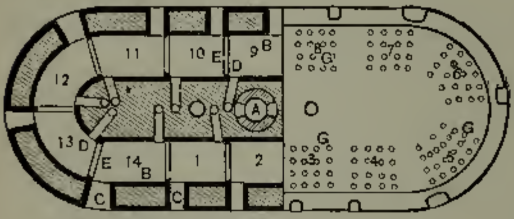

FIG. 77.

goes on, each compartment in turn being charged with fuel and made the combustion chamber. The temperature in that compartment which has just been filled is only high enough to dry the green bricks.

This furnace is very economical of fuel, one ton of soft coal burning $6\frac{1}{2}$ tons of clinker, but it requires much labor. The bricks must be accurately piled in order that open channels may be left beneath the charging holes for the fuel, which is thus made to burn in a column extending from the floor to the top of the furnace. Usually one compartment is emptied each day, and the fire is moved forward.

Revolving furnaces (Fig. 126, p. 598) are largely used for cement burning, and have greatly advanced the Portland cement industry in America. These kilns incline about 5° to 8°, are 60 to 220 feet long, 6 to 8 feet in diameter, and are lined with fire-brick. The fuel is usually powdered coal, blown in at the lower end of the furnace by an air blast; in rare cases oil or natural gas may be used. The mixture of powdered materials (or slurry, in the wet mixing process) enters at the upper end, and is thoroughly calcined during the two or three hours' passage through the furnace and sintered by the heat into little balls or gravel-like lumps. The hot clinker is discharged into an elevator which carries it to the iron coolers, in which air comes in contact with the mass. A little water is sometimes sprinkled into the elevator buckets to " cure " the clinker and insure rapid cooling, which assists materially in the grinding.

The rotary kiln is cheap in its labor account but even the large ones are wasteful of fuel; probably the lowest consumption is about 75 lbs. of coal per barrel of clinker; the Dietzsch and Hoffmann kilns use about one-third this amount of fuel, but require much higher expense for labor, which probably explains the more general use of these types in Europe, where fuel is costly and labor relatively cheap. Much depends on the calcination temperature, which should reach 1400° to 1600° C. (incipient fusion), and there is considerable shrinkage; well-burned clinker is semi-vitrified, hard, and of greenish-black color.

The clinker is then ground in various types of mills (see below), to such fineness that not over 7 or 8 per cent is retained on a sieve having 100 meshes to the linear inch. Only the very fine dust is considered of value in cement.

The **ball-mill** (Fig. 78) consists of a cast-iron drum (D), containing numerous chilled-iron or steel balls (B) of different sizes. The clinker is powdered by the rubbing and pounding of the balls as the drum rotates. The dust passes through the perforated plates (P) and falls on the fine sieves (S). The coarse particles retained by the screens return to the interior of the drum through the openings (C, C) for further grinding.

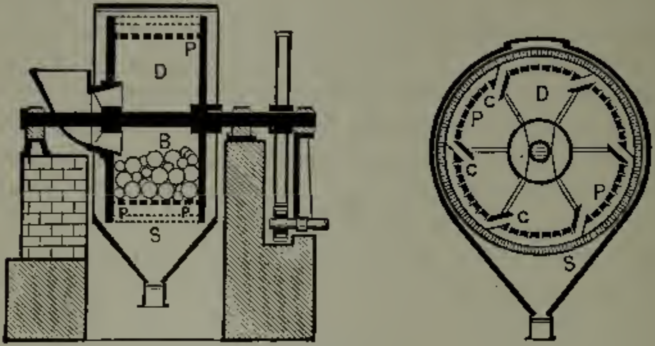

Fig. 78.

The **tube-mill** (Fig. 79) is a horizontal iron tube about 20 feet long by 5 feet in diameter, rotated some 25 times a minute by the gears (G). The tube is half full of smooth quartz pebbles, about the size of goose eggs; these are retained in the tube by a screen (S) at the outlet end, through which the ground cement passes and is discharged through (T). The pebbles are slowly ground up with the cement and a few new ones are added with the clinker at regular intervals. The speed of rotation and the rate of feed of material through the trunnion by the screw (P) determine the fineness of the product. These mills require considerable power and have rather small capacity, but any degree of fineness can be obtained, and the repairs are very moderate. They work equally well on dry or wet materials and are often used to mix and grind slurry.

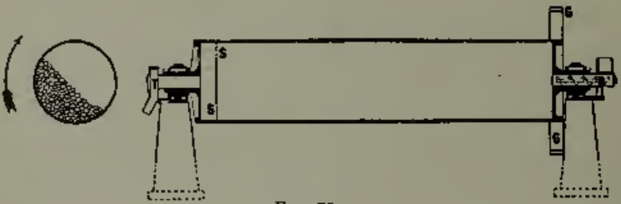

Fig. 79.

The **Hardinge conical mill** (Fig. 80) is a modification of the tube-mill, having somewhat greater efficiency.

The **Griffin mill** is a steel roll, weighing about 400 pounds, revolving on a vertical shaft with a gyratory motion, and pressing by centrifugal force against a steel ring. It has great capacity, and will grind so that about 90 per cent of the product passes a 100-mesh sieve; but the repair account is rather large.

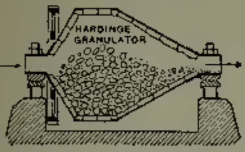

FIG. 80.

The **Fuller-Lehigh mill** consists of a horizontal ring with a ground inner surface, against which several heavy steel balls are made to revolve at a speed of about 160 r. p. m. The grinding effect is due to the centrifugal force developed by the whirling balls.

The **Kent mill** (Fig. 81) consists of three rolls rotating at high speed, within a movable circular ring or die, against which the crushing takes place.

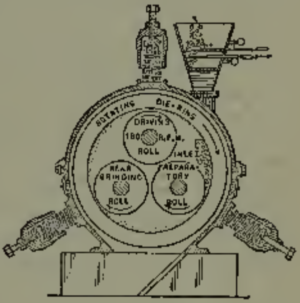

FIG. 81.

The constitution of Portland cement has been much studied, and various views are held as to the proper proportions of the ingredients. Le Chatelier states * that the ratio of the equivalents of lime and magnesia to the silica and alumina should not exceed a maximum equal to three, while that of the total silica, minus the combined iron and alumina, should not be less than a minimum equal to three; thus: —

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} \leqq 3 \text{ and } \frac{CaO + MgO}{SiO_2 - (Al_2O_3 + Fe_2O_3)} \geqq 3.$$

According to Michaelis, the ratio of lime to the acid constituents should fall between

$$\frac{CaO}{SiO_2 \cdot Al_2O_3 \cdot Fe_2O_3} > 1.8 \text{ and } \frac{CaO}{SiO_2 \cdot Al_2O_3 \cdot Fe_2O_3} < 2.2.$$

Newberry † holds that the proportion of lime, by weight, should be to the silica and alumina as shown thus: —

$$\text{Lime} = (SiO_2 \times 2.8) + (Al_2O_3 \times 1.1).$$

The composition of good commercial cements, however, shows some variation, and no definite formula can be assigned to them. The following are typical: —

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* Trans. Am. Institute Mining Engineers, **22** (**1893**), 15.

† J. Soc. Chem. Ind., **1897**, 887.

SiO_2	21.05*	22.80*	19.78*	21.50†	22.04†	21.25†
Al_2O_3	8.95	6.49	8.21	6.60	6.45	6.16
Fe_2O_3	4.40	4.31	4.53	2.60	3.41	3.85
CaO	61.30	61.10	62.69	62.50	60.92	62.69
MgO	1.37	.47	2.09	1.20	3.53	3.00
SO_3	1.28	1.39	1.28	.98	2.25	1.50
Alkalies	.68	.30	—	—	—	—
H_2O, CO_2	.70	2.40	1.10	—	—	0.50
	99.73	99.26	99.68	95.38	98.60	98.95

The cause of hardening of cement has been explained in various ways. Le Chatelier ‡ holds that during the burning a tricalcium silicate (Ca_3SiO_5) is formed by reaction between the clay and the lime, and at the same time, some calcium aluminate and ferrite are formed, besides mono- and di-calcium silicates. By the action of water on the tricalcium silicate, hydrated monocalcium silicate and calcium hydroxide are formed: —

$$1)\ 2\ Ca_3SiO_5 + 9\ H_2O = (CaSiO_3)_2\ 5\ H_2O + 4\ Ca(OH)_2.$$

Then the calcium hydroxide, water, and calcium aluminate may react to form hydrated basic calcium aluminate: —

$$2)\ Ca_3Al_2O_6 + Ca(OH)_2 + 11\ H_2O = Ca_4Al_2O_7 \cdot 12\ H_2O.$$

The formation of the hydrated basic aluminate $[(CaO)_4 \cdot Al_2O_3 \cdot 12\ H_2O]$ is supposed to influence the setting of the cement, but the hardening is ascribed to the first reaction. Richardson § takes the view that Portland cement clinker is largely composed of alit, a solid solution of tricalcic silicate in tricalcic aluminate; and that the setting is due to the decomposition of alit, with formation of crystals of calcium hydroxide. Hydration of the silicates and aluminates is not thought to add to the strength of the cement after setting, but the crystallization of the calcium hydroxide binds the mass together.

Portland cement is usually slower in setting than Roman, but when the hardening has begun, it progresses more rapidly with the former. There is very little increase of hardness after six months. Portland cement is more durable than Roman under most conditions, and is generally stronger. It forms a denser and heavier powder of a greenish gray color, but when hardened has a drab shade resembling the color of the stone quarried at Portland, England, and used much for building in that country; hence the name. Variations in color

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* English. † American.

‡ Annales des Mines, **1887**, 388. J. Soc. Chem. Ind., **1888**, 567, 847. Thonindustrie Zeitung, **16** (**1892**), 1032. Chemiker Zeitung, **1892**, Ref. 342.

§ Proc. Assoc. Port. Cement Mfgr., **1905**, June 15.

of the same brand of cement may show changes in quality; if underburned, it is generally yellowish. The weight per cubic foot varies from about 70 to 90 pounds; the finer the grinding, the less the weight. But as a rule heavy cements are preferred by builders, as they are supposed to be more thoroughly burned; they are, however, slow in setting.

The testing of cement is generally the work of the engineer. Chemical analysis alone is of small use in determining its properties, and physical tests are usually more satisfactory. Committees from the American Society for Testing Materials,* and from the American Society of Civil Engineers,† and other engineering associations have adopted "Standard Specifications" and "Methods of Testing." The tests recommended, are for: —

(*a*) Specific Gravity. (*b*) Fineness. (*c*) Time of Setting.
(*d*) Tensile Strength. (*e*) Soundness.

The **specific gravity** of the cement dried at 100° C. shall not be less than 3.10. The determination is made in Le Chatelier's apparatus, using naphtha of 62° Bé., or kerosene.

In testing for **fineness**, not more than 8 per cent by weight may remain on the No. 100, nor more than 25 per cent on the No. 200 sieve. Use circular sieves, 20 centimeters in diameter, with woven cloth of brass wire 0.0045 inch and 0.0024 inch in diameter respectively, for the sieves. Fifty or 100 grams cement, dried at 100° C., are to be used for the test.

Time of Setting. — The cement shall develop the initial set in not less than 30 minutes, and should set hard in not less than one hour nor more than 10 hours. The test is to be made with the Vicat needle, which is a movable vertical rod, with a plate on the upper end and a short cylinder, 1 millimeter in diameter, at the bottom, the whole supported in a frame. The rod, plate, and foot-piece weigh 300 grams. A paste of cement and water is put into a frame under the needle point, and the depth to which the needle sinks in the soft mass is noted. The set has commenced when the needle ceases to penetrate to within 5 millimeters of the glass plate on which the paste rests, and is terminated when the needle no longer enters the mass.

Time of setting determinations are not exact, and vary with the quantity of water used in the mortar, the temperature of the water and of the air, and the amount of working the mortar may have received during the moulding for the tests. If the set begins in less than half an hour, the cement is called "quick-setting," and is desirable for work under water. Slow-setting cement requires more than half an hour for the set to begin; this is better for most purposes and may be mixed in larger quantities. High temperatures hasten the set of the cement, while a larger proportion of water induces slower setting. The

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* Proc. Am. Soc. Testing Materials, **1904**.

† Trans. Am. Soc. Civil Engineers, **1903**; amended **1904**.

addition of not more than 2 per cent of calcium sulphate, as gypsum or plaster of Paris, retards the set materially. Larger quantities may hasten the set.

For ordinary control work, the time of setting may be determined sufficiently closely by the "normal needle," devised by Gilmore. Two of these are used: one is a wire one-twelfth of an inch in diameter and loaded with a weight of one-quarter of a pound; the other wire has a diameter of one twenty-fourth of an inch and carries a weight of one pound. The cement, mixed to a stiff paste with water, is formed into a pat, one-half an inch thick, and the time noted until no impression is made upon it by the point of the first wire. This is the beginning of the "set." When the second wire will not penetrate, the set is ended.

The tensile strength is determined on a briquette, shaped like an hour-glass, and having at the narrow portion a section exactly one inch square. The minimum requirements shall be within the following limits: —

	Age	Strength
For "neat" cement (*i.e.* without sand)	24 hours in moist air	150–200 lb.
	7 da. (1 da. in moist air; 6 da. in water)	450–550 lb.
	28 da. (1 da. in moist air; 27 da. in water)	550–650 lb.
Sand briquettes (1 part cement, 3 parts sand)	7 da. (1 da. in moist air; 6 da. in water)	150–200 lb.
	28 da. (1 da. in moist air; 27 da. in water)	200–300 lb.

For the sand briquette, a natural sand, obtainable at Ottawa, Illinois, is recommended, but many engineers prefer a standard sand made by pulverizing pure quartz. The sand is sifted and that portion used which passes a No. 20 sieve and is retained by a No. 30. The briquettes must be carefully made to secure uniform results. The cement is mixed with water at about 70° F., filled into bronze moulds, pressed down well, and smoothed off evenly. This is done on a slate or glass plate to prevent absorption of moisture. When set, the briquette is removed and placed in a moist-air closet for 24 hours. It is then kept in water until the test is made, when it is placed in the jaws of a machine, which applies a gradually increasing tension at the rate of 400 pounds per minute. The number of pounds necessary to fracture the briquette is read on a graduated scale beam. The average of three tests (of each neat and sand-mixture) is usually taken as the tensile strength.

The less water used in the cement mortar, the higher the strength, as a rule, especially in the short time tests. For neat cement, the water may vary from 14 to 24 per cent; for sand briquettes, about 12 per cent of the total weight of the sand and cement. The cement and sand should be well mixed, dry; then wet out, and mixed with water in about 2½ minutes, and filled into the moulds at once.

Compression tests are made with small cubes of the cement. This test should show at least ten times the tension resistance. This being difficult to manage, the tensile test is employed instead usually.

Soundness tests are made upon pats of neat cement, 3 inches in diameter, one-half inch thick at the centre and tapering to a thin edge. These are kept in moist air for 24 hours; then one is exposed to air at ordinary temperature for 28 days; another is kept in water at 70° F. for 28 days; a third is exposed to steam in a loosely covered vessel for 5 hours. All of the pats must show no signs of checking, cracking, disintegrating, nor distortion. Faija's test is often used. This consists in placing the test piece in a moist atmosphere at 100° to 105° F., for 6 hours or more, till well set; then it is immersed in water at 115° to 120° F. for the remainder of 24 hours.

Expansion or "blowing" is shown by swelling, cracking, or disintegration of the cement after setting. This is generally supposed to be caused by excess of free lime, or by poor burning, the heat not having been enough to combine the lime with the silica and alumina. The free lime slakes after the cement has set, and the expansion causes disintegration. Magnesia in Portland cement has been thought to cause unsoundness, but up to 4 per cent (as MgO) appears to be harmless, and is allowed by the Standard specifications.

PLASTER OF PARIS

Plaster of Paris is made by heating gypsum ($CaSO_4 \cdot 2\ H_2O$) until about three-fourths of its water of crystallization is driven off. The process, called burning, is carried on in muffle furnaces, kettles, or rotary cylinders. Direct contact with the fuel is avoided, lest the carbonaceous matter may reduce some of the calcium sulphate to sulphide; nor should the flame come in contact with the gypsum, but only the hot gases. Boiler-iron kettles, having a stirring device, are much used, the charge being 5 to 7 tons of finely ground gypsum, which requires about three hours to calcine. Rotary calciners are being adopted because of their economy; these are iron cylinders set at a slight incline, and heated externally by the flame from a furnace. Gypsum, crushed to small size, is fed continuously into the cylinder; the calcined material is friable and easily ground fine.

Gypsum contains about 21 per cent of water of crystallization, while plaster retains 4 to 7 per cent. Moisture begins to escape at about 100° C., but the most favorable temperature for calcining is around 145° C.; if heated to 200° C., all the crystal water is expelled, and the product will combine with water very slowly, the property of rapid setting being lost. Thus the limits of heating are very narrow and much care is needed in the process.

When mixed with water, plaster of Paris forms a paste which soon hardens or "sets," owing to a recombination of water with the burned plaster, to form hydrated calcium sulphate. The theory of this setting has been explained by Le Chatelier.* The composition of the plaster is essentially $(CaSO_4)_2 \cdot H_2O$, a salt which is soluble, and part of which dissolves in the water used in mixing. But as soon as it dissolves, a combination between it and some of the water takes place, forming $CaSO_4 \cdot 2\,H_2O$; this, being much less soluble than the monohydrated salt, at once begins to crystallize from the solution, forming a network of crystals. Then more of the plaster dissolves, becomes fully hydrated, and crystallizes out, increasing the solidity of the "set" by the interlacing of new crystals with those already formed. Thus the cycle of reactions goes on until the plaster is fully hydrated.

The theoretical quantity of water necessary to set plaster is about 18 per cent of its weight; but in fact, from 30 to 35 per cent is generally used. Excess of water renders the mass more plastic and retards the setting. Large excess causes disintegration of the plaster, if left in contact with it for some time after setting, owing to the solution of some of the crystallized calcium sulphate. Since plaster "sets" very rapidly with water, a "retarder," such as glue, dried blood, or vegetable gums, marshmallow root, or fine sawdust, is often added. These colloidal bodies probably decrease the solubility of the calcined plaster and retard the hardening for half an hour or more.

Plaster expands slightly while setting, and hence is valuable for making casts and reproductions. It is used for interior decorative work and also as a cement for joining glass and metal ware. The surface of plaster after setting is rather soft, and if it is desired to increase the hardness, this may be done by mixing alum, borax, or tartaric acid with it, or by adding some alcohol to the water with which the plaster is mixed. However, these substances retard the setting. By painting or dipping plaster casts in melted wax, paraffine or stearin, or in solutions of these in petroleum ether, the pores are filled and the surface is made smooth, so that dirt will not adhere and the articles may be washed. When treated with a solution of barium hydroxide, the surface of the plaster is coated with barium sulphate and rendered insoluble. If plaster is mixed with a solution of glue or size, the material called "stucco" is obtained.

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* Comptes Rendus, Vol. **96**, 717, 1668.

REFERENCES

Die hydraulische Mörter. Michaëlis, 1869.
A Practical Treatise on Limes, Hydraulic Cement, and Mortars. Q. A. Gilmore, 1874.
Chemische Technologie der Mörtelmaterialien. G. Feichtinger, 1885.
Recherches expérimentales sur la Constitution des Mortiers hydrauliques. Le Chatelier, Paris, 1887.
Fabrication et Controlle des Chaux hydrauliques et des Ciments. H. Bonnami, Paris, 1888. (Gauthier-Villars et Fils.)
Zement und Kalk. Rudolf Tormin, Weimar, 1892. (B. F. Voigt.)
A Manual of Lime and Cement. A. H. Heath, London, 1893. (Spon.)
Annales des Mines: — XI (**1887**), 388–465. H. Le Chatelier.
Cements, Limes and Plasters. Edwin C. Eckel, New York, 1907.
The Modern Manufacture of Portland Cement. Percy C. H. West, 1910.
Portland Cement. Richard K. Meade, 2d ed., Easton, Pa., 1911.
Journal of American Chemical Society: — **1894**, **161**. T. B. Stillman.
Journal of the Society of Chemical Industry: —
  1886, 188, 199. **1891**, 927. **1897**, 887. **1910**, 1107.
Trans. Am. Inst. Min. Eng., **27**, 508. P. Wilkinson.
Transactions of the American Society of Civil Engineers: —
  1877. W. F. Maclay. **1885**. E. C. Clarke.
  1885, **1903**; **1904**. Report of Committee on Cement Tests.
  1893. Max Gary.

GLASS

Glass is an amorphous, transparent, or translucent mixture of silicates, one of which is always that of an alkali. The usual silicates employed are those of potassium, sodium, calcium, and lead; the silicates of heavy metals occur in the colored glasses. Glass is not readily decomposed by water or acids (excepting HF). Its behavior towards solvents generally tends to show that it is a mixture of silicates, rather than a definite compound.

Most simple silicates and mixtures of them are difficult to fuse, and when cooled after fusion, have a crystalline structure; but the alkali-lime and alkali-lead silicates fuse easily, and are generally amorphous after fusion. Silicic acid is capable of forming a number of salts of varying acid content and of approximately equal stability. Hence from a fusion of the silicates of two or more metals, the tendency of any particular compound to crystallize is small, and even if a crystal centre is formed, growth is very slow, because of the viscosity of the medium and the major part of the liquid consisting of dissimilar molecular structures. Hence such a mass can be supercooled, the viscosity progressively increasing, and the melt becoming first plastic and finally rigid. Such a supercooled liquid is called a **glass**; it has no melting point, but softens progressively on heating, and if kept thus for some time crystallization, technically called "*devitrification*," will begin, causing a white or porcelain-like appearance. The alkali-lime and alkali-lead silicates are rigid at ordinary temperatures, insoluble in most liquids, decrease in viscosity slowly when heated, so that they are plastic and workable over a large temperature range, and devitrify very slowly. These properties give them their technical importance.

Since the glasses are complex, homogeneous mixtures, all of their properties can be progressively changed by a progressive modification of composition, and use of this is made in the arts.

Soda-lime glass approaches Na_2O, CaO, $6\ SiO_2$, and lead glass, K_2O, PbO, $6\ SiO_2$; but it may vary so much that the formula becomes $5\ K_2O$, $7\ PbO$, $36\ SiO_2$. Of course potash may be substituted for soda, or *vice versa,* in either kind, while the relative proportion of the several ingredients may vary between quite wide limits. But as a rule, the higher the percentage of silica, the harder, more difficultly fusible, and more brittle the glass. Increase of alkali makes it softer, more fusible, and less capable of resisting atmospheric changes and chemical reagents. Increasing the percentage of lime decreases the fusibility and renders it harder, but not so brittle as in the case of high-silica content. If the alkali used be mixed soda and potash, a more fusible glass is obtained than from either alone. Part of the lime or lead may be replaced by oxides of other metals, *e.g.* of iron, manganese, cobalt, copper, barium, zinc, tin, arsenic, etc., and this is generally the case, to some extent, in common glass, and to a greater degree in colored glass. Aluminium oxide may replace some of the silica; the former is often present in considerable amounts, and renders the product tough. Certain fluorides, *e.g.* calcium fluoride, also enter into the composition of some varieties. Besides the above-named oxides, certain borates and phosphates are occasionally used, to replace a part of the silica in glass manufactured for various optical and chemical purposes; these usually contain zinc or barium also. The well-known "optical glass," made in Germany, contains both zinc and boron.

Technically, two kinds of glass are recognized: **lime glass** and **lead glass.** The alkali used may be soda, or potash, or both. Lime glass is most common and generally useful. It is cheaper, harder, more resistive, and less fusible than lead glass; the latter has greater lustre and brilliancy, is heavy and expensive and is used chiefly for cut ware and for optical purposes.

The essential materials for glass making are silica, an alkali, and lime or lead. Silica was formerly derived from quartz or flint; but this is now only used for a particularly fine quality. It is heated to a red heat, and dropped into water, and the friable mass so formed is powdered in a mill. Quartz sand and soft quartzites are the usual sources of silica, and numerous deposits are worked in different countries. Sand of great purity is found in Germany, near Aix-la-Chapelle, and at Nivelstein; in France, at Fontainebleau; in Belgium; in England; and in Australia. In the United States, extensive beds are worked in Berkshire Co., Mass., and in Pennsylvania, along the Juniata River. The Berkshire deposit is a soft white sandstone, which, when crushed, yields sand which is from 99.6 to 99.8 pure SiO_2. The Juniata stone is slightly yellow in color, and the sand is from 98.8 to 99.7 pure SiO_2. The most troublesome impurity in sand is iron; for white glass, there should never be more than 0.5 per cent Fe_2O_3.

Alkali is derived from the carbonate or sulphate of soda or potash, and these also must be free from iron. Carbonate fuses more readily with the sand than does sulphate, but since the latter is cheaper, it is much used. It is *essential* to mix carbon in some form with the sulphate, to assist in reduction. For better grades of glass, charcoal dust is used, but for common glass, powdered coal is the reducing agent. The exact nature of the reaction with sulphate appears somewhat uncertain: —

$$Na_2SO_4 + SiO_2 + C = Na_2SiO_3 + SO_2 + CO.^*$$

For lead glass, sulphates are not generally used, since some sodium sulphide is formed by the reduction of the sulphate, and this reacts with the lead, forming lead sulphide, which darkens the glass.

Attempts to use salt directly in the glass furnace, as a source of alkali, have not proved satisfactory. It is quite volatile at the temperature of the furnace, and the presence of air or steam is necessary for its decomposition by the silica.

For potash, crude pearlash may be used; but in the better grades of glass the refined pearlash is employed. Sulphate of potassium is difficult to reduce, and is not much used.

Lime is derived from chalk or limestone. For very fine glass, pure marble dust, as free as possible from iron, is employed. For common grades, less pure limestone is used. It may contain a high percentage of silica and considerable alumina, but magnesia or iron in large amounts is objectionable. Magnesia makes the glass hard and infusible. In cheap glass, limestone is sometimes replaced in part by felspar, porphyry, or granite. Carbonates of both alkali and lime are advantageous in the glass mixture, since, as the mass fuses, the escaping bubbles of carbon dioxide serve to stir up and mix the ingredients more thoroughly.

Lead is added as litharge (PbO), or red lead (Pb_3O_4). The latter is preferred, since the oxygen liberated from it is thought to assist in decolorizing the glass by oxidizing the iron; it also prevents reduction of metallic lead. It is essential that the litharge and red lead be free from copper and silver.

Besides the above requisites, it is customary to employ other ingredients in every glass mixture, to assist in the decolorization or fusion. The commonest decolorizing material added is pyrolusite (binoxide of manganese, MnO_2). Iron, when in the *ferrous* condition, imparts a green color to glass; but when in the *ferric* state, it is much less troublesome, since it only gives a pale yellow color. By the oxidizing action of the pyrolusite, ferrous iron is converted to the ferric condition; moreover, the silicate of manganese has a violet or pink color, and so helps to neutralize the green. Only a very small

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* Lehrbuch der technischen Chemie, H. Ost, 8te Auf. 257.

percentage of pyrolusite should be thus used. The remedy is not a permanent one, and if the glass is exposed to the sunlight for a long time, it develops a violet shade, as may often be observed in the window panes of old houses.

Arsenious acid (As_2O_3), or nitre ($NaNO_3$), is often added to the materials for colorless glass. The former is reduced to metallic arsenic, which volatilizes. It affords a very clear and lustrous glass. Zinc oxide is often used to decompose any sodium sulphide, which would give a yellow tinge to the product.

In common bottle glass and other cheap grades, where color is no objection, blast furnace slag is often used. This generally needs the addition of soda, to render it more fusible and plastic.

The formulæ for glass mixtures vary much in the different factories, not only because of variations in the composition of the glass produced, but also because the materials are of different degrees of purity. These are often empirical recipes, not based on analysis of the raw materials.

The fuel for glass making is an important item. A quick-burning material, yielding a long flame, without smoke or soot, is desirable. For fine grades, wood is still employed in some places, but good coal is now most common. In this country the discovery of natural gas had a great influence on the glass industry, and within a few years most of the larger plants were moved into the gas territory, Pittsburgh becoming the centre of the manufacture. With the decline of the natural gas supply, producer gas (p. 41) or oil has been substituted as fuel. Gas is an ideal fuel for this purpose, since it is clean, easily managed, and gives a regular heat. It is generally employed in regenerative furnaces (Fig. 23, p. 44). Crude petroleum, or the residuum from kerosene distillation, is much used and is a good fuel. Whatever the mode of heating, only the flame and hot gases should come in contact with the pots or their contents.

There are several forms of glass-furnaces. The common **pot furnace** has the pots placed in a circle around a central opening in its bed, through which the flame and hot gases come up from the grate, which is below the hearth. The furnace is roofed with a rather flat arch, which deflects the flame down upon and around the pots. When open pots are used, it is essential that no soot or smoke enter the furnace, and much care is necessary in firing. In some forms, the fuel is introduced by mechanical means from beneath the grate, so that the fire burns on top of the pile of coal. This prevents the entrance of cold air into the furnace, and also consumes all smoke.

The **Boetius furnace** (Fig. 82) is used abroad, and is best adapted for closed pots. Coal or coke is charged at (A), and air enters through (B, B). The flame passes through (C) into the upper compartment (D), containing the pots. The products of combustion escape through (E, E).

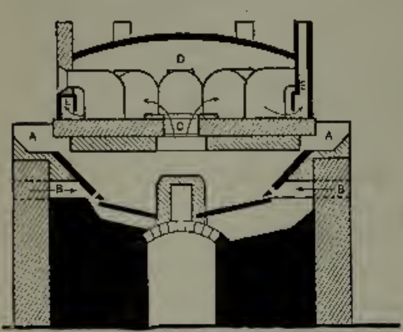

Fig. 82.

Siemens gas furnace (Fig. 23, p. 44) is much used because of its economy of fuel, both as a pot furnace and as a **tank-furnace.** The last named is more economical where a large quantity of one kind of glass is to be made. It replaces the expensive and fragile pots by a single large deep hearth or tank, at one end of which the raw materials are continually introduced, while the glass is withdrawn at the other. Figure 83 shows a plan and elevation of a tank-furnace, in which the batch is introduced at (A). The gas-flame issues from (C, C) and plays over the surface of the charge. The batch (B) soon fuses and the liquid mass flows towards the opposite end of the tank. At (F) are elliptical " **floaters** " of fire-clay, one end of which rests in recesses in the wall, while the free ends meet in the middle of the furnace. The current of melted glass flowing towards (D) constantly presses these floaters together and prevents their separation. The liquid mass thus passes *under* the floaters and collects in the compartment

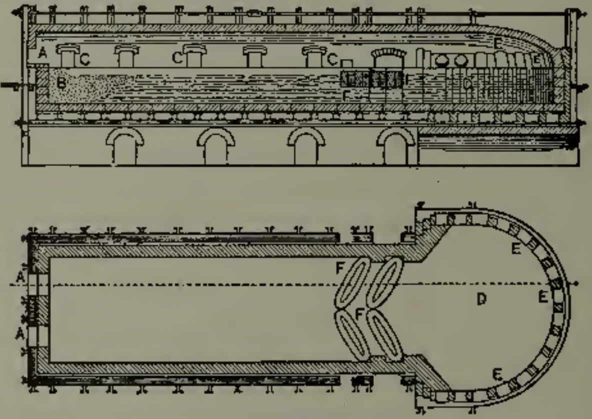

Fig. 83.

(D), from which it is withdrawn through the openings (E, E). At (B) the temperature is very high, and as the glass flows slowly towards (F), the refining takes place. In (D) the temperature is lower and the glass has cooled sufficiently for working. The impurities, rising to the surface during the melting and refining, are retained by the floaters so that the glass in (D) has a clean surface and is free from bubbles. Small rings of fire-clay may be kept floating on the glass near the working doors (E, E); by dipping the glass from the centre of these rings, it is obtained free from any impurities which may be on the surface of the melt in (D). A typical furnace of this kind may be about 75 feet long by 16 feet wide and 5 feet deep, to the level of the doors (E, E).

Glass-furnaces must be made from very refractory materials. The dome and arches are usually silica, or Dinas bricks, or ganister, but the bed is generally fire-clay, as this is less attacked by the contents of a pot when one breaks. The life of a furnace is very uncertain, but may be several years. If allowed to cool, it is generally necessary to reline it before starting again.

Pots for glass making are very carefully constructed, only the best material being used. The breaking of a pot in the furnace is a serious matter, often resulting in the loss of the glass and there is more or less loss of time.

Fig. 84.

Glass-pots are of two kinds, open and closed. **Open pots** (Fig. 84) are circular vessels, about as wide as they are deep, *i.e.* from 3 to 5 feet, and usually slightly broader at the top than on the bottom. They are preferred for a quick melt, and are generally used for glass which contains no lead.

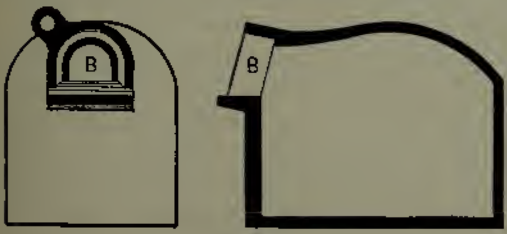

Fig. 85.

Closed pots (Fig. 85) are usually longer in one direction, and are about 5 feet by $3\frac{1}{2}$ feet, by 4 feet high. The neck of the opening is built into the wall of the furnace in such a manner that neither flame nor fire gases can come into contact with and injure the glass, and consequently cheaper fuel may be used; but these pots heat more slowly than do open ones. They are always used for lead glass.

Clay rings are sometimes placed in the pots, so that the glass may be withdrawn without contamination from the floating impurities. Sometimes a partition is constructed across the pot (Fig. 86), the raw materials being introduced and melted on one side, and the refined glass, free from impurities, having passed under the partition, is worked out on the other side.

Fig. 86.

The material of the pots is fire-clay; but the necessary degree of plasticity, with the required infusibility, are possessed by but few clays. To avoid excessive shrinkage when the new pot is heated, a large proportion of burned clay from old pots, entirely free from any adhering glass and ground to a coarse powder, is mixed with the new clay. The mass is then moistened and well kneaded by treading, and is then allowed to stand and "age" for a long time, to increase the plasticity. The pots are built up by hand, the bottom being formed first, and the sides constructed on it. The clay is laid on in small lumps, and each lump is carefully pressed into place by the workman before another is added. From three to five inches is usually added to the height of the pot each day. When finished, it is allowed to stand in a room at constant temperature and protected from draughts of air, for several months, to dry thoroughly. In order to prevent too rapid drying, which might cause cracking, it is generally covered with canvas or paper for the first few weeks.

Before placing it in the glass-furnace, a new pot is heated very slowly in a special furnace, until it is brought up to the temperature of the former, into which it is then transferred, while still hot, through an opening in the wall. The wall must be taken down, the broken pot removed, and the new one introduced, without allowing the furnace to cool; hence the operation is difficult, and requires much skill on the part of the workmen. Once introduced, a pot is kept in constant use, and never allowed to cool; for, if it should, it would crack when heated again. Its life is very uncertain, but a good one will sometimes last for months. The first charge in a new pot is broken glass (cullet), which forms a glaze over the surface and protects it from the solvent action of the melted raw materials.

The **general process of glass making** is as follows: The finely ground raw materials are thoroughly mixed, sometimes by regrinding the mixture or "batch." The batch is shovelled into the pot, together with a certain amount of broken glass called "cullet"; this melts at a comparatively low temperature, and thus assists in liquefying the rest of the charge. More of the batch is added, until the pot is filled to the desired height with the fused mass; then volatile substances, such as arsenious acid, used in decolorizing the glass, are added.

During the melting, much gas (CO_2, SO_2, and O) escapes, and the bubbles rise through the melt, stirring it and causing frothing. A considerable amount of the alkali and other constituents volatilize. The reactions involved are variously written by different authorities:

(*a*) 1) $Na_2CO_3 + CaCO_3 + 2\ SiO_2 = Na_2Ca(SiO_3)_2 + 2\ CO_2$.*
2) $2\ Na_2SO_4 + 2\ SiO_2 + C = 2\ Na_2SiO_3 + CO_2 + 2\ SO_2$.*
3) $Na_2SiO_3 + CaCO_3 + SiO_2 = Na_2Ca(SiO_3)_2 + CO_2$.*
(*b*) $2\ Na_2SO_4 + 6\ SiO_2 + C = 2(Na_2O, 3\ SiO_2) + 2\ SO_2 + CO_2$.†

When the melt has come to a state of quiet fusion, the temperature is generally raised somewhat, and the liquid glass allowed to stand for a time. This is called "**refining,**" and its object is to form a homogeneous mass, free from bubbles and bits of uncombined silica or other matter. The scum which collects is skimmed off; it is called "**glass gall,**" and consists of undecomposed sulphates and chlorides of lime and alkali, alumina compounds from the pot, and various other impurities. If too little carbon is used in the batch, the melt is covered with a layer of fused sodium sulphate; this is known to the workmen as "**salt water.**" Samples of the glass are examined during the refining, and these determine the exact time of heating. After refining, the glass is too liquid to blow, or to work to advantage, and is cooled until it becomes pasty.

The quantities of materials used in the batch, for some typical glasses, are shown in the following table: —

	SiO_2	Na_2CO_3	Na_2SO_4	$CaCO_3$	CaO	MnO_2	Pb_3O_4	K_2CO_3	Coke	Slag
French Plate (Soda-lime)	100	34	—	14.5	—	0.25	—	—	—	—
Bohemian (Potash-lime)	100	—	—	—	18	—	—	40	—	—
Window (Soda-lime)	100	5	37.5	35.8	—	0.4	—	—	4	—
Lead flint	100	—	—	—	—	—	60	20	—	—
Bottle glass (Green glass)	100	—	25	34	—	—	—	—	3	5

Glass is known under various names in commerce, according to the method of its manufacture or the uses to which it is put; for example, plate, crown, flint, and window glass.

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* Wagner, Chemical Technology, 608.

† Ost. Lehrbuch d. technischen Chemie, 5te Auf., 237.

Plate glass is cast on a large iron plate or "casting table," made up of thick, narrow segments of cast iron, bolted together and planed on top. These tables were formerly cast in one piece, and, being large and thick, were very expensive. But when put to use, they soon became warped and dished, owing to unequal expansion of the top and bottom; this caused much loss of time and glass in the subsequent grinding of the plate. The built-up table is much cheaper and retains its even surface much longer.

The melted glass is poured on the table and spreads out in an even layer. But to give the plate a uniform thickness and to smooth down any inequalities of the surface, a heavy iron roller, travelling on adjustable guides at the edge of the table, is passed over it. The height of these guides determines the thickness of the plate. Both the casting table and the roller are heated before use, so that the glass may not be cooled too rapidly. As soon as the plate is rolled, it is transferred to the floor of the **annealing furnace**, or "**lehr**," which is directly in front of the casting table, and which has been heated to the temperature of the glass. The floor of the oven consists of a series of iron plates supported on rollers; as each new sheet of glass is introduced the entire series is moved forward towards the outlet. As the furnace is heated only at the inlet end, the temperature gradually decreases towards the outlet, and the glass slowly cools during a number of hours. All glass must be annealed. This process probably allows the molecules to arrange themselves so that there is no considerable internal stress when the mass is cold. Unannealed glass which has been suddenly cooled is always under high internal strain, which makes it exceedingly brittle, and may even cause it to fly to pieces spontaneously, or when slightly scratched.

When removed from the annealing furnace, the plate is uneven and rough, and may be somewhat devitrified on the surface. It is fastened on a horizontal table, and heavy cast-iron rubbers are made to slide over its surface with a rotary motion, while coarse sand and water are sprinkled on it. When the glass is smoothed and of a uniform thickness, it is polished by rubbing with buffers, covered with leather or felt, and used with fine emery dust or putty powder. About one-half of the thickness of the plate is cut away during the grinding and polishing.

Plate glass is usually a soda-lime glass. The batch is melted and refined as has been described, great care being taken to remove all the "gall," which is skimmed off immediately before the casting. An especially strong pot is used, which will stand the strain of lifting from the furnace while full of melted glass. The furnace is constructed with brick-lined, cast-iron doors, which open to permit the removal of the pot. The melting and annealing furnaces are often joined, so that the latter may be heated with waste heat.

The chief uses of plate glass are for windows and mirrors. A considerable quantity of " rough plate," unground, as it comes from the annealing furnace, is used for skylights and for flooring.

Window glass is always blown. It is usually a soda-lime glass, and the batch is melted and refined in the usual manner, either in pots or in tanks. After the refining, the glass is allowed to become pasty, and then the blower begins his work. His chief tool is the " pipe," a straight piece of iron tubing, four or five feet long, usually provided with a mouthpiece. He dips the pipe into the soft glass, which is called " metal," and gathers a lump on the end. Then, by blowing through the pipe, while whirling it between the palms of his hands, he forms a hollow globe of glass. This is reheated in a special furnace (" glory-hole ") until soft, rolled on a flat surface, and then swung in a vertical circle, with occasional blowing through the pipe, until the globe has elongated into a hollow cylinder, closed at one end and opening into the pipe at the other. In order to have plenty of room for the vertical swinging, the workman stands on a bridge placed across a rather deep pit. The closed end of the cylinder is reheated until soft, and then blown out; the small opening thus made is enlarged by means of the " widening tongs." The pipe is detached by touching its point of attachment with a wet stick, and the edges of the still soft glass are trimmed with shears. A hollow cylinder, open at both ends, is thus formed, and is cut lengthwise with a diamond. It is then put into the **flattening furnace**, in such a position that the cut is on the upper side. The heat being sufficient to soften the glass, the cylinder slowly opens, and spreads out on the floor of the furnace in a flat sheet. It is then transferred to the annealing furnace for blown ware. This consists of a long oven, heated at one end and cool at the other. A system of endless iron bands carries the glass slowly from the hot to the cool end of the oven. Sometimes the glass to be annealed is placed on a large horizontal table, usually built of slabs of stone, and carefully balanced, so as to revolve easily and slowly, by means of a gear, while a segment passes through a narrow opening in the side of the flattening furnace, where it is exposed to the high temperature. The glass is thus slowly carried out of the furnace into a cooler compartment, from which it is removed when nearly cold. This table is chiefly used for window glass.

The glass sheets are now cut to marketable size, without any polishing. As the surface of blown glass is fused and not polished, it is brilliant and hard; hence, it is less easily scratched or etched, and is more durable than plate glass when exposed to the weather.

Glass-blowing is an exceedingly fatiguing labor, and only men of strong constitution and good lung power can do it. The mass of glass which a good workman will handle at one time averages about 18 pounds, and from it he will form a cylinder over a yard long and a foot in diameter. A skilful glass-blower can form all kinds of glass utensils by the use of his pipe and other tools. Wine glasses, tumblers, bottles, and lamp chimneys, for example, are often entirely blown. But much glass ware is blown in moulds, or pressed. Glass-blowing machines are now in use for common bottles, lamp chimneys, fruit jars, etc., and in some cases window glass, carboys, and other large articles are machine blown.

Crown glass is a form of blown glass in which the globular balloon first blown is flattened by pressing against a flat surface. The end of an iron rod is smeared with a coating of melted glass and attached to the centre of the flattened surface. The pipe is then detached, leaving a small hole. By reheating and rotating the rod swiftly about its *longitudinal axis,* the balloon opens out, forming a circular plate or disk, 4 or 5 feet in diameter with the rod at the centre. But they are not of the same thickness at the edge and middle; where the rod was attached, there is a thick rounded mass called the " bull's-eye." This must be cut out, so large window panes cannot be made from crown glass. Thus it is not an economical form of glass-blowing, and the industry is practically abandoned. A little is now made to supply a small demand for the " bull's-eyes " for decorative purposes. Crown glass has a very brilliant surface.

Flint glass now means any transparent, colorless glass.

In **cut-glass** ware, the design is cut in the solid glass, which has been given its general form by blowing or pressing. Sometimes the design is formed in the pressed ware, and the surface only is cut and polished. Glass-cutting is done on a soft steel, copper, or sandstone wheel, the cutting edge of which is fed with sand or emery and water. The polishing is done on similar wheels of wood, fed with rouge or putty powder. Lead glass is nearly always used for cutting, since it is softer and more brilliant than other varieties.

Pressed glass is made by the use of a die or mould; these moulds are expensive, but owing to the great mumber of pieces of the same form and design that are made with slight labor, pressed ware is cheap.

"**Tough**" or "**tempered**" **glass** is produced by a special method of annealing, the articles so treated being capable of withstanding blows and sudden changes of temperature. This tempering is done by plunging the article, while still so hot as to be somewhat soft, into a bath of oil heated to 100°–300° C. This sudden "quenching" hardens the surface of the glass, but causes internal stresses. If scratched or cut slightly, toughened glass is apt to fly to pieces, sometimes with great violence. And even after standing a long time spontaneous fracture often occurs. It is mainly used for lamp chimneys.

A process for making hardened glass plates and window lights is employed in which cold metallic surfaces are applied to the glass plates while the latter are still plastic. The sudden chilling imparts an exceedingly hard surface to the glass, so that it can be used in exposed situations, such as in street lamps.

A **compound glass** is a recent invention to replace the hardened or tempered glass. Articles are formed of two layers of glass, the inner layer having a low coefficient of expansion while the outside layer has a high coefficient. This glass is particularly recommended for lamp chimneys and chemical vessels which must endure sudden changes of temperature. The ratio between the two coefficients must be very carefully maintained.

Colored glasses are produced by adding to the ordinary batch certain metallic oxides or salts, or even finely pulverized metal. These dissolve in the glass, and impart a characteristic color.

Green glass is produced by the use of ferrous oxide, chromic oxide, or a mixture of cupric and iron or chromium oxides. The color produced by ferrous oxide is a dull green, of no particular beauty. Copperas or iron filings are added to the batch to form the ferrous silicate necessary for the color. Chromic oxide (Cr_2O_3) imparts a better green. It is usually produced by adding potassium bichromate ($K_2Cr_2O_7$) to the batch. If an excess of chromium oxide is present, the uncombined portion separates as minute crystals, disseminated through the glass, producing *chrome aventurine*. A mixture of cupric and ferric oxides produces green glass, owing to the combined effect produced by these oxides individually.

Yellow or **amber glass** is made by adding sulphur or carbonaceous matter to the batch, producing sodium or potassium sulphides, which color the glass. A common method is to introduce wood or charred horn into the melted glass. Cadmium sulphide is sometimes employed. No sulphur compound can be used with lead glass. A rich yellow stain is obtained by the use of metallic silver or silver chloride; this is much used in making church windows, and was known in the Middle Ages. A peculiar greenish yellow, fluorescent glass is produced with uranium oxide, but it is expensive.

Orange glass of various shades is made by adding selenium (as a selenate with a reducing agent), or a mixture of ferric oxide and manganese dioxide.

Blue glass is made with cobaltic oxide (Co_2O_3) or cupric oxide. A very small percentage (0.1) of cobaltic oxide produces a deep blue color. If more than 5 per cent is used, the color is so deep that the glass may be ground for pigment (*smalt*). Owing to the intensity of its color, cobalt glass is much used for " flashing " on the surface of colorless glass. To do this, the blower dips his pipe into the pot of colored glass, and, collecting a small lump, dips it into the pot of colorless glass, or *vice versa.* By blowing he forms a sheet of colorless glass which is coated on one side with a very thin layer of colored glass, both firmly welded together. Both glasses must have the same composition and the same coefficient of expansion. A light greenish blue is obtained by the use of a small quantity of cupric oxide.

Violet is produced by a small amount of pyrolusite, free from iron. An excess of manganese, especially if much iron is present, gives a deep yellow or brown.

Red glass is made with metallic gold or copper, cuprous oxide, or selenium oxide. Gold yields a bluish red, while copper and selenium give deep ruby red. For gold ruby a minute quantity of gold chloride is added to the batch; on cooling the glass is colorless or reddish yellow. The ruby color appears on reheating and is due to colloidal precipitation of metallic gold in the glass; if overheated the color changes to a dull red brown, owing to coagulation of the colloidal gold. Gold ruby is generally "flashed," owing to its intense color.

For copper ruby, cuprous oxide (Cu_2O) as "hammer scale," is used; a small quantity of iron filings may be added to reduce any cupric oxide. The pot metal is also nearly colorless or pale green and requires careful reheating to develop the colloidal copper precipitate. This glass is also used for "flashing."

Selenium oxide yields a beautiful deep red in the pot metal, thus avoiding the troublesome second heating; but the color is less intense than with gold or copper, and flashing is not employed.

White, " opal," or " milk " glass is made by adding cryolite or fluorite, with felspar, to the batch for common glass. Calcium phosphate, as bone-ash, may also be used. These substances crystallize in the glass when the melt is kept near its fusion point for some time, and thus cause the opalescence. Large quantities of tin or zinc oxides produce a translucent milk glass.

Black glass is obtained by using a large excess of pyrolusite, iron, or copper oxides. The so-called " smoked glass," used for optical purposes, contains some nickel.

Enamel is an easily fusible glass, usually containing lead and boric acid, or phosphate or stannate of sodium or potassium. It is usually white, blue, or gray, the color being produced by adding proper oxides. It is used for coating metallic (iron) vessels, pottery, (tiles, flower-pots, bricks, etc.), and porcelain. For cooking vessels it must be free from lead, and is composed of sand, borax, soda, and calcium phosphate or white clay (kaolin). Enamel must have a coefficient of expansion about equal to that of the iron on which it is placed, otherwise the glaze is soon destroyed by heating and cooling.

Iridescent glass is made by exposing the hot glass to the vapors of stannic chloride ($SnCl_4$), or hydrochloric acid; these attack the surface of the glass and alter its composition. It was formerly supposed that the art of making this glass was invented by the Romans, and later was lost. However, the old Roman glass was not originally iridescent, but has become so through exposure to dampness and carbon dioxide. The surface has been partly decomposed, the alkali dissolving, thus producing a thin layer of glass having a different composition and physical structure from the main body. This thin film causes interference of the light rays and produces a play of colors when viewed in different positions.

Mirrors were formerly coated with an amalgam of tin. Tin foil was covered with mercury, and the glass, carefully cleaned, was laid on the amalgam, excess of mercury being forced out at the sides, and the amalgam adhering firmly to the glass.

But the silver mirror is now the only kind made. A coating of metallic silver is deposited on the glass from an ammoniacal solution of silver nitrate by the use of a reducing agent. Ammonium tartrate, or a solution of glucose or milk sugar in caustic soda, is generally used for this purpose; or aldehyde is sometimes used. The glass is carefully cleaned and covered with the silver solution containing the reducing substance, and heated gently on a steam or hot-air bath. The thin layer of metallic silver deposited adheres to the glass, and is washed and dried, and covered with a protecting varnish to prevent the hydrogen sulphide in the air from tarnishing the reflecting surface.

Plate glass is generally used for the best mirrors. Blown glass, which is used for the cheaper ones, is very apt to contain bubbles and striæ, causing distortion of the image.

Tradition assigns the discovery of glass to the Phœnicians. Glass making is a very old industry, and was known to the early Egyptians, since glass beads have been found in mummy cases at least 3000 years old. Glass articles have also been found in the excavations at Nineveh. From Egypt, the industry was transferred to Rome, and on the fall of the Western Empire the art was carried to Byzantium. Byzantine glass attained a high degree of perfection ; but in the middle of the thirteenth century Venice became the centre of the industry, and Venetian glass-blowers were remarkably expert in the production of beautiful and delicate patterns. Finally, Bohemia took the lead in the manufacture of glass, and has retained a front rank ever since.

Window glass was made by the Romans to a small extent, and specimens of such glass were taken from the ruins of Pompeii. In England, it first came into use in houses during the reign of Elizabeth, but previously to this it had been used in cathedrals and churches. From the records of York cathedral, it is shown that during the time of Archbishop Wilfrid (669–709 A.D.) "glass was placed in the windows so that birds could no longer fly in and out and defile the sanctuary." The contract for the glass in the great West Window, given by Archbishop Melton, is dated 1330. The work was finished before 1350, and the price paid was 6*d*. per square foot for white, and 1*s*. per square foot for colored glass. This window is 54 feet high by 30 wide, and is to-day regarded as one of the finest examples of stained glass in England. The great East Window (77 feet high and 32 feet wide) was glazed by John Thornton in 1405–1408, for which he received 4*s*. per week. These examples demonstrate the high degree of perfection to which the glass industry had advanced during the Middle Ages.

At the present time, Belgium and England lead in the production of window and plate glass, while Germany, France, and the United States also manufacture enormous quantities. Austria and Germany are the leading producers of blown ware.

REFERENCES

Glass Making. Powell, Chance and Harris. 1883.

U. S. Census, **1880**. — Report on the Manufacture of Glass. J. D. Weeks.

Die Glas-Fabrikation. R. Gerner, Vienna, 1880. (Hartleben.)

Handbuch der Glas-Fabrikation. Dr. E. Tscheuschner, Weimar, 1885. (Voigt.)

Die Fabrikation und Raffinirung des Glases. Wilhelm Mertens, Vienna, 1889. (Hartleben.)

Verre et Verrerie. L. Appert et Jules Henrivaux, Paris, 1894. (Gauthiers-Villars et Fils.)

Journal of the Franklin Institute. **1887**. Glass Making. — C. H. Henderson.

Proceedings of Engineers' Society of Western Pennsylvania. **1895**, 119. A Study of Glass. — Robert Linton.

Elements of Glass and Glass Making. B. F. Biser. 1899.

Jena Glass. H. Hovestadt. 1902.

Journal of the American Chemical Society. **1902**, 893. G. E. Barton.

CERAMIC INDUSTRIES

Clays are natural hydrated silicates of aluminum, formed by the weathering of felspar or felspathic rocks, such as granite. The hydrolysis of felspar may be represented thus: —

$$Al_2O_3,\ K_2O, 6\ SiO_2 + CO_2 + 2\ H_2O = Al_2O_3,\ 2\ SiO_2 \cdot 2\ H_2O + K_2CO_3 + 4\ SiO_2.$$

Clays which have not been transported by natural waters from the place where they were formed are called *primary; secondary* clays have been washed from their original beds and deposited elsewhere. Primary clay derived from pure felspar contains little impurity other than silica, and is called **kaolin**, or **China clay**. It is a white, powdery mass, essentially hydrated silicate of aluminum and silica, nearly all the alkali having been leached out. Kaolin is characterized by its capacity to undergo progressive hydration in contact with water; in the early stages this hydration is merely on the surface of the particles, but as it penetrates deeper and becomes more complete, the clay assumes markedly colloidal properties. Its aqueous suspensions become tolerably permanent (*e.g.* river silt), and in the solid state it is very plastic, *i.e.* it can be readily moulded, and surfaces pressed together coalesce. The water of hydration can be driven off by heat, whereupon the plasticity is lost, and the mass becomes hard and stonelike. These facts are the basis of the ceramic industry.

The rocks from which primary clays are formed are seldom homogeneous, and the various components have different rates of decomposition and hydration. The clay then consists of a mixture of particles of different composition and colloidal character. The formation of secondary clays usually involves mixing of various primary deposits, and the particles of such clays are more diverse in character. Kaolin itself is almost infusible, but if the clay contains in an appreciable amount particles of low melting point (unweathered felspar, quartz, and metallic oxides), on heating, these finely divided particles disseminated in the mass serve as a flux for the rest of the clay, and cause it to soften, or even to melt, at temperatures far below the fusion point of the major part of the mass. Thus a clay may be of such composition that if rendered homogeneous (*e.g.* by melting) its fusion point is very low, but in the clay itself none of the various particles are of low fusion point; such a clay will soften only at very high temperatures, but once softening begins, the mass will quickly liquefy.

Very difficultly fusible clays are generally primary, as among the constituent particles of secondary clays, some are likely to be of low melting point. **Fire-clays** are very difficultly fusible. They are usually found underlying coal beds. In composition they are kaolins containing free silica as quartz. They may contain a little more iron than good China clay, but are free from alkalies.

Secondary clays have had more opportunity for thorough hydration than primary, and are hence more plastic; these colloidal clays are called **pipe-** or **ball-clays**, and are also known as "fat" clays to distinguish them from the non-plastic or "lean" clays.

Fat clays absorb much water and have great binding power, so that they are easily shaped by the potter. But on drying, and especially when burned, they shrink much. This shrinkage is counteracted by mixing with the fat clay a certain amount of "leaning" material, such as silica, pulverized burned clay, or "grog," the ground, unglazed body of pottery. Fat clays are usually more fusible than lean clays.

Highly hydrated, plastic clays can lose a large part of their water without much modification of structure, if dried at temperatures below 100° C. They still rehydrate if wet. All clays lose water of chemical composition below a red heat, and then lose capacity for rehydration and plasticity. All stages of dehydration are accompanied by shrinkage, roughly proportional to the original plasticity; if excessive, this causes cracks in drying and burning; it is controlled by mixing plastic with non-plastic clays, or "grog." Since the physical properties of the product are determined by the proportions of the various clays employed, in making ware to meet definite requirements, a complex mixture of clays is usually necessary.

Clay is used in all degrees of hydration; in the form of a colloidal suspension, or "slip," it makes possible the forming of articles by "casting" in plaster moulds; when dehydrated to the form of a plastic solid mass, it is used on the potter's wheel. Dried at a low temperature, it loses its plasticity and becomes hard, as in sun-dried bricks (*adobe*); it loses chemically combined water below a red heat, and an association of the aggregates occurs, which renders it inert and incapable of rehydration; at higher temperatures, the particles of lowest melting point fuse and cement together the remaining granules; finally fusion may go so far that the mass becomes semivitreous, but complete fusion is avoided to prevent deformation of shape.

Because of their nature and origin, clays are complicated mixtures, each component differing in chemical behavior for varying degrees of hydration; hence neither the empirical analysis, nor the so-called "rational analysis" is of much value to the potter. The latter is a determination of "clay substance" or kaolin, felspar, quartz, etc. (by their different behavior to solvents) and merely emphasizes the differences between clays. The plasticity, fusibility, shrinkage, and color of the product after burning, and its coefficient of expansion are the important properties, and these must be experimentally determined for each clay. The variations in clays are shown in the following analyses: —

CHEMICAL ANALYSES

	GERMAN* (SENNEWITZ)	BOHEMIAN* (ZETTLITZ)	VIRGINIAN† (KAOLIN)	OHIO† (FIRE-CLAY)	ENGLISH† (CORNISH STONE)
SiO_2	64.9	45.6	50.02	74.93	73.57
Al_2O_3	23.8	39.0	35.18	17.19	16.48
Fe_2O_3	0.8	0.5	0.36	0.79	0.27
CaO	—	0.6	0.12	0.29	1.17
MgO	0.5	0.1	0.07	0.46	0.21
Alkalies	1.4	0.5	3.39	1.61	5.84
H_2O	8.4	13.6	10.57	5.44	2.45
	99.8	99.9	99.71	100.71	99.98

RATIONAL ANALYSES

Clay substance	63.8	100.0	84.12	48.24	33.57
Quartz	35.5	0.0	6.55	49.72	41.10
Felspar	0.7	0.0	9.04	2.75	25.31
	100.0	100.0	99.71	100.71	99.98

All clays have a peculiar and characteristic odor when breathed upon or wet.

The preparation of clay for the potter is simple. It is mined, and allowed to weather for several months, which increases its plasticity by promoting hydration. This is probably aided by certain

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* Lehrbuch der technischen Chemie. 5te. Auf. H. Ost, 262.

† Chemistry of Pottery. K. Langenbeck, 10, 111, 165.

enzymes, of bacterial origin in some cases. Fine clays to be used for the better grades of ware are then thoroughly "slipped" with water in a "blunger" (a vat with mechanical stirrers), and thus levigated. The coarse particles of quartz, mica, and undecomposed felspar are separated, and only the clay substance, with a little finely divided quartz, remains in suspension. The fine mud, called "slip," obtained by settling the wash waters, is pressed in cloth bags or it is filter-pressed. It is then ready for use.

Ceramics comprise two general divisions: (*a*) articles having a non-porous body, and (*b*) articles having a porous body. **Non-porous ware** is hard, impervious to liquids and gases, and has a semi-vitrified appearance on the fractured surface. It is burned at a very high temperature, and is chiefly made from kaolin, with just enough plastic material to enable the workman to form the desired article. This division includes porcelain and stoneware. **Porous ware** is less dense, has an earthy appearance on the fractured surface, and permits the passage of gases and liquids through its pores. It is made from plastic clays, and burned at a low or moderate temperature. It comprises bricks, terra cotta, common crockery, and some kinds of stoneware.

There are two kinds of **porcelain**, the hard and the soft, or "fritted." Both are harder than glass, and very resistive to chemical action.

Hard porcelain softens only at the highest attainable temperature, and, when burned, forms a perfectly homogeneous mass, which is translucent. The body is composed of kaolin, quartz, and felspar, in definite proportions. It is glazed with pure felspar, or a mixture of quartz and felspar, with sufficient lime to form a difficultly fusible glass. This glaze, which must have the same coefficient of expansion as the body, is very perfectly welded on to the body, by a second burning at a high temperature; and no distinct line of demarcation between the body and the glaze can be seen on a fractured surface. Berlin, Sèvres and Meissen ware are examples.

Soft porcelain consists of a kaolin body, with ball-clay, bone-ash, and felspathic materials added. This is burned at a high temperature, and glazed with a lead-boric-acid glass, which is fused on to its surface by a second much lower heating. The glaze does not penetrate so perfectly, but forms a more superficial layer than is the case with hard porcelain. English china, stone ware, and Parian ware are soft porcelain.

In preparing the clay for porcelains, the powdered materials are thoroughly mixed, wet, and the " slip " kneaded and allowed to age for several months. The articles are formed on the potter's wheel, a horizontal revolving table, driven by foot or machine power. Sometimes the slip is cast in porous moulds of gypsum or burned clay, which absorb the water, leaving the mud on the face of the mould. Or the partly dried mud is pressed in moulds to form one surface of the article, the other being completed on the wheel, as is the case with dishes and plates. The articles are very slowly dried at atmospheric temperature, and then burned at a low red heat, to give them sufficient coherence to permit of glazing.

The finely powdered glaze mixture is stirred up with water to form a cream, into which the articles are dipped and at once withdrawn. A layer of the glaze adheres to the surface, and, after drying, the article is ready for the second or glaze burning. In order to protect them from direct contact with the fire in the kiln, they are enclosed in fire-clay boxes, called " saggers." These are piled in the kiln in columns or " bungs," extending from the bottom to the top. In order to allow sufficient freedom for shrinkage, the porcelain is supported on a " cockspur," a small tripod of fire-clay. The contraction of porcelain on burning is nearly 13 per cent of its original volume. After burning, the ware is sorted; much is lost owing to warping, to bubbles in the glaze, and to discolorations resulting from smoke and from iron oxide in the material.

The body of all ware to be glazed is called " biscuit " after the first firing; that of soft porcelain which has been hard fired is called " Parian." Both are used for statuettes, medallions, and reliefs.

Stoneware, which is also a non-porous body, is made from refractory material, and burned at high temperatures. But the color of the resulting ware may range from white and gray to yellow and brown. It is not attacked by chemicals, and withstands temperature changes fairly well. The finest quality is the well-known " **Wedgwood** " ware, which comes in various colors, and is usually not glazed. The gray stoneware, decorated with blue, so much used for drinking-mugs and ornamental vases, is also of this group. Yellow and brown varieties are much used for mineral water-bottles, *bombonnes*, condenser tubes, and glazed pipes in chemical factories. The clays are less pure than those for porcelain, and the ware is burned without saggers, at a very high temperature. A " salt glaze " is used, to form which common salt is thrown into the kiln, and, volatilizing, combines with the silicates of the stoneware to form double silicates of soda and alumina on the surface of the ware; or the articles are " slip glazed " by applying an easily fusible clay as " slip," before firing.

The kilns for potters' use are of several kinds. A common form is the **up-draught kiln**, in which the flame enters at the bottom and passes up between the " bungs," and out at the chimney above. A better type is the **down-draught kiln**, which is sometimes built in two stories. The lower story is filled with the ware to be fired at the highest temperature, and the upper with that to be burned at a less heat. The flame from the grate passes up through flues in the kiln walls, and enters the lower chamber near the top. It then goes down between the bungs, and, through openings in the floor, into other flues in the walls, around the upper chamber, and thence to the chimney. This kiln is economical of fuel, affords very even temperature in the lower chamber, and utilizes the heat which is lost in the up-draught kiln. A special form of **Hoffmann's ring furnace** (p. 185) is also employed for pottery and brick burning. In a new form of kiln, the bungs are arranged on cars, which travel slowly through a long gallery, towards the firing chamber. The waste heat from the hot chamber enters the gallery at the end next the firing room, and, coming in contact with the pottery, heats it to a temperature corresponding to its distance from the inlet flue. The cars move through the furnace into a second long gallery, where the heat from the saggers warms the air which is passing into the furnace, thus utilizing the waste heat. The firing compartment usually contains two loaded cars; and the grate being at one end of the firing room, the pottery in each car gets a preliminary firing before it reaches the hottest part of the kiln. As soon as one car is fired, it is pushed into the cooling gallery, the rear car is moved into the hottest compartment of the kiln, and another is introduced from the preliminary warming gallery. This furnace is economical of fuel, gives an even temperature, and the time of firing being greatly reduced, there is less loss of saggers and pottery.

Porous ware, the second division of ceramics, is manufactured extensively in all countries. The finest grade is " **faience**." This is made from a white clay, which is washed, levigated, and aged, much as for porcelain. The better grades are burned in saggers at a high temperature, and glazed with a transparent lead glaze at a much lower heat. **Majolica** also belongs to this group, being a colored porous body, covered with a non-transparent glaze.

Between faience and common pottery no sharp line can be drawn.

The color ranges through cream, yellow, brown, and red, and the body consists of more or less fusible clay, with a still more fusible lead glaze, which is often colored with metallic oxides. The clays for common pottery are generally "slipped," and strained through fine sieves to remove stones and coarse grains. The articles are fashioned on the potter's wheel and are *air dried.* They are then dipped in a glaze made of litharge and clay, shaken to a cream with water. Or the dry mixture is powdered over the surface from a pepper box. Or they are given a "salt" glaze as before described. They are burned without saggers, and at a temperature only sufficient to fuse the glaze.

Tiles are a special form of pottery, consisting of flat, thin plates, much used for floors, panels, and architectural purposes. They are finer ware than common brick, and more care is taken in the preparation of the body and in the burning. There are three classes, vitrified, encaustic, and glazed.

Vitrified tiles consist of single pieces, made by one burning at a very high temperature, so that the entire body of the tile is semi-fused. They are not glazed, and are a form of stoneware much used for pavements and floors, because of their hardness.

Encaustic tiles are made from two or more clays, generally of different colors. A facing of fine clay may be put on a back of commoner quality. The ornamental design is made by inlaying the face with other clays, which burn to different colors. All the materials must have the same coefficient of expansion, so that no cracks form between the different parts of the design. These tiles are generally used for ornamental purposes, and are often covered with a transparent glaze, necessitating two burnings.

Glazed tiles are made with a body (which may consist of more than one clay) of uniform color, covered with a transparent glaze, colored or not, according to the effect desired.

The dry clay, flint, felspar, Cornish stone,* "grog," and other materials in the mixture for the body of the tile, are put into a revolving drum (**Alsing mill**), along with a number of round flint stones. After five or six hours' grinding, the mixture is complete. The dry powder is then sifted through a fine sieve. There are two methods of forming the tile, the "dust body" and the "wet body" process. In the **dust body method** the sifted clay mixture is *dampened* by spread-

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* Cornish stone is partly weathered felspar, being thus a mixture of kaolin, felspar, quartz, and mica. It is mined in England, and much used as a flux and fusible ingredient in porcelain and tiles.

ing on a wet plaster of Paris floor. It is shovelled over and allowed to remain on the floor until the particles of clay will just stick together when pressed in the hand. It is then filled into a metallic mould which contains the intaglio for relief designs; it is then heavily pressed in a screw or hydraulic press. This compacts the clay, and gives sufficient coherence, so that the green tile may be removed. It is exceedingly brittle, and must be handled very carefully. It is well dried in a room where there is a good circulation of air. To prevent discoloration, tiles are burned in saggers in which they are loosely packed in quartz sand to prevent their twisting and bending, since they become very soft at high temperatures.

In the **wet body process** the slip is moulded in plaster of Paris moulds. After standing half an hour, or more, until the water has all been absorbed by the plaster, the clay cast is removed, dried slowly, and burned as in the case of dust body tiles.

Glazes, both for hollow ware of all sorts and for tiles, are of three kinds, engobe, enamel, and transparent.

The **engobe** is a fusible clay, felspar, or alkali, applied in a very thin coating. It forms a thin glaze, usually opaque, which is intended to support a second thicker glaze or enamel.

Enamels are usually transparent glazes, holding in suspension opaque substances such as oxide of tin. A mixture of litharge and tin oxide (" ashes of tin ") is very often used for enamel.

Transparent glazes are practically lead or lime glass. This is sometimes, though rarely, used as " raw glaze," *i.e.* the materials are ground fine, mixed, and applied to the ware as a cream with water. This is difficult to do, owing to the great density of the litharge, which settles out of the cream, on standing even a short time. To avoid this separation and loss, and to allow the use of substances soluble in water, *e.g.* borax, soda-ash, or boric acid, the glaze is generally " fritted " or semi-fused, before making it into a cream with water. The powdered and thoroughly mixed material, together with coloring substances if desired, is heated in a sagger until it forms a coherent mass, but is not completely fused. The frit is then powdered in a ball mill. Fritted glaze is much more uniform than raw, and there is no tendency to segregation of its components.

In all kinds of glazed ware, it is very essential that the glaze and body shall have the same coefficient of expansion, or cracking of the glaze is liable to occur. This is called " **crazing**," and is caused by the glaze contracting too much in cooling; the scaling off of glaze and attached body from high points of the tile, called "**shivering**," is caused by insufficient contraction of the glaze. To prevent these defects the glaze or the body is so modified that the coefficients of expansion are the same. The exact adjustment of this factor is a matter of experience. The usual methods employed are, — to render the body less plastic by the addition of lean clay, grog, or quartz, thus increasing the silica, which increases the expansion of the body; or to modify the glaze by the addition of silica or boric acid for greater expansion, or of lime, lead, or alkali, to increase the contraction. Boric acid, lead, and alkali make it more fusible, and the temperature of the intended burning must be kept in mind when adding these ingredients. Boric acid and lead also increase the brilliancy of the glaze. The addition of certain coloring matter to glazes also increases the tendency to craze. Alumina is essential in a glaze to prevent devitrification during the burning.

Terra cotta has a soft porous body, and is not glazed. Its color depends on the character of the clay. Generally a highly ferruginous clay is used, which has a deep red color when burned. It is extensively employed for architectural effects and for tiles.

Bricks are probably the most important of the porous ware. They are made from common clay, which usually contains considerable impurity, lime and iron oxide often being present in large quantities. The preparation of the clay is a simpler process than for pottery. After digging it is usually weathered for several months, and then screened, to remove pebbles of quartz or limestone.* It is then "pugged" or "tempered," by mixing thoroughly with water and the ingredients to make the desired "body"; in the case of a fat clay, these are sand, grog, or other clays. This is done in a "pug mill," a tank containing a revolving stirring apparatus, which pushes the mass out at the bottom in proper condition to be used at once. The paste is moulded into bricks, by hand for the finer sort, and by machinery for the common grades. The latter are apt to be uneven and rough. The moulded bricks are dried in the air, usually in the yard, under a light shed. They are turned over frequently during the drying, which must not be too rapid, lest the bricks crack.

The firing is done in kilns which may be built of the air-dried brick, numerous channels being left for the passage of flame and hot gases. This mode of burning results in several grades of brick,

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* *Limestone pebbles* are very injurious, since the burning converts them into lumps of lime within the brick, and when the latter is wet or exposed to weather the lime is hydrated, and, expanding, disintegrates the brick.

owing to the unequal distribution of heat. Or closed kilns, such as the Hoffmann ring furnace (p. 185), may be used. This gives a more even product than the open kiln.

In this country wood and coal are used for fuel, but gas is frequently employed abroad. The temperature in the kiln for common brick seldom goes higher than 1000° C.; but for hard, paving brick it may be raised to 1200° or 1300° C., producing incipient fusing. The heat also affects the color of some bricks; high temperature yields a dark red, gray, or bluish black, according to the amount of ferroso-ferric oxide (Fe_3O_4) formed. Clays containing much lime yield yellow or cream-colored brick, if iron is also present.

Common brick will fuse if exposed to high heat, and are not suitable for lining fireplaces, furnaces, or ovens.

Fire-brick are made from fire-clay, with the addition of a large amount of "grog" or silica. These must resist great heat, and not shrink nor warp. The clay is prepared similarly to that for common brick, but more care is taken in the mixing. The bricks are also heavily pressed to increase the density. The burning is at the highest temperature possible, so that no shrinkage will occur later when the bricks are in use. They are brittle, and must be supported by a backing of common hard brick.

Bricks, the body of which are magnesia, chromite, silica, etc., mixed with just enough plastic clay to make them workable and to cement the grains of the body when burned, are largely employed in chemical furnaces to withstand high temperature corrosion of various types of charge.

REFERENCES

Handbuch der gesammten Thonwaarenindustrie. Bruno Kerl, Braunschweig, 1879.
Traité des Arts ceramiques ou des Poteries. Alexandre Brongniart.
Leçons de ceramique. A. Salvetat.
La Faience. Th. Deck.
Report on the clay deposits of Woodbridge, South Amboy, etc. Public Documents of New Jersey.
A Practical Treatise on the Manufacture of Bricks. C. T. Davis.
Pottery and Porcelain of the United States. E. A. Barber.
Die Steingut-Fabrikation. Gustav Steinbrecht, Leipzig, 1891.
Ziegel-Fabrikation der Gegenwart. Herman Zwick, Leipzig, 1894.
Seger's gesammelte Schriften. H. Hecht und E. Cramer, Berlin, 1896.
The Chemistry of Pottery. Karl Langenbeck, Easton, Penn., 1895.
Clays. Heinrich Ries, New York, 1906. (Wiley & Sons.)
Clay and Pottery Industries. J. W. Mellor, London, 1914.
The Silicates in Chemistry. W. Asch and D. Asch. Trans. by A. B. Searle, New York, 1914.

PIGMENTS

Pigments are mineral or organic bodies, usually insoluble in water, oils, and other neutral solvents, and are used to impart color to a body, either by mechanical adhesion to its surface or by admixture with its substance. In most cases there is no chemical combination between the pigment and the body it colors.

The color of a pigment depends upon the amount and kind of light which it *reflects*. It is essential that the pigment be opaque (possess large capacity to absorb transmitted light) in order that it may have a good "covering power" or "body"; *i.e.* it should entirely conceal the surface to which it is applied. Many pigments are prepared by chemical precipitation, but some of the most important are not.

Pigments form the basis of paint, which consists of a mixture of a pigment with some drying oil, or with water containing gum or size. It is used for decorative and protective purposes; if used for outside work, the pigment should be insoluble in water.

The durability of a paint depends on the chemical stability of the mixture of pigments and vehicle composing the film, and on its mechanical strength, resistance, and impermeability. These properties are best secured by using a mixture of relatively coarse and fine pigments; the first form a skeleton of large particles, giving strength and rigidity, and the latter render the mass impermeable by filling the voids between the coarse particles. Thus while coarse pigments (barytes, silica, chalk, etc.) are almost valueless alone, their addition, in quantities up to 10 per cent, greatly increases the wearing qualities of paints containing fine pigments (white lead, zinc oxide, etc.). Furthermore mixtures of fine pigments, — which differ from each other in size of particle, — are better than the pure pigments alone. This has been established in the case of white pigments; with colored pigments, chemical changes in the pigment, vehicle, or both, frequently complicate the matter.

WHITE PIGMENTS

White lead is the most important of all pigments, and is a very old one, the native carbonate, *cerussite*, having been used by the Romans. But as this mineral is restricted in its distribution the artificial product was in time brought into use. The so-called Dutch process of making white lead is the oldest known, reference being made to it as far back as 1622. With a few modifications, it is still in use, and yields a product which for many purposes is preferred by painters to the lead manufactured by the numerous newer processes. It usually has more covering power and a better color.

White lead is a basic lead carbonate, and analyses of the best samples give as constitutional formula about 2 $PbCO_3$, $Pb(OH)_2$, in which there are two molecules of $PbCO_3$ to one of hydroxide. This appears to be the best ratio. But the white lead of trade varies a good deal, according to the method and conditions of making. In some cases it is nearly pure $PbCO_3$, and in others the proportion of carbonate to hydroxide is as high as three to one, or more. But some hydroxide is necessary in order that the white lead may have a good covering power. Then, too, the hydroxide is supposed to combine with the oil chemically to form a "lead soap," which perhaps dissolves in the excess of oil to form a kind of varnish.

There are three general methods employed in white lead making, besides numerous patent processes. These are: —

The Dutch, or Stack process.

The German, or Chamber process.

The French, or Thenard's process.

The **Dutch process** consists in exposing sheet lead to the direct action of moisture, acetic acid vapors, and carbon dioxide. The corrosion is effected in earthenware pots 8 inches in depth by 5 inches in diameter, glazed inside, and made in the form of crucibles, each containing a shelf. On this shelf is a spiral or "buckle" of thin sheet lead, made by rolling up a sheet of lead 2 feet long by 4 inches wide; or cast buckles of various forms to expose a large surface to the fumes, may be used. In the lower compartment is dilute acetic acid, containing from 3 to 5 per cent $C_2H_4O_2$. A large number of these pots so charged are packed in a shed or brick building, having an opening on one side reaching from the ground nearly to the roof. A layer of ashes is spread over the floor first, and then a layer 4 or 5 feet thick of spent tan bark which is moist and ready to ferment. This is well packed down, and the pots placed side by side upon it until the whole space is filled, excepting about 6 inches next the walls, which is solidly filled in with the tan. More lead buckles or lead gratings are placed across the tops of the pots, so as to form a layer of metallic lead about 4 inches deep. Then about 6 inches above this, and supported by timbers or blocks, is a board floor upon which the next layer of tan, about one foot deep, is placed, and the pots upon it as above described. The doorway is boarded up as the filling continues, and the "stack," as the alternate layers of pots and tan are called, is carried to within a few feet of the top of the shed. For a stack 20 by 12 by 18 feet in size, 40 or 50 tons of lead are required, about 3 tons of lead and 200 gallons of acid being used in each layer of pots. Very soon after packing an active fermentation of the tan sets in, the temperature rising to about 55°–60° C. This heat is sufficient to vaporize the acetic acid and water, and these vapors attack the metallic lead, forming a basic lead acetate. Great quantities of carbon dioxide are liberated during the fermentation, and this decomposes the lead acetate, forming basic lead carbonate, or white lead. The reactions, aside from those of fermentation, may be represented by the following: —

1) $Pb + 2\ C_2H_4O_2 = H_2 + Pb(C_2H_3O_2)_2$. (Normal lead acetate.)

2) $3\ Pb(C_2H_3O_2)_2 + 2\ H_2O = 2\ Pb(C_2H_3O_2)_2, Pb(OH)_2 + 2\ C_2H_4O_2$.

3) $2\ Pb(C_2H_3O_2)_2, Pb(OH)_2 + 2\ CO_2 + 2\ H_2O =$
$2\ PbCO_3, Pb(OH)_2 + 4\ C_2H_4O_2$.

Some authorities consider the reactions to be as follows: —

a) $Pb + H_2O + O = Pb(OH)_2$.

b) $Pb(OH)_2 + 2\ C_2H_4O_2 = Pb(C_2H_3O_2)_2 + 2\ H_2O$.

c) $Pb(C_2H_3O_2)_2 + 2\ Pb(OH)_2 = Pb(C_2H_3O_2)_2, 2\ Pb(OH)_2$. (Basic lead acetate.)

d) $3\ \{Pb(C_2H_3O_2)_2, 2\ Pb(OH)_2\} + 4\ CO_2 =$
$3\ Pb(C_2H_3O_2)_2 + 2\ \{Pb(OH)_2, 2\ PbCO_3\} + 4\ H_2O$.

Thus the acetic acid, or the neutral lead acetate, is regenerated, and attacks more of the metallic lead, and the process repeats itself. But the action is very slow, the time usually allowed for a stack to work being about three months. If horse dung is used instead of the tan bark, as it formerly was, the process is quicker, taking about two months; but the sulphur compounds formed in this fermentation darken the white lead more or less.

Usually the metallic lead is nearly all corroded and converted into white lead, but never completely, and the product is seldom equally good in all parts of the stack. Well-corroded buckles retain their shape, although they become rather more bulky and of a grayish white color, and have a firm, porcelain-like structure. When soft and powdery, the product is not so satisfactory. The "corrosions" are taken to the grinding room and put through rolls, which break them into fine powder; the uncorroded lead is rolled out into plates and scales, which are retained on the sieves when the mass is screened. The white lead passes through, and is reduced to a fine pulp by wet grinding in an edgestone or horizontal mill, and then levigated; salt is often added to the water to accelerate the sedimentation. The coarser particles from the first settling tanks are returned to the mills and reground. In the final settling tanks is left a heavy white mud, which may be dried in steam-jacketed copper pans. Usually the wet mud is mixed with about 9 per cent of raw linseed oil, in mechanical mixers of the helical screw type. The oil combines mechanically with the pigment and the mixture settles, while the water, now almost free from lead, is drawn off from above. The paste of lead in oil contains so little water that it is not further dried as a rule, but is packed directly for shipment. This method avoids the dust produced in handling the dry pigment.

The white lead comes in trade either dry or mixed with about 9 per cent of raw linseed oil. If it is slightly yellow, due to stains from the colored liquids in the tan, or to tarry matters in the acetic acid, or to overheating in the drying, a little indigo or Prussian blue may be added to neutralize this. One ton of the metallic lead yields about 1¼ tons of the white lead; but the process is always somewhat uncertain both as to quantity and quality of the product. Sometimes very little corrosion takes place, and this may vary in different parts of the stack. The process is slow, a large plant is required, and the capital invested lies idle; hence the price of white lead is somewhat higher than the simplicity of the method would at first glance appear to warrant.

To obtain good results by the Dutch method the lead must be very pure. If any silver, copper, or iron is present, the color of the white lead will be damaged. Antimony, arsenic, bismuth, and zinc are said to retard the corrosion very much.

The **German, or chamber, process** is an artificial method of producing about the same conditions as prevail *inside the stack* in the Dutch method. The reactions are the same. Lead plates are hung or arranged on shelves in a closed chamber, provided with a door and window for filling and for watching the process. Dishes of acetic acid are placed on the floor, or acetic acid vapor is introduced from stills outside, the room is heated by steam to about 38° C., and carbon dioxide is introduced. This is much more rapid than the Dutch method, usually requiring about five weeks, but the quality of the product is not so satisfactory. There are difficulties to contend with in the rate of flow of the acid vapors, steam, and carbon dioxide, and in the regulation of the temperature. Too much acetic acid vapor causes loss of lead as neutral acetate; too much carbon dioxide precipitates normal lead carbonate; too little acetic acid or too high a temperature, with excess of water vapor, may form lead oxide, which, being yellow, injures the product. Many modifications of this process have been invented, and some of them are worked more or less successfully. In one form, the chamber is fitted with tracks, on which cars are run, carrying the sheet lead in frames. A car can be run out, and another introduced, without much loss of time or cooling of the chamber. The white lead made by this method is ground and levigated as already described.

Carter's process is much used and produces white lead of good quality. Atomized lead, made by blowing a jet of superheated steam against a fine stream of melted lead, is put, in two-ton charges, into rotary wooden cylinders, 6 feet in diameter by 10 feet long; dilute acetic acid is sprayed in, and carbon dioxide with air admitted through the centre of the head, while the barrel revolves slowly. The constant stirring accelerates the process, and corrosion is complete in about 15 days. The tumbling of the mass also serves to pulverize the white lead. The carbon dioxide is made by combustion of good coke with excess of air. *Coleman's process* is similar but the carbon dioxide is used under pressure.

The **French process, or Thenard's method,** depends on precipitation of a basic lead carbonate from a solution of a basic salt by means of carbon dioxide. The solution generally used is a basic lead acetate, prepared by boiling litharge with neutral acetate. The reactions are: —

1) $2\ PbO + Pb(C_2H_3O_2)_2 + 2\ H_2O = Pb(C_2H_3O_2)_2, 2\ Pb(OH)_2$.

2) $3[Pb(C_2H_3O_2)_2 \cdot 2\ Pb(OH)_2] + 4\ CO_2 =$
$3\ Pb(C_2H_3O_2)_2 + 2[2\ PbCO_3, Pb(OH)_2] + 4\ H_2O$.

The reactions are carried out in the apparatus shown in Fig. 87.* The litharge is mixed with the solution of neutral lead acetate in the tank (A), which is heated by a steam pipe. When saturated, the mixture is run into the settling tank (B), where the undissolved

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* After Hurst, Painter's Colours, Oils and Varnishes.

litharge deposits. The clear solution of basic lead acetate is then run into the precipitating vessel (C), where it is treated with carbon dioxide, introduced through the pipes (D, D). The basic lead carbonate falls as a heavy white precipitate, while a solution of neutral lead acetate remains. After settling, the solution is drawn into the tank (E), from which it is pumped back into (A), where, after adding a small amount of acetic acid, it is used again. The white lead is collected in (F), from which it is taken to be filtered and washed. The carbon dioxide used must be pure and concentrated, and is made by heating calcium carbonate with coke, in a special furnace (G). The gas is passed through water in (H) to remove impurities, and then goes to the precipitating vessel.

The precipitation requires from 10 to 14 hours or more, varying, as does also the quality of the product, with the quantity and strength

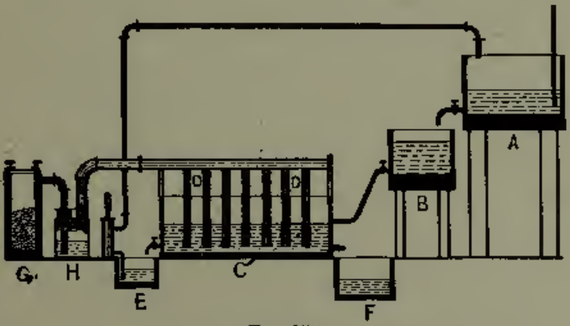

Fig. 87.

of the solution of basic acetate. The white lead separates in a granular or crystalline form, and is washed, ground, and dried, as in the methods already described. It is said to have less covering power than the amorphous powder produced by the Dutch method.

Many chemical processes based upon the precipitation of a basic lead carbonate from solutions of various lead salts, have been proposed, such as **Milner's process**, the **Kremnitz process**, and certain electrolytic processes, but these as yet have not developed industrially.

Methods depending upon the precipitation of basic lead solutions with sodium carbonate have the disadvantage of forming crystalline product.

Many **electrolytic processes** have been proposed: thus in modification of the chamber process, lead is placed on shelves, covered with carbon or tin plates, through which an electric current passes.

More rapid corrosion of the lead thus charged, by the carbon dioxide and acetic acid vapors, with formation of a granular product, is claimed.

It has been proposed to make a precipitated lead hydroxide by electrolysis with lead anodes and inert cathodes, in a bath of sodium nitrate, the hydrate being then treated with a solution of sodium bicarbonate; but this method of corrosion of the lead is expensive and has not proved a success.

A general method for the electrolytic production of insoluble salts the formulæ of which may be written as MA, in which M is the metal and A the anion of the salt, is to employ anodes of the metal M in an electrolyte containing two soluble salts, NA and NB, N being a suitable metal, usually an alkali, and B an anion whose salt with M is soluble. At the anode the salt MB is formed and diffuses out into the solution, where it is precipitated by double decomposition with NA. The precipitate not being formed on the anode itself is non-adherent and hence does not interfere with the electrolysis, as would otherwise be the case. A specific illustration of this method is the **Lückow process.*** The electrolyte, composed of solutions of 80 parts sodium chlorate and 20 parts sodium carbonate, is diluted to such a degree that it contains 1.5 per cent of anhydrous salts, since dilute liquors yield the purest product. The liquid is kept slightly alkaline, and carbon dioxide is passed into it to replace the carbonate precipitated with the white lead. The cathodes of crude lead and the anodes of pure, soft lead, each having an area of 20 to 30 sq. dcm., are placed about 12 to 15 mm. apart, and the current density is 0.5 ampère per sq. dcm. with a voltage about 2. The voltage varies somewhat according to the conductivity of the electrolytes and the distance between the pairs of electrodes.

Owing to the high price of white lead, it is frequently adulterated with barytes ($BaSO_4$), lead sulphate, lead carbonate, or calcium carbonate. Barytes is the most common adulterant, being cheap and heavy. A pure white lead should dissolve in dilute C.P. nitric acid, without leaving a residue. (Common nitric acid will not yield a perfect solution, as it contains sulphuric acid.)

White lead is very heavy, having a specific gravity of 6.47. A cubic foot of the dry powder weighs about 185 pounds. It has great value as a pigment, owing to its covering power, its perma-

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* Mineral Industry, VIII, 392; IX, 438. J. Soc. Chem. Ind., **1895**, 975; **1897**, 743.

nency, and the readiness with which it mixes with other pigments. But it turns dark on contact with hydrogen sulphide, or if mixed with pigments containing sulphur, such as ultramarine, cadmium yellow (CdS), or vermilion (HgS). It is not suitable for painting the interiors of houses where gas or coal is burned. It is nearly insoluble in water, but, if taken into the system, will in time produce very dangerous poisoning; and too much care cannot be taken in the manufacture to prevent the fine dust from flying about. Sponges are worn over the mouth by the workmen, especially in the grinding room. An exhaust fan should be employed to draw the dust away from the workmen.

Owing to the cost and poisonous character of white lead, **substitutes** are used to some extent. These are lead sulphate, sulphite, and oxychloride. Lead sulphate is the base of "**sublimed white lead,**" the chief white lead substitute. By heating galena and coke in a blast of hot air, part of the lead is reduced to the metallic state, and part converted to sulphate and oxide, which, together with some metallic lead, sublime as "lead fume." This is collected in chambers and subjected to a second heating in a blast of hot air, which finishes the conversion to sulphate. The zinc present in the galena also passes off with the fume, and is converted to zinc white by the hot-air blast. The color of the sublimed white lead is sometimes improved by treating with sulphuric acid. It has good covering power and color, and is not readily affected by hydrogen sulphide. It mixes well with other pigments containing sulphur, and is non-poisonous.

Lead sulphite is made by precipitating a basic acetate solution with sulphur dioxide gas, or by subliming mixed lead and zinc ores with carbon, with a limited supply of hot air.

Pattinson's white lead is an oxychloride of lead ($PbCl \cdot OH$), made by precipitating a hot solution of lead chloride with one-half the quantity of milk of lime necessary for its complete decomposition. The pigment has good body and color, but is not now used.

White zinc, or **Chinese white,** is zinc oxide (ZnO). It is made by distilling metallic zinc in fire-clay retorts, and leading the vapors into a flue through which air is drawn. On contact with the air, the hot vapor at once inflames and burns to the oxide, which is collected in a series of settling chambers, or in large bags of cotton cloth, the gas and air escaping through the meshes of the cloth. Instead of the metal, zinc ores mixed with carbon (*e.g.* coke or coal), are heated in special furnaces or retorts, the vapors being burned with air as before. But ores containing cadmium cannot be used, because cadmium oxide also sublimes, and being brown, discolors the product. The oxide is also formed by calcining zinc carbonate or hydroxide. The natural carbonate, Smithsonite, is, however, seldom pure enough, and precipitated carbonate must be used. This is too expensive to compete with the combustion process.

Zinc white is very permanent, and works well in water and in oil, of which latter it requires a large amount, usually about 20 per cent of its weight.

Zinc sulphide is sometimes substituted for zinc white. This has more body than the oxide. If the vapors of zinc and sulphur are brought together, zinc sulphide is formed; it is collected in settling chambers from which the air is excluded. As a rule, pure sulphide is not used, but a mixture of sulphide and barium or strontium sulphate. Zinc sulphide whites are permanent, have good body and color, and mix well with oil and with other pigments, excepting those containing lead or copper.

Lithopone is a mixture of barium sulphate and zinc sulphide. Hot solutions of barium sulphide and zinc sulphate are mixed; the precipitate, after filtering and washing, is dried, ground with a little ammonium chloride, and the mass heated red hot and quenched by pouring into water. After grinding and levigating, a fine white powder is obtained, which works well in oil, has good body, is not readily affected by hydrogen sulphide, and is somewhat cheaper than white lead. It finds much use in paints and varnish enamels, for oilcloths, and as filler in rubber compounding.

The barium sulphide required is made by reducing barytes with coal dust, by calcining in a rotary furnace or in a reverberatory. The charge is then lixiviated, hot, and the solution clarified by filtration.

Barytes, or barium sulphate, occurs native in large quantities. The mineral is finely ground, treated with hydrochloric acid or with sulphuric acid to remove iron, and then levigated. Precipitated barium sulphate (*blanc fixe*) is obtained as a by-product in some chemical industries, and is used to a considerable extent as a filler and pigment. It has more body than barytes.

Barytes is very heavy, is not affected by sulphur nor other chemicals, and may be mixed with all pigments. It has little body, and does not work well in oil, having a streaky appearance when applied, and drying very slowly. Owing to its weight, one of its chief uses is to adulterate white lead.

Gypsum, terra alba, or **mineral white,** is used to some extent as a pigment, especially for wall-paper printing. The mineral is simply ground, and treated with acid to remove the iron. Precipitated calcium sulphate is a by-product of many chemical operations, and is largely used as a filler in paper making, and for weighting cloth, under the names "Crown filler" and "Pearl hardening."

Whiting, or **Paris white,** is calcium carbonate. It is prepared by grinding and levigating pure chalk, which occurs in large deposits in England, France, and other countries. Precipitated calcium carbonate is a by-product from many chemical processes. Whiting is much used to modify the shade of other pigments, and as the bases of whitewash. When mixed with from 15 to 18 per cent of linseed oil, it forms **putty.**

Kaolin, or **China clay** (p. 212), is sometimes used to modify the shade, or to adulterate other pigments. Its chief uses as pigment are in wall-paper printing, and as filler in cloth and paper.

BLUE PIGMENTS

Ultramarine is the most important blue pigment. It occurs in nature as the mineral *lapis lazuli,* but in such small quantities, and the cost of preparation is so great, that this is of no importance as the source of the pigment.

Ultramarine is probably a double silicate of sodium and aluminum, together with a sulphide of sodium. But the composition varies in different samples having the same physical properties. The presence of sulphides seems necessary for the color, since, if treated with acid, hydrogen sulphide is evolved, and the color disappears. Numerous formulæ have been proposed for ultramarine. Soda ultramarine, poor in silica, is $4(Na_2Al_2Si_2O_8) + Na_2S_4$;* that high in silica is $2(Na_2Al_2Si_3O_{10}) + Na_2S_4$.*

Soon after the introduction of the Leblanc soda process, blue spots, resembling natural ultramarine in color, were noticed in soda furnaces lined with siliceous material. This suggested the possibility of artificial ultramarine. In 1828, Guimet in France and Gmelin in Germany succeeded in making it. Guimet kept his method secret, but Gmelin published his. Afterwards, green, violet, and yellow ultramarine were discovered. A white ultramarine is supposed to be the basis of all others, and to it is assigned the formula:

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* Annalen der Chemie, **194**, 1. — R. Hoffmann.

$Na_2Al_2Si_2O_8 + Na_2S$.* Green ultramarine is probably not a distinct chemical compound, but a mixture of ultramarines.

None of the above ultramarines, excepting blue and green, has any commercial importance.

The materials used for making ultramarines are China clay, sodium carbonate or sulphate, carbon, sulphur, and sometimes siliceous matter. The purity of the material is important as affecting the shade of the color; iron is especially liable to make it dull. There are two methods of making it, the sulphate of soda, or indirect method, and the soda-ash, or direct method.

In the **sulphate method**, kaolin, anhydrous sodium sulphate, and charcoal, or pure coal, are powdered and thoroughly mixed. The carbon is necessary to reduce the sulphate to sulphide. Sometimes rosin is used as a reducing substance. The kaolin should contain 2 SiO_2 to 1 Al_2O_3, and be as finely powdered as possible. The mixture is packed in crucibles † having tight-fitting covers, and is heated at a bright red heat for about 8 hours. The furnace is allowed to cool very slowly, care being taken that no air has access to the contents of the crucibles. When cold, the mass is dull green and porous, and when ground and washed constitutes the **ultramarine green** of commerce. It is obtained by this process only.

To make the **blue ultramarine**, the green powder is subjected to a "coloring" process. It is spread in shallow trays in layers about 1 inch deep, and sprinkled with powdered sulphur. On heating, the sulphur ignites, and is allowed to burn itself out with access of air. Sometimes muffles are used, the sulphur being added in small quantities at a time, and the charge stirred with mechanical stirrers during heating. A part of the sodium sulphide is probably changed to the sulphate or other soluble salts, and the crude blue results. It is powdered and washed to remove soluble salts (Na_2SO_4, Na_2SO_3), and sometimes boiled with a sodium sulphide solution to remove any free sulphur, which is injurious to the copper print rolls in calico printing. It is then ground and levigated, the different grades being used for different purposes. The shade is usually modified to match certain standards, by blending several lots of colors.

The **soda-ash, or direct, method** yields blue ultramarine at one

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* Annalen de Chemie, **194**, 1. — R. Hoffman.

† In modern plants, muffle furnaces are replacing the crucibles for making the green ultramarine. But these must be built very carefully to exclude the air; then they need much time for cooling, usually requiring 10 days or more.

heating, which may be done in muffles or in crucibles. The usual charge is about 2½ tons, and consists of soda-ash, kaolin, charcoal, and sulphur, ground fine and packed firmly on the floor of the muffle, forming a layer about 14 inches thick. A layer of tiles, luted together with clay, is placed on top of the charge, and the front of the furnace is bricked up, a loose brick being left so that samples may be taken out to determine the time of heating. The process is very slow, requiring 3 or 4 weeks, of which 10 or 12 days are required for the slow cooling of the muffle; during all this time great care is necessary to exclude the air. The mass forms two layers, one bright blue, and the bottom greenish blue. These are separated, washed, and levigated. By using large crucibles instead of the muffle, the time of heating is reduced somewhat, but the breakage and extra labor more than offset the gain.

To make an ultramarine which is less sensitive to acids, and which will withstand the alum used in paper making, a high percentage of silica in the pigment is necessary. For such a product, it is customary to use the soda process, and to add powdered quartz, sand, or diatomaceous earth to the charge.

The first heating is very important in all processes of making ultramarine blue; about 700° C. is the proper temperature. If overheated, the mass may fuse. Exclusion of air is necessary to prevent oxidation and loss of sulphur, which causes the product to turn dull green, brown, or gray.

Ultramarine blue is much used in wall-paper and calico printing; for neutralizing the yellow color in paper pulp, crystallized sugar, and cotton and linen goods; for laundry blue; for paint; for printers' ink; and for coloring mottled soaps. It is a very fast color to light, soap, and alkalies, but is quickly destroyed by even weak acids.

Ultramarine violet is made by heating the blue, rich in silica, to 175° C., in an atmosphere of chlorine and steam. Some of the sodium is thus converted to salt, and removed by washing. The violet may also be formed by heating the blue to about 200° C., with 2 or 3 per cent ammonium chloride, in the presence of air. It is not much used, as it has little tinctorial power.

Ultramarine red is made by heating the blue to not over 145° C., in an atmosphere of dry hydrochloric acid gas, or in the vapors of nitric acid. It is of but little importance.

Prussian blue, or **Berlin blue**, is the ferrocyanide of iron (ferric-ferrocyanide), $Fe_4[Fe(CN)_6]_3$. To make it, a dilute solution of copperas ($FeSO_4 \cdot 7\ H_2O$), acidified with sulphuric acid, is precipitated with potassium ferrocyanide solution. After decanting the liquor the white precipitate of ferrous-ferrocyanide is oxidized with nitric acid, or with bleaching powder and hydrochloric acid. Exposure to the air also causes oxidation, but the color thus obtained is not so good.

Chinese blue is a very pure and carefully prepared Prussian blue. In order to lighten the shade, and to make the pigment easier to grind, a certain amount of alum is added to the copperas solution before precipitating.

A blue which is soluble in water results if the iron solution is poured into the ferrocyanide solution in a slow stream, or if Prussian blue is boiled in a ferrocyanide solution. In both cases, the ferrocyanide must be in *excess*.

Prussian blue is not affected by acids, and mixes well with oil, but fades a little on exposure to the light. The color is destroyed by alkalies, and consequently it cannot be mixed with any substance having an alkaline reaction. It has great tinctorial power, but is transparent, and lacks body. It is dissolved by oxalic acid, yielding a blue solution, formerly much used for blue ink.

Turnbull's blue, a deep reddish blue precipitate, is obtained by precipitating a ferrous salt with potassium ferricyanide [$K_3Fe(CN)_6$], instead of the ferrocyanide. This is similar to Prussian blue.

Smalt is a potash-cobalt glass, made by fusing pure sand and potash with cobalt oxide (Co_2O_3), in a furnace similar to a glass furnace. The crude cobalt oxide, called "zaffre," is made by carefully roasting smaltite ($CoAs_2$), cobaltite ($CoAsS$), or cobalt-nickel pyrites [$(CoNi)_2S_3$]. The ore is carefully sorted by hand, and iron pyrites and other impurities removed; then it is ground and sometimes levigated, and roasted in a reverberatory furnace. A large part of the arsenic and sulphur passes off as oxides. The arsenic trioxide (As_2O_3) is condensed in long flues or chambers, while the sulphur dioxide escapes to the chimney. A small amount of the sulphur and arsenic is left in the zaffre to combine, during the fusion, with the iron, copper, nickel, and other injurious metals, forming a speiss, which, being heavier than the glass, settles to the bottom of the pot. The blue glass is refined (p. 203) until all the impurities have settled, and is then ladled out into water. This granulates it, and the sand so formed is ground under edge-runners and levigated. The medium-fine deposit is the best grade, the finest being too light-colored. The coarse and the very fine are usually remelted.

Smalt is a very permanent color, fast to light, and not affected by acids nor alkalies. But it does not work well as a paint either in oil or in water, and is expensive; hence it is now largely replaced by ultramarine. The composition of commercial smalt varies much; it may contain from 2 to 16 per cent of cobaltous oxide (CoO), but it is often difficult to get a good test for the cobalt.

Imitation smalt is sometimes made of sand, colored with ultramarine. A simple test with acid detects this at once. Prussian blue is shown by treating with alkali.

Cobalt blue is made as follows: alumina is heated to a red heat in a crucible with basic cobalt phosphate, made by adding sodium phosphate to a cobalt nitrate solution. Alum and sodium carbonate solutions are mixed, and aluminum hydroxide precipitated. These two products are thoroughly washed, and one part cobalt phosphate is mixed with 8 parts aluminum hydroxide, and the mixture heated to a red heat until the blue color develops. The pigment is then ground wet, washed, and dried. This yields a good oil color.

Copper blues are not important. **Mountain blue** is the ground mineral azurite, a hydrated copper carbonate [$2\ CuCO_3, Cu(OH)_2$].

Bremen blue is a copper hydroxide containing some copper carbonate and oxychloride. A mixture of common salt, copper sulphate, and metallic copper in small pieces is kept in tubs for several weeks, being well stirred frequently. A paste of green oxychloride is formed, which is washed free from all soluble salts. A small quantity of hydrochloric acid is then added, and left for several hours. Finally, a solution of caustic soda is added, and thoroughly mixed until the paste acquires a blue color. After washing well and drying, it is ready for use.

The copper blues are altered somewhat by exposure to the weather. They are readily darkened by hydrogen sulphide or sulphur fumes, so cannot be mixed with pigments containing sulphur. They dissolve in acids and in ammonia, and become black when heated, owing to the formation of cupric oxide (CuO). They are opaque in water, but become slightly transparent in oil and lose body. They are at best a greenish blue.

Indigo is an organic substance (p. 521) somewhat used as a pigment in laundry blue and soap.

GREEN PIGMENTS

Ultramarine green is not largely used as a pigment. Its preparation is described on p. 232.

True **Brunswick green** is the oxychloride of copper, made by allowing metallic copper to stand for a number of weeks in a solution of common salt which contains sulphates. The insoluble pigment is washed through a sieve to remove copper chips, and then dried at a low temperature to prevent decomposition. It is a good pigment, working well with oil, and having a fair coloring power; but the color is rather pale.

The pigment now sold under the name of Brunswick green is generally a mixture of Prussian blue, chrome yellow, and barytes, the proportion of each depending on the shade desired. These greens are prepared by the dry or the wet methods. In the former, the dry ingredients are mixed in a paint- or edgerunner-mill. But the shade is inferior to that produced by the wet method. In this, copperas ($FeSO_4 \cdot 7\ H_2O$), lead acetate, barytes, and potassium ferrocyanide and bichromate are used. The iron and lead salts are dissolved separately, and mixed while stirring in the barytes; some lead sulphate is thus precipitated also. Then, while still stirring actively, the mixture of potassium ferrocyanide and bichromate solution is added. After a few moments' further stirring, the pigment is allowed to settle, and the liquor is decanted. Then the precipitate is washed by decantation, filtered, and dried carefully. Or the dry ingredients are finely powdered, and then stirred up thoroughly with water in a tank until, on settling, the liquor is nearly colorless. The precipitate is washed as above described.

These greens are sometimes sold under the names Victoria, Prussian, or chrome green. They work very well in oil, have good covering power, and are fairly permanent; but they cannot be mixed with pigments containing sulphur or alkaline substances, nor used where exposed to hydrogen sulphide gas. Alkalies act both upon the Prussian blue and the chrome yellow, causing them to turn red or brown. Sulphur darkens the chrome yellow.

Chrome greens are valuable pigments, having a light yellowish green color. The basis is chromic oxide (Cr_2O_3). By precipitating a solution of a chromic salt with soda, chromium hydroxide [$Cr(OH)_3$] is obtained. This is washed, dried, and calcined at a red heat, until the water is expelled, and chromic oxide results.

Guignet's green * is a chrome green made in the dry way. A mixture of 3 parts potassium bichromate with 8 parts boric acid is heated to dull redness in a reverberatory furnace for four hours. The porous mass is then washed, ground, and dried. In composition, this green is a hydrated chromic oxide, containing a very small quantity of boric acid. A chromium borate is formed by the calcination, which is decomposed by the water, forming hydrated chromic oxide ($Cr_2O_3 \cdot 2\,H_2O$), or $Cr_2O(OH)_4$, and regenerating boric acid.

Guignet's green is permanent, mixes well with oil and with all other colors, and has good covering power. It is one of the most valuable pigments.

Chrome greens, consisting of chromium phosphate, are sometimes made by boiling potassium bichromate with sodium phosphate and a reducing agent. These are not so good as the oxides, and have paler shades.

Copper greens containing only copper salts are of little importance. Only two need be considered here.

Mountain green, malachite, or **mineral green**, is a basic copper carbonate [$CuCO_3$, $Cu(OH)_2$], occurring as the mineral malachite, which is much used for ornamental bric-a-brac and lapidary work. When ground very fine, it is sometimes used as a pigment, and is permanent in the light, mixes well with oil, and has fair covering power. It is blackened by hydrogen sulphide. An inferior imitation of the natural product is made by precipitating copper sulphate solution with sodium or potassium carbonate containing a little white arsenic (As_2O_3).

Verdigris is not of constant composition, but is a basic copper acetate, corresponding nearly to the formula [$2\,Cu(C_2H_3O_2)_2 + CuO$]. It is sometimes made by covering copper plates in heaps of the residue from wine presses. Fermentation of the mass produces acetic acid, which, together with the moisture, forms a layer of verdigris on the copper. This is scraped off, washed, and levigated. A better product is obtained by wetting cloths in vinegar or in pyroligneous acid, and spreading them between the copper plates. Verdigris is not a good pigment, being altered by moisture and light.

By dissolving copper oxide, or carbonate, in acetic acid, and evaporating the solution, a crystallized salt having the composition

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* Bulletin de la Société de Paris, **1**, 9. Guignet, — Fabrication des Couleurs, 149–153.

$Cu(C_2H_3O_2)_2$, $Cu(OH)_2 \cdot H_2O$ is obtained, which is called "distilled verdigris" in trade. This, however, is not a pigment.

Copper and arsenic greens surpass all others in brilliancy and beauty, but, being exceedingly poisonous, cannot be used for many purposes. **Scheele's green**, which is chiefly copper arsenite ($HCuAsO_3$), is made by dissolving arsenious acid in a hot solution of potassium carbonate, and pouring the liquid into a solution of copper sulphate. The precipitate is carefully washed and dried. It is a grass-green pigment, having little coloring power, and now seldom used.

Paris, or **emerald, green** is an aceto-arsenite of copper,

$$[Cu(C_2H_3O_2)_2 \cdot Cu_3As_2O_6],$$

prepared by adding a thin paste of verdigris in water to a boiling solution of arsenious acid in water; some acetic acid is then added, and the mixture boiled until the precipitate is of the desired shade; or the color will develop by simply allowing the mixture to stand for some days. By Galloway's process, sufficient sodium carbonate is added to a copper sulphate solution to precipitate one-fourth of the copper. Then acetic acid is added until the precipitate is just redissolved, and the liquid is heated to boiling. A hot solution of sodium arsenite (arsenious acid dissolved in sodium carbonate) is then added, and the mixture well stirred. The green precipitate is filtered, washed, and dried at a low temperature. For the finest pigment, the solutions should be dilute.

Paris green has a peculiar light green shade possessed by no other pigment. It is permanent, works well in oil, and has a good covering power. But owing to its poisonous character its use as a pigment is much restricted. Nearly the whole of the present production is used to exterminate potato beetles and other insects injurious to vegetation.

Terra verde is an earthy pigment, containing ferrous silicate as its chief ingredient. Green earths are found in numerous places, but the best are from Cyprus and Italy. They are a dull pale green, and are permanent, but have little covering power.

YELLOW PIGMENTS

The most important yellow pigments are chrome yellows and yellow ochres; others are used but little.

Chrome yellows have as a basis the chromate of lead, zinc, or barium, are all made by precipitation and each has a shade peculiar to itself. **Lead chromate** is made from the lead acetate, or nitrate, and potassium bichromate. The reactions are as follows: —

a) $2\,Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2\,KC_2H_3O_2 + 2\,C_2H_4O_2 + 2\,PbCrO_4$.

b) $2\,Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2\,KNO_3 + 2\,HNO_3 + 2\,PbCrO_4$.

In order to modify the shade, lead, barium, or calcium sulphate is mixed with the chromate in the grinding-mill. Or a portion of the lead is precipitated as sulphate or carbonate along with the chromate; this is done by mixing sodium carbonate or sulphate with the potassium bichromate. Chrome yellows are called "pure" when lead sulphate has been used to modify the shade.

The precipitate is well washed by decantation, and the pulp freed from water in the filter press, or in a centrifugal machine, or by pressing in cloth bags. It should be dried at a low temperature, and well ground either dry or in oil. For the best color, the lead nitrate should be used in slight excess. When lead nitrate is used in making the chromate, it is customary to recover the potassium nitrate from the liquor and first wash-waters, the free nitric acid being neutralized with pearlash before evaporating. The excess of lead salt is precipitated from the waste liquors on the addition of the pearlash.

Chrome yellow is sometimes made by digesting lead sulphate with a hot solution of potassium bichromate until the desired shade is developed.

Lead chromate is a brilliant yellow, mixes well with oil, and has great covering power. It is blackened by hydrogen sulphide, and should not be mixed with pigments which contain sulphur, or are strongly alkaline. When treated with a caustic alkali, lead chromate is converted into a basic salt, having a red or orange color. These basic chromates are prepared for pigments, and sold under the name of *chrome orange* and *chrome red.* They are made by boiling chrome yellow with calcium or sodium hydroxide. The following is the reaction involved: —

$$2\,PbCrO_4 + 2\,NaOH = Na_2CrO_4 + PbCrO_4 \cdot PbO \cdot H_2O.$$

Quicklime gives a paler color than caustic soda. Chrome red is also made by digesting white lead with potassium bichromate and caustic soda.

Zinc chromate is made from zinc sulphate and neutral potassium chromate. The neutral salt $ZnCrO_4$ forms only in concentrated solutions of the precipitant, and hydrolyzes instantly on contact with water to basic chromates, which precipitate, and to free chromic acid in solution. The composition of the precipitate varies and is determined by the concentration of the acid solution with which it is in contact. Indefinite washing with water will remove all of the chromic acid, but after the basicity has reached approximately $4\ ZnO \cdot CrO_3$, the loss of acid is slow, owing to the insolubility of the precipitate. Zinc chromate is also made by boiling zinc oxide with potassium bichromate. The pigment has a light lemon color, is permanent, not affected by sulphur, and can be mixed with other pigments. It is soluble in mineral acids, and is decomposed by caustic alkalies.

Barium chromate is much like the zinc salt, but is a greenish yellow color. It is made in the same way as is the zinc chromate, but from barium chloride. It is not used to any extent.

Yellow ochres and **Siennas** are natural mineral products, varying from bright yellow to brown. The color is due to hydrated oxide of iron, and in Sienna there is a little manganese oxide. The pigments contain sand and clay in large quantities, and are decomposition products from iron-bearing minerals. The Siennas are usually finer grained and contain less gangue mineral than the ochres. They occur in beds in the earth, and the only preparation necessary is grinding and levigating. They are very permanent, mix well with oil and with other pigments, have good covering power, and are cheap. If ochres and Siennas are calcined, the water of hydration is removed from the ferric hydroxide, and the color becomes orange or red. Burnt Sienna, made by heating raw Sienna to a low red heat, is reddish orange in color.

Cadmium yellow is cadmium sulphide (CdS), and is made by precipitating a cadmium solution with hydrogen sulphide. If the solution is strongly acid, the color becomes more nearly orange.

It is a brilliant yellow, very permanent, and mixing well with oil and with other pigments, excepting lead and copper compounds. It is chiefly used as an artist's color. Sometimes cadmium yellow is made by using ammonium sulphides instead of hydrogen sulphide to precipitate the pigment; but in this case free sulphur is present in the precipitate, and causes changes in the color when mixed for use.

Orpiment is arsenic trisulphide (As_2S_3). It is found native as a mineral, which is simply ground for pigment. It is also extensively made by precipitating a dilute solution of arsenious acid in hydrochloric acid with hydrogen sulphide; or by subliming a mixture of arsenious acid and sulphur from a retort. The pigment obtained by either method is finely ground.

Orpiment is a very bright yellow, mixes well with oil, and has good covering power; but it is not permanent on exposure to light, and cannot be mixed with many other colors. It is also very poisonous. It is sold under the name of **royal yellow**, or **king's yellow**.

Litharge is lead monoxide (PbO), made by oxidizing metallic lead at a high temperature, in rotating cast-iron drums, heated by an external fire. The drums have shelves or ribs inside, which pick up the melted lead and cause it to fall in thin films through the current of air drawn in by a fan. It is not so important as a pigment as for the preparation of "boiled linseed oil" (p. 357). It is also extensively used in making lead glass and in pottery glazes.

Another variety of lead monoxide, having a lighter yellow shade, is "**massicot**," which is formed by oxidizing lead at so low a temperature that no fusion of the product takes place. It is chiefly prepared for the manufacture of red lead (p. 242).

Yellow lead oxide is also made by heating white lead.

Gamboge is a gum-resin obtained from a tree (*Garcinia Morella* Desr.) of Siam. Incisions are made in the bark of the tree, and the sap is collected in bamboo receivers, in which the yellow resin is left on evaporation. Gamboge emulsifies with water, and is used as a water-color paint. It cannot be used as an oil paint except when mixed with alumina.

Indian yellow, or **purree**, is made by heating the urine of cattle that have been fed with leaves of the mango tree, the color being produced by an excessive secretion of bile, which has passed into the urine. The pigment precipitates, and is pressed and dried; it consists of salts of *euxanthic acid*, an organic body. It is a bright yellow, but not permanent in the light, and is very expensive.

ORANGE PIGMENTS

Orange mineral is lead tetroxide (Pb_3O_4), prepared by heating white lead in the presence of air. It is usually made from the scum which collects on the surface of wash-waters used in levigating white lead.

$$2\ PbCO_3, Pb(OH)_2 + O = Pb_3O_4 + 2\ CO_2 + H_2O.$$

In composition and properties it is similar to red lead (below), but has a slightly lower specific gravity (6.95).

Chrome orange has been described in connection with chrome yellow (p. 239).

Antimony orange is antimony trisulphide, made by precipitating a moderately concentrated solution of antimony chloride with hydrogen sulphide. The precipitate is washed in dilute hydrochloric acid, and then levigated. It must be dried at a low temperature.

It has a bright orange color in oil or water, is permanent and of good body, but is decomposed by alkalies. It is chiefly used for vulcanizing rubber, producing the red " antimony rubber " of commerce.

RED PIGMENTS

Red pigments form a numerous and important group, containing some of the brightest and most permanent colors.

Red lead is lead tetroxide (Pb_3O_4), having the same chemical composition as orange mineral (p. 241), but differing in its physical properties. It is made by the direct oxidation of metallic lead. The process is carried on in two stages. In the first or " drossing " operation the lead is converted into massicot by heating with free access of air in a reverberatory furnace to a temperature just above that of melted lead (340° C.). The temperature must be very carefully regulated, for if the massicot melts it passes into ordinary litharge, from which red lead cannot be made. As fast as a layer of oxide forms it is pushed to the back of the hearth with a " rabble "; finally, the unoxidized lead is allowed to run off, and the massicot is raked out and cooled. It is pale yellow, of granular texture, and contains pellets of unoxidized lead. It is finally ground and levigated, and then transferred to the second or " coloring process "; it is heated to a dull red heat in a muffle or reverberatory furnace with access of air. The mass is stirred frequently to assist the absorption of oxygen, and to develop the color. Samples are taken at intervals, until the desired shade is obtained, which usually takes from 40 to 48 hours; then the furnace is allowed to cool. The product is usually ground before packing for market.

Red lead is somewhat variable in color, but is a good pigment of great covering power and brilliancy. It has a specific gravity of 8.5. Chemically, it is regarded as a mixture of lead monoxide and peroxide ($2\ PbO + PbO_2$), but commercial samples vary some from this formula. When treated with dilute nitric acid, the monoxide dissolves, leaving the peroxide as a brown powder; this constitutes a test for red lead, since no other red pigment turns brown with nitric acid.

A large use of red lead is for glass making, for which a very pure grade is necessary. Owing to its oxidizing effect with linseed oil, it is extensively used, mixed with this oil, as a lute in plumbing and gas fitting. It is much used as a protective paint for iron and steel.

Chrome red is a basic lead chromate ($PbCrO_4$, $PbO \cdot H_2O$), made by boiling chrome yellow with caustic soda or with lime, as described on p. 239. It is also made by boiling white lead with a solution of neutral potassium chromate. When the desired shade is developed, the pigment is washed, ground, and levigated.

It is a fairly bright red, of good body, working well in oil. Like all lead pigments, it is darkened by sulphur and hydrogen sulphide. It is sold as **Chinese red, American vermilion,** and **Victoria red.**

An imitation of chrome red is made by coloring white lead, orange lead, or barytes with some of the coal-tar dyes, especially with eosins.

Red ochre is made by calcining ordinary ochre at a low red heat until more or less of the water of hydration is driven off. The shade depends on the time of heating, — the longer the calcination the more purple the product. Red ochres are essentially ferric oxide with alumina, silica, and lime. The native oxides, *hematite* and *limonite,* are seldom used for pigment, being hard to grind. But in a few places soft deposits of hematite are found, which yield a pale red pigment without further treatment than grinding. These ochres are sold as **Indian red, light red, Venetian red,** etc.

Iron reds are now being prepared in large quantities, chiefly as by-products from other manufactures. These are sold as **rouge, colcothar, Venetian red,** etc., and all contain ferric oxide as the coloring matter.

When fuming sulphuric acid is made by the dry distillation of copperas (p. 82), a residue of ferric oxide remains in the retort. This is ground, levigated, and sold as colcothar. It is nearly pure Fe_2O_3.

In the manufacture of galvanized iron or tinned ware, the rolled sheet iron is dipped into a bath of acid to dissolve any oxide from its surface before putting it into the bath of melted zinc or tin. These acid "dipping liquors" contain much iron, which is precipitated by adding soda-ash or lime, and used as pigment. If sulphuric acid is used in the dipping liquors, and is neutralized with lime, the precipitate consists of ferric hydroxide, with more or less calcium sulphate. By calcining, a light red pigment, called Venetian red, is formed.

Many metallurgical operations yield liquors containing much iron, which is precipitated with lime, forming Venetian red.

These iron reds are very permanent and valuable pigments. They work well in oil, mix with all other pigments, have very good body, and are cheap, but the color is not so bright as in some pigments. The covering power is, however, largely dependent upon the methods of precipitation and ignition, which are carefully guarded trade secrets. The density of samples of practically identical composition may vary three- or four-fold.

Vermilion is mercuric sulphide (HgS). It occurs in nature as the mineral *cinnabar*, but the pigment is now all made artificially. It is one of the brightest reds, and has been known for a long time. It is made in two ways, by the wet and by the dry process. In the **wet process**, 100 parts of mercury are ground with 38 parts of flowers of sulphur until thoroughly incorporated; then the mass is digested at about 45° C., with a solution of 25 parts caustic potash in 150 parts water. The mixture is stirred frequently, and any water lost by evaporation is replaced. After 2 or 3 hours the mass becomes brown, and then gradually turns red. When the desired color is acquired, which usually takes about 8 hours, the pigment is at once washed by decantation, since further action of the potash dulls the color. The pigment is ground and dried carefully. The temperature must be kept between 40 and 45° C., for if overheated it becomes brown. Solution of potassium or sodium polysulphide may be used instead of the potash. The brilliancy of the color may be increased by treating with hydrochloric or nitric acid.

The **dry methods** yield the best product. The **Dutch process** consists in heating mercury and sulphur together in shallow iron pans until they combine to form a black mercuric sulphide (HgS, *ethiops mineral*). This is pulverized, and introduced into earthenware retorts in small amounts at a time. The larger part of the black sulphide sublimes into the upper part of the retort as a bright red powder. This is ground, washed, treated with acid, and levigated.

Chinese vermilion is the finest quality, and its manufacture was long kept a secret. Now it is known to be made by a process similar to the Dutch method, but owing to the patience and care exercised by the Chinamen a very fine product is obtained.

Vermilion is a very heavy, opaque, and brilliant pigment. Owing to its weight, it settles out of the oil when used for paint, causing difficulty in applying it evenly. It is permanent, and not readily affected by acids and alkalies. When heated in a closed tube, it turns black, and finally sublimes unchanged, thus furnishing a good test for its purity. It is sometimes adulterated with red lead, iron reds, or carmine lakes, but these leave a brown or black residue when heated. Vermilion is very expensive.

Vermilionettes are brilliant red pigments, produced by coloring neutral white bodies, such as barium sulphate, lead sulphate, or white lead with coal-tar dyes of the eosin class. The white base is stirred up with a solution of the dye, and lead acetate or alum is added, which precipitates the color upon the white base. Orange mineral is sometimes mixed with vermilionettes to brighten the color. These work well in oil, have good body, and are brilliant, but fade on exposure to the light.

Realgar, the disulphide of arsenic (As_2S_2), occurs in nature in small quantities as a brilliant red mineral which, when ground, furnishes a fine pigment. But the chief supply is obtained artificially by fusing together white arsenic (As_2O_3) and sulphur in the proper proportions, or by distilling arsenical ores with sulphur. The crude product is remelted, and arsenic or sulphur added, as need be, to give the desired shade. As a pigment, realgar is subject to the same disadvantages as orpiment (p. 241). It is much used, however, in preparing "Bengal lights," and for unhairing hides for tanning.

Antimony red, or **antimony vermilion**, is an oxysulphide of antimony, made by precipitating an antimony chloride solution with thiosulphate of soda. On heating the solution to 55° C., a red precipitate separates. This is washed and dried at about 50° C. It is also prepared by dissolving tartar emetic in tartaric acid solution, mixing with sodium thiosulphate, and heating to 90° C.

Antimony red is used for oil and water colors, and to some extent in calico printing. It has good body, and is permanent if not mixed with alkalies or with alkaline vehicles.

Carmine pigment belongs to the class of pigments, called "**lakes**," which are metallic salts of organic color acids. The coloring matter in carmine is the organic substance carminic acid ($C_{17}H_{18}O_{10}$), obtained from the bodies of the cochineal insect. The lake is prepared by extracting the crushed insects with hot water, filtering, and adding a solution of alum or tin chloride, and cream of tartar. After standing, the pigment precipitates. Or the lake may be precipitated at once by adding sodium carbonate to the mixed solutions. The extraction is done in tinned copper vessels, and hard water is said to improve the color of the pigment.

Carmine is a very bright scarlet, the tin salt being brighter than the aluminum. It works well in oil and as a water color, but fades on exposure to sunlight. It is soluble in strong caustic alkalies.

Cochineal lake, crimson lake, Florentine lake, and others, are carmine lakes containing a larger proportion of alumina or metallic base than does carmine.

Madder lakes and **Brazil-wood lakes** are prepared by precipitating extracts of these substances with alum and tin, by adding sodium carbonate. They furnish red pigments of various shades, but lacking in covering power.

Yellow lakes are made from fustic, Persian berries, or quercitron bark extracts, in the same way as the madder lakes are made.

Many of the coal-tar dyes may be precipitated as lakes, and a great number of pigments are thus prepared. But many of them are deficient in covering power, and lack permanency on exposure to the light.

BROWN PIGMENTS

Umbers are ochres containing more manganese than Sienna contains. They are complex mixtures of silica, alumina, iron, manganese, lime, and other matter. There are two varieties, raw and burnt. Raw umber has received no further treatment than grinding and levigating. Burnt umber has been calcined at a low, red heat, whereby more or less of the water of hydration of the iron oxide has been driven out, giving a darker shade to the product. The best umber comes from Cyprus, but many other localities furnish it in various shades. It is very permanent, has good covering power, and mixes well with all other pigments. It is not affected by acids nor alkalies, and is cheap.

Vandyke browns are indefinite mixtures of iron oxides and organic matter. They are obtained from certain bog-earth or peat deposits, or from ochres containing bituminous matter. They are also made artificially from charred organic substances, such as bark, cork cuttings, or bone dust. Mixtures of lampblack, yellow ochre, and iron oxide are also sold as Vandyke browns. These pigments are permanent, mix well with all other colors, and have good body.

Sepia is an organic pigment obtained from the cuttle-fish (*Sepia officinalis*), that secretes it as a dark liquid, to be discharged in the water to hide his movements when disturbed. It is contained in a small sac, which is removed and dried. To purify the pigment, it is dissolved in caustic soda, and the decanted solution is acidified with hydrochloric acid. The pigment thus precipitated is washed and dried.

Sepia is a dark brown, fine-grained pigment, very permanent and capable of mixing with all other colors. It is chiefly used as a water color by artists.

BLACK PIGMENTS

Black pigments nearly all contain carbon as the base. The most important is **lampblack**, which is the soot produced by the incomplete combustion of organic substances, mostly of an oily or resinous nature. The knots and refuse from pitch pine and hemlock, the crude mineral oils, residues from petroleum refining, and the "dead oils" from coal-tar furnish much lampblack. The temperature of burning is low and the air supply limited, so that a large part of the carbon remains unconsumed and is deposited as soot in a series of chambers, through which the combustion products are led. Some oil may *distil* into the chambers, mixing with the product, increasing its liability to spontaneous combustion in storage, and lowering its value for paint, as it dries very slowly.

Carbon black is made by burning natural gas * so that the flame impinges upon a rotating, horizontal iron plate. The sudden lowering of the temperature of the flame causes a deposit of carbon, which is removed from the plate as it rotates, by a fixed scraper. An automatic conveyer carries the pigment to the grinding and sifting apparatus. The product is free from oily matter and mixes readily in water, but with difficulty in oil. It is much used for printing-ink, paint, rubber mixing, coloring cement mortar, etc.

Carbon from different sources varies widely in both covering power and color. When obtained from hydrocarbons, the higher the molecular complexity of the substance burned, the less the density of the product, and the browner the shade, although many brown products grind black in oil. Ivory black is the densest and blackest pigment, though high-grade bone-black develops great brilliancy in a paint.

Ivory-black is made by heating the refuse from ivory working in closed retorts until all organic constituents are decomposed. The

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* Mining and Engineering World, **1911**, Oct. 28. J. Soc. Chem. Ind., **1894**, 128.

retorts must not be opened until quite cold. The charred mass is ground fine, and yields the finest quality of black pigment with respect to deadness of the black when ground in oil. It is an intense black, but since it acts like bone-char on organic coloring matter, it cannot be mixed with most pigments of an organic nature.

Bone-black is an inferior black, made from bones charred in a retort. When coarsely pulverized, it is extensively used for decolorizing syrups and oils. It is finely powdered for pigment, and is much used in making leather blacking, where the calcium phosphate and carbonate in it are also of importance.

Charcoal from soft wood, ground very fine, is sometimes used as a pigment, and to mix with other blacks. It is not so soft and fine as lampblack.

Graphite is employed as a pigment in pencils, crayons, and in stove-blacking. It also forms the basis of a protective paint for metal. It is a dull black, very inert and permanent.

Manganese ores, such as pyrolusite (MnO_2) and hausmannite (Mn_3O_4), are sometimes powdered for pigments. But they act as "dryers" when used with oil, and are rarely used in paint.

Black lake, made from logwood decoction and potassium bichromate with copper sulphate, is a blue black, but not permanent.

Tannate of iron blacks, derived from tannin liquors, copperas, and alum, also fade on exposure to the light.

REFERENCES

Lehrbuch der Farbenfabrikation. I. G. Gentele, Braunschweig, 1880.
Das Ultramarine. C. Fürstenau, Wien, 1880. (Hartleben.)
Die Erd- Mineral- und Lackfarben. Dr. Mierzinski, Weimar, 1881.
Chemistry of Pigments. J. M. Thomson. Lecture before the Society for the Encouragement of Arts, Manufactures, and Commerce. London, 1885.
Fabrication des Couleurs. Ch. Er. Guignet, Paris, 1888.
Oel und Buchdruckfarben. Louis E. Andes, Leipzig, 1889. (Hartleben.)
Die Fabrikation des Ruses und der Schwaerze. H. Koehler, Braunschweig, 1889.
The Chemistry of Paints and Painting. A. H. Church, London, 1890.
Painters' Colours, Oils, and Varnishes. G. H. Hurst, London, 1892.
Pigments, Paints, and Painting. George Terry, London, 1893. (Spon.)
Die Fabrikation der Mineral- und Lackfarben. J. Bersch, Leipzig, 1893.
Die Fabrikation der Erdfarben. Dr. Josef Bersch, Leipzig, 1893.
Handbuch der Farben-Fabrikation. Dr. S. Mierzinski, Leipzig, 1898.
Chemistry and Technology of Mixed Paints. M. Toch, New York.
Modern Pigments and their Vehicles. Frederick Maire, New York, 1908.
An Introduction to the Chemistry of Paints. J. N. Friend, London, 1910.
Paint Technology and Tests. H. A. Gardner, New York, 1912.
Journal of American Chemical Society, **1880**, 381. — H. Endemann.
Journal of the Society of Chemical Industry: —
1887, 719. Rawlins. **1890**, 1137. Wunder. **1891**, 709. **1892**, 357. Weber.
Jour. Ind. Eng. Chem., **1914**, 54.

BROMINE

Bromine is widely distributed in nature as bromides, usually accompanying common salt and magnesium chloride. The world's supply is obtained from "bittern," the mother-liquor of the salt industry. Stassfurt furnishes about two-thirds of the supply, and the remainder is extracted from the brines found in Michigan, Ohio, and West Virginia, along the Kanawha and Ohio rivers. The American product in 1913 was about 572,400 pounds. Small quantities are obtained from the mother-liquors of the Chili saltpetre industry, and in Europe from kelp.

Bromine is present in the mother-liquors as magnesium bromide, and to a small extent as sodium bromide; the liquors also contain large quantities of sodium and magnesium chlorides. Several methods of extraction are in use, — the continuous and periodic processes being old, while recently direct electrolysis of the waste brine has been introduced. The bromine is liberated by the current before the chlorine is set free.

The **continuous process** depends on the decomposition of the magnesium bromide by chlorine gas. A sandstone or earthenware tower is filled with broken brick or burned clay balls; chlorine gas and steam are introduced at the bottom of the tower, and rising between the balls, meet descending streams of hot bittern. By reaction between the chlorine and the magnesium bromide, the bromine is set free. The chlorine stream must be regular, and so controlled that no excess is used; otherwise some bromine chloride is formed. Part of the bromine dissolves in the liquor as soon as set free, and this liquor flows into a special receiver, heated by steam; here it is boiled to drive out the bromine, which, together with water vapor, passes back into the tower, entering at the bottom, and mixing with the chlorine. At the top of the tower, the bromine vapor passes out into an earthenware worm-condenser, which empties into a closed vessel. An outlet pipe from the top of this receiver passes into a small tower, filled with moist iron turnings or scrap iron. Any uncondensed vapors of bromine, passing out of the receiver, combine with the iron to form ferrous bromide, which is used for making potassium bromide.

In this process, any bromine chloride formed in the tower is decomposed, before it can pass into the condensing worm, by the fresh bittern entering at the top of the tower. Bromine chloride is a volatile liquid, and would contaminate the bromine. The exhausted bittern from the heating-vessel goes to waste. The chlorine gas necessary is made in special stills from manganese binoxide and hydrochloric acid.

The **periodic process** depends on the following reaction: —

$$MgBr_2 + 2\,H_2SO_4 + MnO_2 = MgSO_4 + MnSO_4 + 2\,H_2O + 2\,Br.$$

This is carried on in sandstone stills, heated by steam. A charge of pyrolusite, sufficient for several days, is put into the still, and the bittern, heated to 60° C., is run in. The quantity of sulphuric acid to be added is carefully gauged with each charge of bittern in order that none of the magnesium chloride shall be decomposed. Usually, a little of the magnesium bromide is left in the bittern, since the high temperature necessary to decompose the last traces would also decompose some of the chloride, which would form bromine chloride, and contaminate the product. The bromine distils over into a condensing worm, as above described. The exhausted bittern is drawn off after each charge, and goes to waste. At the present time, considerable potassium chlorate is used instead of pyrolusite for the oxidizing agent. This is especially advantageous if the bittern contains much calcium chloride, since only one-half as much sulphuric acid is necessary, and there is, consequently, less difficulty from calcium sulphate. Neither the stills nor the tower should be lined with pitch or tar, since these substances absorb much bromine.

The crude bromine obtained by either process contains some bromine chloride, lead bromide from the pipe-joints and connections, and some organic matter. It is purified by shaking with ferrous, sodium, or potassium bromide, and redistilling from glass retorts. The bromine chloride is thus decomposed, and the salts of the heavy metals remain in the still. Very pure bromine is obtained by neutralizing with barium hydroxide solution, evaporating to dryness, and calcining at a red heat. The barium bromate and chlorate formed in the neutralizing are decomposed to form barium bromide and chloride. By extracting the mass with alcohol, the bromide is dissolved. The barium bromide obtained by evaporation of the alcohol is decomposed with pyrolusite and sulphuric acid, the pure bromine passing to the condenser as vapor.

Operations with liquid bromine must be carried on in the open air, or in a strong draught. If inhaled, the vapors are suffocating, and cause great irritation of the air passages. The liquid attacks the skin, and causes sores which heal very slowly.

Bromine is largely used in making certain coal-tar dyes, such as the eosins; for sodium and potassium bromides; and to some extent as a chemical reagent, and for making organic bromides. It is considered dangerous freight by transportation companies, and so only its salts, especially potassium bromide, are usually shipped.

"**Solidified bromine**" is a convenient form for laboratory work. This consists of sticks of diatomaceous earth, pressed with size or molasses, burned till coherent, and soaked in liquid bromine. The porous material absorbs from 50 to 75 per cent of its weight of the liquid.

Potassium bromide is made by decomposing iron bromide with potassium carbonate. The ferroso-ferric bromide (Fe_3Br_8), made by adding more bromine to ferrous bromide, is usually employed.

$$Fe + Br_2 = FeBr_2.$$

$$3\ FeBr_2 + 2\ Br = Fe_3Br_8.$$

$$Fe_3Br_8 + 4\ K_2CO_3 + 4\ H_2O = Fe_3(OH)_8 + 8\ KBr + 4\ CO_2.$$

The solution is filtered and evaporated, yielding cubical crystals of the salt, free from bromate, which is always formed when bromine is neutralized directly with alkali.

Potassium bromide is used in medicine and in photography, especially in the preparation of silver bromide plates and films.

Sodium bromide is similar to the potassium salt, is used for the same purposes, and is made in the same way; but it does not crystallize so well.

REFERENCES

Berichte über die Entwickelung der chemischen Industrie. — A. W. Hofmann, 1875, 129.
Moniteur scientifique, 1879, 905. — H. S. Welcome.
Handbuch der Kali-Industrie, E. Pfeiffer, 321. Braunschweig, 1887.
Die Gewinnung des Broms in der Kaliindustrie. M. Mitreiter, Halle, a. S., 1910.
Salt Deposits in Ohio. Bull. 8, vol. IX (1906), Rep't. Ohio Geol. Survey. J. A. Bownocker.

IODINE

Iodine is obtained from the ashes of seaweed, and from the mother-liquors of the Chili saltpetre industry.

Along the coasts of France, Scotland, and Norway, seaweed is collected and burned * at as low a temperature as possible. The ash, called *kelp,* or *varec,* contains from 0.5 to 1.5 per cent of its weight of iodides of sodium and potassium. It is lixiviated, and the filtered solution is systematically evaporated. First, sodium sulphate, and then common salt, crystallizes. By further evaporation, sodium carbonate, together with more salt and potassium chloride, separates. The mother-liquor is then treated with sulphuric acid to decompose the alkali sulphides and sulphites formed by reduction of the sulphates during incineration. This precipitates sulphur, and the sodium sulphate formed crystallizes. The mother-liquor, still holding the iodides in solution, is then heated to 60° C. in iron retorts with lead covers, and having pipes leading to condensers.† Small quantities of pyrolusite are introduced into the retort periodically, when the following reaction takes place: —

$$2\,NaI + 3\,H_2SO_4 + MnO_2 = MnSO_4 + 2\,NaHSO_4 + 2\,H_2O + I_2.$$

Pyrolusite is added as long as iodine distils off; but excess must be avoided, lest bromine and chlorine be set free from the salts still present in the liquor, and combine with the iodine to form tribrom- or trichlor-iodine (ICl_3).

Sometimes the iodine liquor is decomposed by leading chlorine gas into it, the same as in making bromine (p. 249). The crude iodine precipitates as a paste, and is washed and then dried on porous plates. Much care is necessary to avoid an excess of chlorine, since this forms volatile iodine trichloride (ICl_3), and causes loss.

By heating the acidified iodide solution with ferric chloride or

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* By burning the seaweed in closed retorts, the loss of iodine by volatilization is reduced.

† The condensers, called *udells*, are bottle-shaped vessels of earthenware, arranged horizontally, 5 or 6 in a series, the neck of one entering the bottom of the next. In the lower side of each is a small hole, through which the condensed water drains off. Each still has two sets of udells, which are left in position during repeated charges of the still, until they are filled with solidified iodine. Recently the condensers have been made of seven or eight lengths of plain earthenware pipe, each length 3 feet long by 1½ feet in diameter, and the joints luted with clay.

potassium chlorate, the iodine is liberated, and distils off, with some water, and no trichloride is formed, thus: —

a) $2\ NaI + 2\ FeCl_3 = 2\ FeCl_2 + 2\ NaCl + I_2$.

b) $6\ NaI + KClO_3 + 3\ H_2O = 6\ NaOH + KCl + 6\ I$.

Another method is to mix the kelp with a little water and sulphuric acid, and to add potassium bichromate: —

$$6\,NaI + 10\,H_2SO_4 + K_2Cr_2O_7 = 6\,NaHSO_4 + K_2Cr_2(SO_4)_4 + 7\,H_2O + 6\,I.$$

The precipitated iodine is washed, dried, and sublimed.

It has been proposed to heat the kelp directly with powdered bichromate, decomposition taking place at a red heat, and the iodine subliming: —

$$6\ KI + K_2Cr_2O_7 = 4\ K_2O + Cr_2O_3 + 6\ I.$$

The seaweeds of the Pacific coast of America may also furnish iodine in large quantity, when the market conditions will warrant its recovery.

The recovery of iodine from the **mother-liquors** of **Chili saltpetre** is now most important. The iodine is chiefly in the form of sodium iodate ($NaIO_3$), and the process depends on the following reaction: —

$$2\ NaIO_3 + 5\ SO_2 + 4\ H_2O = Na_2SO_4 + 4\ H_2SO_4 + I_2.$$

In practice, the sulphur dioxide is used in the form of sodium bisulphite solution, containing some neutral sulphite. This is made immediately before use by leading sulphur dioxide gas into sodium carbonate solution until the liquid contains one part of neutral sulphite to two of acid sulphite. The requisite quantity of this acid sulphite liquor is added to the mother-liquor, and thoroughly agitated; the precipitated iodine is collected on filters made of coarse bagging or canvas, and after washing is pressed heavily to remove excess of water. The reaction is probably as follows: —

$$2\ NaIO_3 + 3\ Na_2SO_3 + 2\ NaHSO_3 = 5\ Na_2SO_4 + I_2 + H_2O.$$

But since some sodium iodide is also present, the excess of bisulphate employed decomposes it according to the reaction: —

$$NaIO_3 + NaI + 2\ NaHSO_3 = 2\ Na_2SO_4 + I_2 + H_2O.$$

Sometimes the iodine is precipitated as cuprous iodide (Cu_2I_2) by adding copper sulphate and sodium bisulphite to the mother-liquors, but this is now less frequently done than formerly. The cuprous iodide was shipped to Europe, and used to make potassium iodide by treating with potassium carbonate.

The liquors from which the iodine has been separated are returned to the lixiviation tanks for the treatment of the crude " caliche " (p. 145).

The crude iodine obtained by any of the above processes is purified by resubliming in iron retorts, the vapors being condensed in earthenware receivers. The temperature of the retorts must be very low in order to form large crystals, and the condensers must not be so cool as to cause sudden condensation of the vapors.

The chief uses of iodine are in the manufacture of coal-tar dyes and organic compounds, and in medicinal preparations.

The most important iodine derivative is potassium iodide (KI). This is made in several ways: —

(*a*) Iodine may be dissolved in a caustic potash or carbonate solution, the solution evaporated to dryness, and the mixture of iodide and iodate so obtained calcined with powdered charcoal at a low red heat, to decompose the latter salt.

$$6\,I + 6\,KOH = 5\,KI + KIO_3 + 3\,H_2O.$$

$$2\,KIO_3 + 3\,C = 2\,KI + 3\,CO_2.$$

The calcined mass is lixiviated, filtered, and crystallized. Very pure materials are needed in this process.

(*b*) A better method is to form ferroso-ferric iodide, and decompose this with pure potassium carbonate. Metallic iron is dissolved by digesting with iodine and water, forming ferrous iodide, which is then treated with sufficient iodine to form the ferroso-ferric salt: —

$$Fe + 2\,I = FeI_2.$$

$$3\,FeI_2 + 2\,I = Fe_3I_8.$$

$$Fe_3I_8 + 4\,K_2CO_3 + 4\,H_2O = Fe_3(OH)_8 + 8\,KI + 4\,CO_2.$$

This method, if carefully worked, yields a very pure salt, entirely free from potassium iodate. The precipitated ferroso-ferric hydroxide is granular, and more easily washed than is ferrous hydroxide.

(*c*) Barium iodide is made by agitating barium sulphide solution with iodine. The clear solution is then boiled with potassium sulphate solution, the precipitated barium sulphate filtered off, and the filtrate evaporated until the potassium iodide crystallizes: —

$$BaS + I_2 = BaI_2 + S.$$
$$BaI_2 + K_2SO_4 = BaSO_4 + 2\ KI.$$

Potassium iodide is chiefly used in medicine as an alterative and diuretic. A small quantity is used in photography.

Lead, mercury, and ferrous iodides are used to a small extent in medicine, but these are not important.

REFERENCES

Wagner's Jahresbericht über die Leistungen der chemischen Technologie, **1879**, 334. E. Schering. (Jodkalium.) 337. G. Langbein. (Jod-Gewinnung in Chili.)
Journal of the Society of Chemical Industry: —
1893, 128. J. Buchanan. (Extraction of Iodine in Chili.)

PHOSPHORUS

The discovery of **phosphorus**, about 1675, is attributed to an alchemist, Brand, at Hamburg. Urine which had been evaporated to a thick syrup was heated in an earthenware retort with sand, the phosphorus distilling off. It was known only as a chemical curiosity until Scheele, in 1775, made it from bone-ash; soon after it assumed commercial importance. Bone-ash is still a leading source, but the mineral phosphates, being cheaper, are now used.

Normal calcium phosphate [$Ca_3(PO_4)_2$] is reduced by carbon only at excessively high temperatures, and then forms calcium phosphide rather than the free phosphorus. Free phosphoric acid is, however, reduced to phosphorus. In the old process, tricalcium phosphate (as bone-ash) was decomposed with sulphuric acid to form monocalcium phosphate and calcium sulphate. By leaching with hot water, the monocalcium phosphate was dissolved, and the solution, after decantation from the sulphate, was evaporated in lead pans, when powdered charcoal or coke was stirred in, and the mass heated in iron pans until dry. The dry mixture was charged into earthenware retorts and heated moderately at first, and then to very high temperatures. The moderate heating reduced the monocalcium phosphate to calcium metaphosphate, which in turn was decomposed by the carbon, forming tricalcium phosphate, phosphorus, and carbon monoxide. The reactions were as follows: —

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = CaH_4(PO_4)_2 + 2\ CaSO_4.$$
$$CaH_4(PO_4)_2 = 2\ H_2O + Ca(PO_3)_2.$$
$$3\ Ca(PO_3)_2 + 10\ C = Ca_3(PO_4)_2 + P_4 + 10\ CO.$$

This left one-third of the phosphorus combined with the calcium, but by adding silica to the mixture, *all* of the phosphorus is liberated, according to the reactions: —

$$Ca(PO_3)_2 + 5\ C + SiO_2 = CaSiO_3 + 2\ P + 5\ CO.$$
$$Ca_3(PO_4)_2 + 5\ C + 3\ SiO_2 = 3\ CaSiO_3 + 2\ P + 5\ CO.$$

The **electric furnace process** of Readman,* Parker, and Robinson. for the direct reduction of calcium phosphates in a continuous-acting

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* J. Soc. Chem. Ind., **1891**, 445. U. S. Pat. No. 482,586 (**1892**).

furnace (Fig. 88) has now replaced the older methods. The retorts employed in the old process, to withstand the chemical action of the charge, had to be made from materials which are poor conductors of heat, and hence the wear and tear was heavy, and the heat efficiency low. Electrical heating develops the energy within the retort itself, and allows the retort walls to be kept relatively cool. Owing to the high temperature attained by this method of heating, silica (as sand) may be introduced directly in the charge, all of the phosphorus being set free to distil out of the furnace, while a fused slag is separated and tapped off at the base of the furnace.

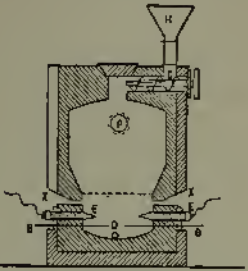

FIG. 88.

An intimate mixture of carbon, phosphate, and flux is heated; the gases and phosphorus vapors pass by the pipe (P), to the condenser, while slag is tapped off at intervals, through (O). Fresh charges are introduced through (H), by the conveyer (C). The carbon electrodes (E) are in metal sockets passing through the walls of the furnace. The working holes (X) are closed with clay when the furnace is running. This method avoids the use of sulphuric acid, the concentration and handling of phosphoric acid, uses no earthenware retorts, and saves time; it is further claimed that less coke is used.

The crude phosphorus made by any of the above processes contains sand, carbon, clay, and other impurities. It is purified by melting under warm water, and straining through canvas bags; formerly chamois leather was used. Or it is redistilled from iron retorts. Sometimes it is treated with a 3 per cent solution of potassium bichromate and its equivalent of sulphuric acid, in a lead-lined agitator which is heated by steam coils. After a couple of hours' agitation, the phosphorus is nearly transparent, and of a light yellow color. It is washed with hot water, filtered through canvas bags, and moulded into "sticks" by pouring into glass or tin tubes placed in cold water. For shipment, phosphorus is packed in water in tin boxes, the lids of which are tightly soldered.

Yellow or **ordinary phosphorus** is a pale yellow, translucent, waxlike mass of 1.82 specific gravity, very inflammable, and combining directly with oxygen, sulphur, and the halogens. It melts at 43.3° C. under water, and at 30° C. when dry; it distils at 269°.* It is very soluble in carbon disulphide, sulphur chloride, and phosphorus

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* J. B. Readman, Thorpe's Dictionary of Applied Chemistry, Vol. IV., 205.

trichloride, slightly so in caustic soda solution, but insoluble in water. It is exceedingly poisonous, less than 0.15 gram being a fatal dose. Persons working continuously with yellow phosphorus are subject to necrosis, usually appearing first in the jawbones.

The chief uses of yellow phosphorus are in making matches and phosphor-bronze, and for rat poison.

Amorphous or **red phosphorus** is made by heating the yellow variety for several hours in closed retorts at 250° C. If an autoclave be employed, and the temperature raised to 300° C., the pressure inside the vessel makes the process much more rapid. The hard mass thus produced is ground under water, and the powder boiled with caustic soda solution to remove any unchanged yellow phosphorus. Carbon disulphide is sometimes used instead of caustic soda, but this is expensive and easily inflamed. After boiling in water, filtering, and drying by steam heat, the amorphous phosphorus is packed dry. Red phosphorus is a reddish brown, opaque substance, having a specific gravity of 2.25. It is not affected by heating in the air until the temperature reaches 260° C., at which point it inflames. By heating in an atmosphere of nitrogen or carbon dioxide, it distils, returning to the yellow variety. It is insoluble in carbon disulphide, caustic soda, and in water, and is not poisonous. The chief use of red phosphorus is in the manufacture of "safety matches."

MATCHES

In about 1812, the so-called "chemical matches" were invented. Sticks were dipped in melted sulphur, and the "head" coated with a mixture of sugar and potassium chlorate. It was fired by dipping into a bottle containing asbestos moistened with sulphuric acid.

Friction, or **lucifer, matches** were invented in 1827, in England. The heads were a mixture of antimony trisulphide and potassium chlorate, made into a stiff paste with water and gum. They were ignited by rubbing on sand or emery paper. The antimony trisulphide was soon replaced by phosphorus, and the potassium chlorate by nitre. At the present time, lead peroxide, red lead, or manganese dioxide are used instead of nitre as the oxidizing substance. Chlorates are used, but sparingly, since they form explosive mixtures.

Soft wood, generally pine or spruce, is cut by machines to form the sticks, which are thoroughly kiln-dried. They are then fixed in a frame so that each stick stands alone, and the end of each stick is well soaked in melted sulphur, paraffine, or stearic acid. The igniting mixture is made by slowly stirring phosphorus into a warm solution of dextrine or glue; the oxidizing materials are then added, and the paste stirred until cold. It is frequently colored with ultramarine, lead chromate, chalk, or lampblack. It is then spread evenly in a thin layer on a table, and the prepared sticks dipped into it once or twice. After drying, the heads are sometimes dipped in thin shellac or other varnish, to protect them from the moisture in the air.

Safety matches are made without yellow phosphorus. The match head is generally sulphur, or antimony trisulphide, with potassium chlorate, or bichromate, as the oxidizing material. Sometimes red lead, lead peroxide, or manganese dioxide is used as a part of the oxidizing material. The surface upon which the match must be lighted is coated with a mixture of red phosphorus, antimony trisulphide, and dextrine, or glue. Powdered glass or emery is used to increase the friction.

The compositions used on matches are carefully guarded as trade secrets, and are different in different factories. One is given as follows: —

Head Composition		Rubbing Surface	
$KClO_3$	5 parts	Sb_2S_3	5 parts
$K_2Cr_2O_7$	2 parts	Red Phosphorus	3 parts
Glass Powder	3 parts	MnO_2	1½ parts
Gum	2 parts	Glue	4 parts

The friction of the match head on the prepared surface develops sufficient heat to convert a little of the red phosphorus to the yellow variety, which at once combines with some of the potassium chlorate and antimony sulphide, evolving enough heat to inflame the mixture on the head.

To prevent the burned stems from smouldering, the sticks are sometimes soaked in a solution of magnesium sulphate, alum, or sodium phosphate before making the head.

In some countries, *e.g.* Switzerland, the manufacture and sale of matches containing yellow phosphorus is prohibited. In this country their production has been eliminated by the imposition of a prohibitive tax of 1 cent per 100 matches.

REFERENCES

Chemical News, **1879**, 147. J. B. Readman. (Manufacture of Phosphorus.)
Chemiker-Zeitung, **1881**, 196. A. Rossel. (Matches without Phosphorus.)
Journal of the Society of Chemical Industry: —
  1890, 163, 473. J. B. Readman. (Manufacture of Phosphorus.)
  1891, 445. J. B. Readman. (Manufacture of Phosphorus.)

BORIC ACID

Boric acid $[B(OH)_3]$ occurs in volcanic regions, especially in Tuscany, as a constituent of the vapors, called *soffioni,* which escape from hot springs and from openings in the ground, called *fumeroles.* In some places the water has evaporated from the *fumeroles,* and the boric acid has crystallized, forming the mineral *sassolite.* Combinations of boric acid with sodium, magnesium, and calcium are found in various places: as, **tinkal** (native borax), $Na_2B_4O_7 \cdot 10\ H_2O$; **boracite,** $2(Mg_3B_8O_{15})$, $MgCl_2$; **borocalcite,** $CaB_4O_7 \cdot 6\ H_2O$; and **boronatrocalcite** (ulexite), $Na_2B_4O_7$, $(2\ CaB_4O_7)$, $18\ H_2O$.

In Tuscany, natural or artificial ponds (lagoons) are formed around the *fumeroles,* or a series of masonry basins or tanks are constructed over them, and the *soffioni* made to bubble through water in these, thus washing most of the boric acid from the vapors. These tanks are so arranged that the water from one flows into another at a lower level; in the final basin, a solution containing about 2 per cent boric acid is obtained. The solution is evaporated, either in lead-lined vessels, heated by the steam from the *fumeroles,* or in cement-lined tanks, having coils through which the steam passes. Calcium sulphate deposits freely during the evaporation of the solution, which is concentrated to 1.08 specific gravity. It is then crystallized in lead-lined wooden vats. The crystals are drained for some hours, and dried on a floor also heated by steam from the *fumeroles.* The crude boric acid is purified by recrystallization. In many places in Tuscany, bored wells are sunk from 200 to 300 feet, and the vapors escape from these as from the natural *fumeroles.*

Boric acid is made in California, and in Chili, by boiling calcium borates, suspended in water, with sulphur or sulphurous acid: —

$$Ca_2B_6O_{11} \cdot 5\ H_2O + 8\ S + 10\ H_2O = 2\ CaSO_4 + 6\ B(OH)_3 + 6\ H_2S.$$

$$Ca_2B_6O_{11} \cdot 5\ H_2O + 4\ SO_2 + 6\ H_2O = 6\ B(OH)_3 + 2\ Ca(HSO_3)_2.$$

Much boric acid is made from the **boracite** in the Stassfurt salts. The mineral is crushed, and treated with just enough hydrochloric acid to decompose it. A rather vigorous reaction takes place, and the mass becomes pasty. It is dissolved in boiling water, and carefully tested for free hydrochloric acid; if none is present, the solution of boric acid is decanted from the sediment of clay and sand, or filtered through linen bags, and is crystallized in lead-lined or iron tanks.* Sulphuric acid is also used to decompose the boracite, in which case the mother-liquors from the boric acid contain magnesium sulphate; this is recovered as Epsom salt. The following reactions are involved: —

1) $(2\,Mg_3B_8O_{15}), MgCl_2 + 12\,HCl + 18\,H_2O = 7\,MgCl_2 + 16\,B(OH)_3$.

2) $(2\,Mg_3B_8O_{15}), MgCl_2 + 7\,H_2SO_4 + 18\,H_2O =$
$7\,MgSO_4 + 2\,HCl + 16\,B(OH)_3$.

The actual quantity of acid used is determined for each lot of salt.

Boric acid forms pearly white, laminated crystals, very slightly soluble in cold water, but dissolving readily in hot water. It has but little taste. When heated, it loses water, and at 140° C. forms pyroboric acid ($H_2B_4O_7$). At a red heat, all the water is expelled, and boric anhydride (B_2O_3) results; this is stable and non-volatile, even at high temperatures. Consequently, it will decompose nearly all metallic sulphates, carbonates, and nitrates when fused with them, forming metallic borates. Hence it is used as a flux. Boric acid is chiefly used in the preparation of borax; in enamels and glazes for pottery; in making Guignet's green; as an antiseptic in medicine and surgery; and for preserving fish, meat, and milk.

Borax, sodium biborate ($Na_2B_4O_7$), is the only important salt derived from boric acid. It is found native in Thibet, Ceylon, and California. But little is known of the method of preparing borax in Thibet. It comes from that country as *tinkal*, an impure, crystallized borax, containing lime, magnesia, sulphates, and chlorides and a greasy substance added presumably to protect the crystal from efflorescence and breakage. The *tinkal* is purified by dissolving in hot water, and adding lime-water and calcium chloride, to precipitate the grease as lime soap. After filtering, the borax is crystallized by concentrating the solution.

Borax was formerly obtained by evaporating the water and by washing the mud from the beds of several ponds (Borax Lake, and others) in Lake, Inyo, Kern, and San Bernardino counties in California; this was succeeded by its recovery from various dry lake beds, so-called "marshes," in the Death Valley region, where the surface efflorescence, or crusts, consists of a mixture of borax, soda, salt, and sulphate. At present nearly all borax produced in this country is made

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* F. Wittig (Zeit. angew. Chem., **1888**, 483), recommends iron crystallizing tanks, because lead-lined vessels buckle and leak, owing to the changes of temperature. The iron soon becomes polished, and yields perfectly clean crystals.

from ulexite or "cotton ball" ($NaCaB_5O_9 \cdot 8\ H_2O$) and colemanite ($Ca_2B_6O_{11} \cdot 5\ H_2O$), found in Inyo, San Bernardino, and Ventura counties.

The ore in small lumps is roasted at low heat in a rotary furnace, to expel water and cause the colemanite to fall to powder, which is sifted to remove the refuse calcite, sand, clay, etc. The powder is boiled in sodium carbonate and bicarbonate solution until decomposed, the calcium carbonate settled, and the brown solution of borax run into large iron crystallizing vats, which are sheathed with wood to prevent too rapid cooling. To form good crystals, the solution should cool very slowly, and the vats are usually covered to prevent the formation of surface crust. Wires are suspended in the vat for the borax to crystallize upon, which requires from 7 to 10 days. Impure crystals deposit on the bottom and sides of the vat, and are generally recrystallized from water. The sodium bicarbonate is added to prevent the formation of metaborate. The reactions are as follows: —

$$2\ Ca_2B_6O_{11} \cdot 5\ H_2O + 2\ Na_2CO_3 + 2\ NaHCO_3 = 4\ CaCO_3 + 3\ Na_2B_4O_7 + 11\ H_2O.$$

$$4\ NaCaB_5O_9 \cdot 8\ H_2O + 2\ Na_2CO_3 + 2\ NaHCO_3 = 4\ CaCO_3 + 5\ Na_2B_4O_7 + 9\ H_2O.$$

The sludge from the decomposing vat is boiled with water, filter-pressed, and the liquor sent to the next decomposing operation, while the mud is thrown away.

A borocalcite called *pandermite*, found in Asia Minor and some other localities, is worked in somewhat similar manner.

Much of the boric acid produced in Italy is converted to borax by boiling it with sodium carbonate; the solution is concentrated to 22° Bé. at 104° C., settled and run into shallow, open, crystallizing vats, where the borax deposits within three days; but for recrystallization deep tanks, tightly covered, and lagged to prevent radiation of heat, are used; from 16 to 18 days are required, and large crystals are formed.

Borax comes in trade in two forms: common or *prismatic borax* ($Na_2B_4O_7 \cdot 10\ H_2O$), and *octahedral borax* ($Na_2B_4O_7 \cdot 5\ H_2O$). The former is produced as large, efflorescent, monoclinic crystals, by crystallizing from a solution of 22° Bé., which is permitted to cool to 27° C.; it melts in its water of crystallization when heated, then swells greatly, forming a spongy mass, which fuses at red heat to a transparent glass. Octahedral borax is obtained as regular octahedrons, when a solution of common borax is concentrated to 30° Bé., and cooled only to 56° C. It is permanent in dry air, but absorbs moisture on exposure, and passes into the prismatic variety; it fuses without intumescence, and is preferred as a flux for brazing and soldering.

Borax is used as a flux in welding and brazing metals; in enamel and glazes for metal ware and pottery; in laundry work and in starch to increase the gloss; in soaps, especially those intended for use in hard water; for preserving meat; as a mordant in dyeing; for the ungumming of raw silk; in medicine and pharmacy; and with casein for the preparation of paste.

Perborates,* derivatives of the acid HBO_3, have become important industrially, as oxidizing agents. *Sodium perborate* ($NaBO_3 \cdot 4\ H_2O$), is a stable, crystalline salt, produced from sodium peroxide and boric acid solutions; in cold, aqueous solution it acts like hydrogen peroxide.

REFERENCES

Hofmann's Bericht über die Entwickelung der Chemischen Industrie. **1875**, 324, 343.

Handbuch der Kali-Industrie. E. Pfeiffer, Braunschweig, 1887. (Boracit.)

Chemiker-Zeitung: —
1879, 46. (Boric Acid from Boracite.) **1887**, 605. (Borax in Chili.)

Third Annual Report of the California State Mineralogist, 1883.

Die Stassfurter Kali-Industrie. G. Lierke, Wien, 1891.

California State Mining Bureau, Bul. No. 24. The Saline Deposits of California, 1902.

Zeitschrift für angewandte Chemie: —
1888, 483. F. Witting. (Borax from Boronatrocalcite.) **1891**, 367. **1892**, 241. Dr. Scheuer. (Boric Acid and Borax Industry.)

Journal of the Society of Chemical Industry: —
1889, 857. C. N. Hake. (Borax Lake in California.) **1892**, 683.

Engineering and Mining Journal: —
(Borax.) **53**, 8. **54**, 247.

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* Compt rendu, **1904** (**139**), 796. J. Soc. Chem. Ind., **1904**, 1145; **1905**, 275, 276, 332.

ELECTRIC FURNACE PRODUCTS

The electric furnace * is used for one or more of the following reasons: (*a*) To secure temperatures higher than are attainable with combustion furnaces, thus making possible the production of certain substances previously unknown, or obtained with great difficulty; (*b*) for generating heat at the exact point required, thus avoiding the heat losses and depreciation of plant incident to forcing large quantities of heat through retaining walls; (*c*) for the maintenance of definite conditions (especially reducing atmosphere) within the container.

The successful application of the electric furnace to technical uses by Messrs. Cowles, in Cleveland, Ohio, in 1884, was the beginning of large industries. Various modified forms of the Cowles furnace are now used to produce carborundum, artificial graphite, calcium carbide, phosphorus, alundum, barium hydrate and cyanide, and other products, and in metallurgical operations.

The Cowles furnace (Fig. 89) consists of a crucible (F), into which the movable electrodes (E) pass. The cover has an opening (O) for the escape of the gases. The carbon electrodes are in contact at first, but are slowly separated as the charge and furnace become hot, and the current passes through the mixture in the crucible, or an arc is formed. At (J) the electrodes are joined to the conductors from the dynamos. When the electrodes have been separated until the ammeter readings have become nearly constant, the operation is allowed to go on for some hours. Either direct or alternating currents may be used, when the desired results can be obtained by a high temperature, and are not due to electrolysis.

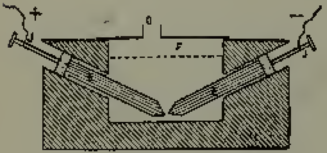

Fig. 89.

In some forms of electric furnaces the heating is accomplished by passing the current through a conductor of relatively high resistance embedded in the charge; the heat from the resistance warms the adjacent portions of the charge.

Carborundum, or **silicon carbide**, was first made on a technical

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* Electric Furnaces and their Industrial Applications, J. Wright, New York, 1905. The Electric Furnace, Alfred Stansfield, 2d Ed., New York, 1914. (McGraw-Hill Co.) Trans. Faraday Society, Jan. **1905** (I), 85.

scale by E. G. Acheson, about 1891, using the Cowles furnace. It is now extensively produced at Niagara and other places, and used as an abrasive, replacing emery and corundum. The charge of 100 parts coke powder, 100 parts sand, and 25 parts common salt, to which a little sawdust is sometimes added, is packed around a horizontal core, twelve feet long, of granulated coke, joining the electrodes, which are embedded in the furnace walls. The heat causes the granulated coke to sinter together; the salt causes adhesion between the particles of the charge. As the reaction proceeds, large quantities of carbon monoxide are evolved, and the furnace is enveloped in blue flames. The reaction is: —

$$SiO_2 + 3\ C = SiC + 2\ CO.$$

After several hours vapors of sodium appear and cause the flame to become yellow; the furnace is permitted to cool, and the core is found surrounded by a crust of crystallized carborundum, with an intervening layer of graphite, formed by the decomposition of some of the carborundum by the heat. The brilliant black carborundum crystals often have a splendid iridescent lustre. The material is sorted by hand, and the carborundum crushed and washed with sulphuric acid to remove traces of iron, aluminum, sulphides, phosphides, carbides, etc. It is then washed with water, and levigated to separate the powder into commercial sizes.

Carborundum is not attacked by acids or by sulphur fumes, is stable in the air and infusible, and is harder than corundum. It is decomposed by fusion with caustic alkalies and nitre, and is attacked by chlorine above 600° C.

Artificial graphite is made by heating amorphous carbon in the presence of ferric oxide or silica, at high temperature, so that the iron or silicon is vaporized and the carbon is left in the crystalline form as graphite. At intermediate temperatures in the presence of carbon, iron and silicon form carbides; at higher temperatures, the carbides dissociate into the elements and the carbon formed by the dissociation is in the form of graphite. Thus iron and silicon act as catalyzers of the graphite formation.

The brick furnace used is similar to the carborundum furnace and has carbon electrodes. Anthracite coal, as raw material, is filled into the furnace around a carbon rod as a core between the terminals, which heats the coal at the start since it is a poor conductor of heat when cold. Nearly all impurities are vaporized and the graphite contains only about 0.5 per cent of ash. This product is used for lubricators, paints, dry batteries, pencils, etc. Articles formed from pulverized amorphous carbon, pressed into moulds, can be "graphitized" in the electric furnace without change of form.

Calcium carbide was first prepared on a commercial scale by T. L. Willson, about 1895, although it had been known as a laboratory product many years before.

By heating an intimate mixture of pulverized lime and coke in an electric furnace, calcium carbide is formed directly: —

$$CaO + 3\,C = CaC_2 + CO.$$

The furnace (Fig. 90) * generally used is made of fire-brick and lined with carbon; it is designed for 3000 to 4000 kilowatts. The iron bottom of the furnace connects with the carbon lining of the bottom, to form one electrode, and the other electrode is suspended so that it hangs free within the hearth. The fused carbide forms a pool under the electrode, which is raised or lowered as need be by the hoist (W). The furnace is tapped at intervals, by means of a special arc, sprung at the end of the pointed, tapping electrode (A), by which a hole can be melted through the furnace wall in a few minutes. For a short time previous to tapping, no fresh charge is introduced and the fused carbide in the furnace forms a thin, liquid bath. The

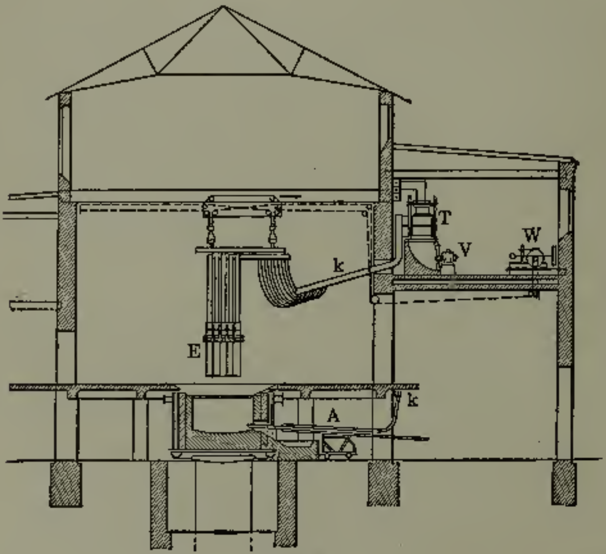

FIG. 90.

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* Electrochem. Ind., **1908** (7), 400.

charge itself serves to protect the fire-brick walls from the intense heat of the arc.

The raw materials, which must not contain water, phosphate, sulphate, nor mangesia, are lime or limestone, and coke, charcoal, or anthracite; these are coarsely pulverized and mixed in proportions of 95 kg. lime to 68 kg. coke. In theory, to produce 100 kg. of carbide, 87.5 kg. of lime and 56.25 kg. of carbon are needed. One kilogram of carbide requires about 4 kilowatt-hours, and 1 ton of carbide is obtained from 1.79 tons of mixture of lime and coke.

Calcium carbide is a hard, crystalline mass, with lustrous surface when freshly broken, but soon tarnishing and decomposing in the air. It reacts at once with water, forming acetylene and calcium hydroxide: —

$$CaC_2 + 2\ H_2O = C_2H_2 + Ca(OH)_2.$$

Commerical carbide contains about 80 per cent CaC_2, and is chiefly used to prepare acetylene gas (p. 324), for the manufacture of calcium cyanamide (below), and somewhat as a germicide in combating *phylloxera*.

Calcium cyanamid,* discovered by Frank and Caro when attempting the synthesis of cyanides (p. 290), is formed when purified and concentrated nitrogen gas (from liquid air) is brought into contact with finely ground calcium carbide, in ovens heated to about 1000° C. The reaction

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C$$

is reversible if the conditions are not kept within certain limits, regarded as trade secrets.

The product from the ovens is a hard cake (black from the free carbon), with about 22 per cent nitrogen and 1 per cent carbide. After fine grinding and careful hydration of the residual carbide, the material goes to the fertilizer trade as "*lime-nitrogen*," or "*nitrolim*." It also finds use in making synthetic ammonia (p. 150); for cyanides by fusion with common salt; and for case-hardening iron, especially for armor plate.

Alundum is the name given to an artificial corundum (Al_2O_3), produced by fusing bauxite in the electric arc furnace. Iron and most other impurities volatilize, leaving nearly pure aluminum oxide in the furnace. The cooled mass is pulverized in crushers and rolls, and sieved to the desired size of grain, for making into wheels and other imple-

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* Zeitsch. angew. Chem., **1903 (16)**, 536; **1910 (23)**, 2405. J. Soc. Chem. Ind., **1903**, 809. Electrochem. Met. Ind., **1907**, 77; **1908**, 341; **1910**, 539; **1915**, 213.

ments for grinding and polishing, and for refractory linings and similar uses. As an abrasive it is harder and tougher than emery, which it has largely replaced.

Barium hydroxide * is made in the electric furnace from barytes, thus: —

1) $4\ BaSO_4 + 4\ C = 3\ BaSO_4 + BaS + 4\ CO.$

2) $3\ BaSO_4 + BaS = 4\ BaO + 4\ SO_2.$

A mixture of ground barytes and coke, in the above proportions, is heated in an electric furnace which may be tapped periodically. The first reaction takes place at once and at moderate temperature, but the second is slower and requires very high heat. The product tapped from the furnace is dissolved in hot water, and the solution of hydroxide and sulphydrate filtered. Crystals of $Ba(OH)_2 \cdot 8\ H_2O$ separate from the solution on cooling, the sulphydrate remaining in the mother-liquor. The crystals are centriffed, washed, and dried. The reduction of the barytes is claimed to equal nearly 97 per cent of the available sulphate, and the product is very pure.

Cyanides ‡ may be made in the electric furnace by heating a mixture of barium carbonate and coal or coke dust until barium carbide is formed, and then introducing nitrogen gas (deoxidized air), whereby barium cyanide is produced. The charge is cooled somewhat before the nitrogen is brought in contact with the mass.

For **electric carbon disulphide process**, see p. 297.

For **electric phosphorus process**, see p. 256.

REFERENCES

Applied Electrochemistry. By M. do Kay Thompson, New York, **1911**. (Macmillan Co.)

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* J. Soc. Chem. Ind., **1902**, 391. Trans. Am. Inst. Elec. Eng., **1902**.

† J. Soc. Chem. Ind., **1900**, 745. U.S. Pat. Nos. 657,937 ; 657,938.

ARSENIC COMPOUNDS

Arsenious acid, white arsenic, or **arsenic trioxide** (As_2O_3) is the most important arsenic derivative. It is made by roasting arsenical pyrites (mispickel), FeAsS; or as a by-product in the preparation of zaffre from cobaltite (CoAsS), or smaltite ($CoAs_2$), and in roasting certain arsenical tin ores before smelting.

The roasting is done in reverberatory furnaces, and the vapors of white arsenic sublime off, and are condensed as a powder in long horizontal canals, or in chambers. The crude product is purified in a small reverberatory furnace, fired with coke, or in cast-iron pots, a number of which are set in a furnace, all being connected with a single condensing chamber or canal. Directly over the pot an iron drum or cylinder is often placed, from the top of which a short pipe leads to the condensing chamber.

After resubliming, the oxide is a white granular powder, which is usually ground before packing for market; or, by a second sublimation under slight pressure in an atmosphere of arsenious acid, it is obtained in an amorphous or vitreous state. For this the pot is heated red-hot, and the "arsenic meal" introduced through an opening in the cap of the drum, which is then closed. The arsenic vapor rises into the drum, and condenses on its walls as a transparent layer of "arsenic glass."

White arsenic, or, as it is commonly called, arsenic, comes in commerce as a powder, and as a "glass." On standing, the latter changes to a crystalline state, and becomes white, opaque, and porcelain-like in structure. It has no odor, and a very slight metallic taste, is difficultly soluble in water, and vaporizes without melting when heated in the open air. It is used in glass-making; when dissolved in glycerine, as a mordant in calico printing; in making various pigments; for preparing fly and rat poisons; as a preservative for green hides; for the manufacture of arsenic salts; for insecticides; in medicine; and formerly, to a great extent, in the preparation of aniline from nitrobenzene.

Arsenic acid, H_3AsO_4, is prepared by heating 4 parts arsenic trioxide with 3 parts concentrated nitric acid (1.35 sp. gr.), and evaporating the solution to a thick syrup, in which form it is usually sent to market. By evaporating it to dryness, and igniting at a red heat, **arsenic pentoxide,** As_2O_5, a hygroscopic body, is formed.

Arsenic acid attacks the skin, producing blisters, but is less poisonous than arsenious acid. It is chiefly used in calico printing, but was formerly much employed as an oxidizing agent in making certain coal-tar dyes (rosanilines).

Sodium arsenate, Na_2HAsO_4, is made by heating white arsenic with sodium nitrate, or by dissolving white arsenic in sodium carbonate solution, adding some sodium nitrate, evaporating to dryness, and calcining the mass. By dissolving in water, and crystallizing, the salt $Na_2HAsO_4 \cdot 12\ H_2O$ is obtained. This usually contains some $NaH_2AsO_4 \cdot H_2O$ (binarsenate).

It is used as a substitute for the "dung-bath" in dyeing alizarines, and in calico printing, to prevent discoloration of the white parts of the pattern by rendering the excess of mordant insoluble, so that it does not "bleed," *i.e.* diffuse into the white portions of the cloth.

Sodium arsenite, $NaAsO_2$ (meta-arsenite), is prepared by neutralizing arsenious acid with sodium carbonate, or hydroxide solution, and boiling for some time. The salt has been used instead of the "dung-bath" in dyeing.

Orpiment and **Realgar** have been described on pp. 240 and 245.

Lead arsenate,* $PbHAsO_4$, or $Pb_3(AsO_4)_2$, made by precipitation of a lead acetate or nitrate solution with sodium arsenate, is a white amorphous powder much used as an insecticide spray in agriculture. It is less injurious to foliage and adheres better than Paris green. It should not contain lead arsenite, which is more soluble and hence affects vegetation seriously.

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* Bul. No. 121, U. S. Bureau Chemistry, Dept. Agriculture, 1910.

WATER-GLASS

The substances sold under this name are silicates of sodium, or potassium, or of both. They are soluble in water, and are generally sold as thick, syrupy liquids.

Commercial water-glass is not of definite composition, but is approximately $Na_2Si_4O_9$. It is prepared by fusing powdered quartz, or infusorial earth, with caustic soda or with sodium carbonate. A small quantity of charcoal is also added, to assist in the complete reduction of the carbonate. Sodium sulphate may be used instead of the carbonate. The fusion is done in a reverberatory furnace, and requires 8 or 10 hours. Sometimes ordinary glass-pots and furnaces (p. 199) are used. The product is a translucent or transparent glass, slightly green, from traces of iron. It is powdered, and boiled in water, best in a digester under pressure, until the soluble matter is dissolved. A small quantity of copper or lead oxide is added, to decompose any sodium sulphide formed during the reduction. After 10 or 12 hours the solution is drawn from the boiler, filtered on cloth, and allowed to settle. It is then concentrated to 140° Tw. (1.7 sp. gr.). The material used must be pure, and especially be free from lime, alumina, etc.

Water-glass is also made by boiling silica in a digester with a solution of caustic soda for a long time at 60 pounds pressure. This yields a solution of the silicate directly, which needs only a little concentrating. Sometimes gelatinous precipitated silica is dissolved in caustic soda, and the solution is evaporated. By using a mixture of equivalent weights of sodium and potassium carbonates, a more soluble glass is produced, which is sometimes called "double soluble glass."

Potassium silicate, which forms a more soluble glass than sodium silicate does, is made in the same way.

Water-glass is readily decomposed by acids, even carbon dioxide setting free silica, and forming a salt of the alkali. It is used extensively as an addition to yellow or laundry soaps; as a fixative for pigments in calico printing; as a vehicle for pigments in fresco painting; for rendering cloth and paper draperies non-inflammable; as a size for paper and fabrics; for preserving eggs; as a preservative for timber and porous stone; in the manufacture of artificial stone; and in cement mixtures for glass, pottery, wood, and leather.

PEROXIDES

Barium peroxide * BaO_2, is made by calcining barium nitrate, and heating the oxide thus obtained in an atmosphere of dry, pure air. The nitrate is packed in crucibles, and heated in a furnace at 880° C. for several hours. The mass fuses, and for the first 3 or 4 hours continues to evolve nitrous gases, but finally becomes solid, though of a spongy, porous character. This is barium monoxide, and must be carefully protected from moisture and carbon dioxide. It is broken up into small lumps, and put into flat iron trays, which are set in wide, cast-iron pipes, through which a current of air can be passed. The air is dried thoroughly, and freed from carbon dioxide before it enters the pipes, by passing it through a drying tower, or drum, filled with caustic soda or quicklime. The pipes are heated to a low red heat (400° C.), and the air passes through them. The barium oxide takes up an atom of oxygen, forming the peroxide, while nitrogen escapes from the pipe. The product is cooled away from contact with air.

By adding an excess of barium hydroxide solution to a solution of hydrogen peroxide, a precipitate of hydrated barium peroxide, $BaO_2 \cdot 8\ H_2O$ is obtained, which is stable. By drying this at 130° C., all the water is expelled, and the pure peroxide remains.

Barium peroxide is a gray or white powder, insoluble in water, but combining with it to form a hydrated compound. It is easily decomposed by dilute acids, and even takes up carbon dioxide from the air. Heated to a bright red heat (1000° C.), it decomposes into monoxide and free oxygen. Its chief uses are for making hydrogen peroxide, and in the preparation of oxygen gas.

Hydrogen peroxide † H_2O_2, is made by decomposing barium peroxide with dilute mineral acids. The finely powdered barium peroxide is actively stirred into diluted hydrochloric acid in which blocks of ice are floating. The temperature must not rise above 15° C. When all the peroxide is dissolved, dilute sulphuric acid in slight excess is added to precipitate the barium. Then to remove iron and alumina, some sodium phosphate is added, with more barium peroxide to make the solution neutral; finally add ammonia to decided alkaline reaction.

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* J. Soc. Chem. Ind., **1890**, 246. L. T. Thorne. Chemiker-Zeitung, **1894**, 68.

† Zeitschr. f. angew. Chem., **1890**, 3. G. Lunge. J. Am. Chem. Soc., **12**, 64. A. Bourgougnon. J. Soc. Chem. Ind., **1902**, 229.

The turbid liquor is rapidly put through a filter-press, and the clear filtrate immediately made slightly acid with sulphuric acid, as the alkaline solution will not keep. Any barium remaining in solution is precipitated with pure sodium sulphate solution, and the liquor settled. Phosphoric acid may be used instead of hydrochloric and gives a stable product; but it is more expensive. The commercial strength is known as a 12-volume solution, *i.e.* $3\frac{1}{2}$ per cent H_2O_2.

By using hydrofluoric acid, the precipitate of barium fluoride may be readily employed to generate more of the acid; if nitric acid is used, a considerable part of the barium is recovered as barium nitrate, with which more barium peroxide can be made.

Hydrogen peroxide is a powerful oxidizing agent towards substances capable of oxidation, but with bodies which give off oxygen readily it acts as a reducing agent, giving up one atom of oxygen to unite with the oxygen from the body in question, forming a molecule of the free gas. It is used extensively as a bleaching agent, especially for animal fibres and tissues, such as silk, wool, hair, feathers, bone, and ivory. It has long been used as a hair bleach for toilet use. As a disinfectant and antiseptic, it finds use in surgery; for restoring the colors of oil paintings which have darkened with age, it is very effective, if the paint contains lead; the lead sulphide is oxidized to the sulphate by the peroxide, the black color of the former being destroyed. Hydrogen peroxide has also been proposed as a substitute for sodium bisulphite and thiosulphate, as the reducing material for chrome tannage processes; also as an antichlor, for use after chlorine bleaching; and as a general antiseptic, for use in the fermentation industries, and as a preservative for milk, beer, wine, and other fermentable liquids.

Sodium peroxide,* Na_2O_2, has recently appeared in commerce as a bleaching material. The technical production depends upon the oxidation of fused metallic sodium, by exposing it to a current of pure dry air or oxygen. The sodium is contained in aluminum trays, which are put on cars, and pushed *slowly* through a wide iron pipe, externally heated to 300° C., while air, purified as described on p. 272, passes through the pipe in the opposite direction. The temperature must not rise above 300° C., and the oxidation must be slow.

Sodium peroxide is a yellowish white, very hygroscopic powder, which is chiefly used as a powerful bleaching agent. It gives off 20

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* J. Soc. Chem. Ind., **1892**, 1004 (Patent to H. Y. Castner); **1893**, 603. Chemical Trade Journal, **11**, 208.

per cent of its weight as active oxygen.* It dissolves in dilute acids without evolving oxygen, *if the vessel be kept cool*, yielding a strong solution of hydrogen peroxide. It dissolves in water with the loss of some oxygen, and a great evolution of heat, which may be sufficient to set fire to inflammable bodies. It is too strongly alkaline for silk or wool bleaching, and should be converted into magnesium peroxide for this purpose. This is easily done by adding magnesium sulphate solution: —

$$Na_2O_2 + MgSO_4 = Na_2SO_4 + MgO_2.$$

The solution of sodium peroxide attacks cellulose, and produces an effect similar to that obtained by "mercerizing" with caustic soda.

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* Barium peroxide liberates 8 per cent of its weight of active oxygen, while a 12-volume solution of hydrogen peroxide liberates only 1½ per cent of its weight of active oxygen.

OXYGEN

Numerous processes have been devised for the technical production of oxygen, but most of them are so expensive, or require such complicated plants, that only two or three are in actual operation on a large scale at the present time.

The **decomposition of potassium chlorate** by heating, with the addition of manganese dioxide, has been much employed, and is still the favorite laboratory method of obtaining a pure gas. The addition of pyrolusite lowers the temperature of the decomposition, and reduces the liability of explosion. It is highly important that the potassium chlorate and pyrolusite be free from carbonaceous matter.

Boussingault's process, as modified by Brin brothers, and worked on a large scale, is often called **Brin's process.*** Boussingault discovered that barium peroxide (BaO_2), when heated to a high temperature, decomposes into the monoxide and oxygen, the latter passing off. Then by heating the barium oxide to a low red heat in a current of air, the peroxide can be regenerated. But his attempts to utilize the process were unsuccessful, because the monoxide soon became inert, and would not absorb oxygen from the air. This was due to the fact that the moisture and carbon dioxide in the air converted the barium oxide to hydroxide and carbonate, which are very stable bodies, even at high temperatures, consequently the regeneration of peroxide rapidly decreased.

As modified by Brin brothers, the temperature of the retort remains constant, while all moisture and impurities are removed from the air. Barium oxide is made from barium nitrate, as described on p. 246, and put into vertical retorts, or long narrow pipes, suspended in a furnace heated by producer gas. When the temperature reaches 700° C., purified air is forced into the retorts under a pressure of 15 pounds per square inch, and the monoxide takes up an atom of oxygen, and forms the peroxide. The air supply is then cut off, and the pump reversed, so as to form a vacuum in the retort, reducing the pressure to about 26 to 28 inches of mercury. Under these conditions, the barium peroxide gives off an atom of oxygen, and is reduced to the monoxide. The gas is pumped into the gasometer, and when it ceases to be evolved the pump is reversed again, and air forced into the retort, to oxidize the monoxide to peroxide again.

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* J. Soc. Chem. Ind., **1890**, 246. L. T. Thorne. **1889**, 82 and 517.

The air is passed through purifiers, one filled with quicklime, and the other with caustic soda; these remove the water and carbon dioxide. By the alternate use of pressure and vacuum, the temperature may be kept constant at 700° C. The oxygen obtained is about 96 per cent pure. The baryta is removed once in six or eight months, and broken up to prevent caking, after which it is returned to the retort. The yield of oxygen gas at each operation is said to be about 10 litres per kilo of barium oxide employed. The cost of the gas in England is from 3*s*. to 7*s*. per 1000 cubic feet.

Deville's process. — By allowing sulphuric acid to drop in fine streams on red-hot surfaces, it breaks up according to the reaction: —

$$2\ H_2SO_4 = 2\ SO_2 + 2\ H_2O + O_2.$$

The gases evolved are passed through cooling coils to condense the water, and then through scrubbers containing water, to remove the sulphur dioxide. The retort is usually filled with broken brick, pumice, or other porous, acid-resisting material. The process has no significance as a method of preparing oxygen alone, but has been used for making sulphuric anhydride, SO_3, the water being first condensed, and the sulphur dioxide and oxygen uniting to form the trioxide. About 114 litres of oxygen are obtained from 1 kilo of sulphuric acid.

Tessié Du Motay process.[*] — This depends on the following reactions: —

1) $2\ Na_2MnO_4 + 2\ H_2O = Mn_2O_3 + 4\ NaOH + 3\ O.$

2) $Mn_2O_3 + 4\ NaOH + 3\ O(air) = 2\ Na_2MnO_4 + 2\ H_2O.$

First, sodium manganate is prepared by mixing a manganese oxide with caustic soda, and heating with free access of air. The following reaction takes place: —

$$2\ MnO_2 + 4\ NaOH + O_2(air) = 2\ Na_2MnO_4 + 2\ H_2O.$$

The sodium manganate is crushed, mixed to a paste with caustic soda solution, containing from 5 to 10 per cent NaOH; this is dried slowly and *completely* in shallow pans, and ignited in a crucible at a white heat, to render it spongy. But it must not fuse. This yields a porous manganate, containing an excess of caustic soda, which is filled into long clay or cast-iron retorts of peculiar construction,[†] set at an incline in the furnace, and heated to a regular temperature of 400°–450° C. Superheated steam is then admitted to the retort, where it deoxidizes the manganate, regenerating the manganic oxide and caustic soda, while oxygen is liberated, and is cooled and collected in a gasometer. Then the process is reversed, and purified air, which has passed through a heating pipe, set in the furnace, is admitted to the retort; it oxidizes the material,

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[*] J. Soc. Chem. Ind., **1892**, 312. F. Fanta.

[†] For details, see J. Soc. Chem. Ind., **1892**, 315.

regenerating the sodium manganate, while pure nitrogen escapes. The cycle of operations is repeated indefinitely. In order that the supply of oxygen may be continuous, the plant is usually built in duplicate, so that the contents of one set of retorts is being oxidized with air, while that of the other is being deoxidized with steam.

The **Lindé refrigeration process*** employs distillation and dephlegmation of liquid air, which is made by the refrigerating effect produced when expanding compressed air from a higher to a lower pressure. At 0° C., each decrease of one atmosphere pressure causes a drop of 0.276° C., in the temperature. The specific heat of a gas increases with increasing pressure, and the cooling effect is greater the lower the temperature at which expansion takes place. With suitable apparatus for heat interchange, the action of an indefinite number of expansions is accumulated and intensified, since the cold gas from each expansion serves to precool the compressed air before the next expansion. Air at 200 atmospheres pressure enters the small copper tube (Fig. 91) † and flows down through the triple coil of the heat interchanger and finally through a copper coil submerged in the liquid air in the bottom of the rectifier. This lowers the temperature so much that the compressed air is liquefied before reaching the valve (A), by which the liquid is admitted to the top of the rectifying column which serves as a dephlegmator. Nitrogen, having a boiling point of – 195.5° C., tends to evaporate much faster than the oxygen boiling at – 182.5° C.; thus separation is effected in the column, oxygen descending as liquid, and nitrogen ascending as gas. The cold outgoing gases pass through the heat interchanger coils surrounding the tube containing the compressed air, from which they absorb heat as they escape into the atmosphere. By allowing much of the liquid oxygen to vaporize also, a residual product of 95 to 98 per cent pure is obtained.

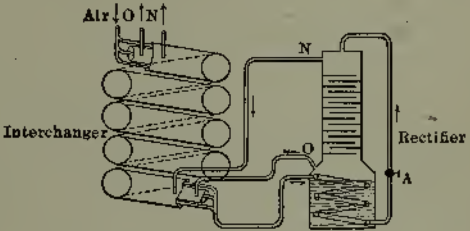

Fig. 91.

The production of oxygen by the **electrolysis of water** (with some sodium hydroxide in solution) is practised commercially in this country and abroad. About 3 cubic feet of oxygen and 6 cubic feet of hydrogen

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* J. Soc. Chem. Ind., **1895**, 984; **1903**, 695. U. S. Consular Rep., **54**, 64.

† Publications of the Lindé Air Products Company, Buffalo, N.Y.

are obtained per kilowatt-hour; each cell takes 350 ampères at 2 volts. The generator consists of an iron tank, about 3 feet diameter and 4 feet deep, whose wall serves as the cathode. Suspended from the inside of the cover is a perforated steel cylinder, serving as anode; an asbestos-cloth diaphragm surrounds the anode, separating it from the cell wall (cathode), and prevents mingling of the oxygen and hydrogen, which pass off by separate pipes from their respective compartments. Both gases are obtained very pure.

Oxygen is used for the oxy-hydrogen and oxy-acetylene flame, in melting platinum and other refractory metals; for autogenous welding and metal cutting; in the calcium light; in purifying illuminating gas; to destroy fusel oil in high wines; and in treatment of asphyxia and heart weakness. Its use has been proposed to hasten melting and refining of glass; for enriching air in the blast-furnace and steel converter; for oxidizing drying oils, and to assist the action of bleaching powder in textile work.

REFERENCES

Chemical Trade Journal, **1887**, 145.
Journal of the Society of Chemical Industry: —
1886, 568. **1889**, 82, 517. **1890**, 246. **1892**, 312. **1895**, 984. **1903**, 695. **1911**, 333. Ozone.
Chemische Industrie, **1890**, 104, 120; **1891**, 71. G. Kassner.
L'Ozone et ses Applications Industrielles. H. de la Caux. Paris, 1910.

SULPHATES

The sulphates of ammonium, magnesium, potassium, and sodium were discussed in connection with the industries to which they are related.

Ferrous sulphate, green vitriol, or **copperas,** $FeSO_4 \cdot 7\ H_2O$, is a by-product of several industries. Pyrites may be exposed to moist air until oxidation takes palce; by lixiviation, a solution of ferrous and ferric sulphates, and sulphuric acid, is obtained, which is run over scrap iron. The reaction reduces all ferric salts, and the clarified and concentrated liquor yields light green crystals $FeSO_4 \cdot 7\ H_2O$.

$$FeS_2 + H_2O + 7\ O = FeSO_4 + H_2SO_4.$$

The basic ferric sulphate from the manufacture of aluminum sulphate from shale (p. 286) yields copperas by treatment with acid and scrap iron. The " sludge acid " of petroleum refining is sometimes used for ferrous sulphate, by diluting and dissolving scrap iron in it. The acid " pickle liquors," used in foundries and wire mills for cleaning the surfaces of castings and wire, are treated with scrap iron to neutralize free acid, and yield more copperas on evaporation, than the market demands; the disposal of the excess is an industrial problem to prevent contamination of surface waters.

Wet metallurgical processes for producing cement copper (p. 616) furnish considerable copperas. Copper sulphide ores, low in copper, are weathered in heaps for several months, and frequently moistened with water. Oxidation of the sulphides forms copper and iron sulphates, and when leached the liquors run into tanks containing scrap iron; copper precipitates and ferric sulphate is reduced to the ferrous state. The solution is clarified and evaporated to crystallize.

All processes for making ferrous sulphate yield dilute solutions, which are best evaporated by over-surface heating (p. 4), to prevent oxidation. The clarified liquid is put into lead-lined tanks, in which strings or wooden rods are suspended; on these the large bluish green crystals of ferrous sulphate form. The crystals effloresce quickly when exposed to the air, and become coated with a brownish white powder of basic ferric sulphate, formed by oxidation; ultimately the entire crystal is converted to this basic salt. By adding alcohol to a ferrous sulphate solution, the salt is precipitated in fine crystals which are more stable in the air than are the ordinary kind.

Ferrous sulphate crystals have 7 molecules of crystal water; when heated to 140° C., 6 molecules of water are expelled, but the last molecule is not removed until the temperature reaches 260° C., when basic salt begins to form. At a red heat, sulphuric anhydride is given off and ferric oxide is left.

Copperas solution oxidizes quickly in the air, and a yellow precipitate of basic ferric sulphate separates. Commercial green vitriol often contains copper sulphate, and sometimes nickel sulphate; if large quantities of these impurities are present, the color is very dark, and the salt is called " black vitriol."

Ferrous sulphate is largely used as a mordant in dyeing; in the preparation of horticultural sprays; for disinfecting purposes; for the purification of water supplies; in the manufacture of ink, Prussian blue, and various pigments; and for precipitating gold from solution in metallurgical processes.

Copper sulphate, blue vitriol, or **"bluestone,"** $CuSO_4 \cdot 5\,H_2O$, is now largely obtained as a by-product in the " parting " of gold and silver with sulphuric acid. The gold and silver alloy is boiled with concentrated sulphuric acid in cast-iron pans; the silver is dissolved, the solution separated from the residue of gold, and the silver sulphate decomposed with metallic copper. Metallic silver precipitates, and copper sulphate remains in solution.

Copper sulphate is also prepared by allowing sulphuric acid to drip on scrap copper with free access of air, the copper being slowly oxidized and dissolved. Or metallic copper, contained in lead-lined tanks, may be treated with hot acid. Scrap copper is often heated red-hot in a furnace, and then sulphur is thrown in, and the door tightly closed. Cuprous sulphide is formed, which is then oxidized at a red heat by admitting air into the furnace. A mixture of copper sulphate and oxide is thus produced, which is treated with hot dilute sulphuric acid, and the solution so obtained is evaporated.

1) $2\,Cu + S = Cu_2S.$

2) $Cu_2S + 5\,O = CuSO_4 + CuO.$

3) $(CuSO_4 + CuO) + H_2SO_4 = 2\,CuSO_4 + H_2O.$

Copper sulphide ores, *chalcopyrite,* and *chalcocite,* and artificial copper mattes are sometimes converted into blue vitriol; but the ferrous sulphate formed crystallizes with the copper sulphate. Such blue vitriol is much used where iron is not injurious. The iron may be removed by roasting the salt until the ferrous sulphate is decomposed into oxide, and then dissolving in water and recrystallizing. Or the solution may be boiled with a little nitric acid or lead peroxide, until the iron is converted to the ferric state, when, by adding copper carbonate, or oxide, or barium carbonate, and boiling again, the iron precipitates.

Some copper ores contain zinc, and yield a bluestone, contaminated with zinc sulphate. The acid " dipping liquors " from copper and brass works are also used for blue vitriol, but these are generally contaminated with zinc. The hammer-scales (copper oxide), produced in rolling and working sheet copper, are often dissolved in dilute acid to form blue vitriol.

Copper sulphate forms deep blue crystals, containing 5 molecules of water. In dry air the crystals effloresce and fall to a white powder, but all the water does not escape until the mass is heated to 240° C. The anhydrous salt is a white powder, and will abstract water from alcohol or organic liquids. Bluestone is largely used as a mordant in calico printing, and in dyeing; for preparing other copper salts and pigments; in the preparation of germicides and insecticides (Bordeaux mixture, etc.), for batteries, and electrolytic baths; in metallurgy, and in most operations where a soluble copper salt is desired.

Zinc sulphate or **white vitriol**, $ZnSO_4 \cdot 7\ H_2O$, is not of very great importance. It is made by roasting zinc blende (sphalerite), or zinc-lead ores,* and leaching the mass with water or dilute sulphuric acid. Or scrap zinc is dissolved in dilute acid. The solution may be purified from copper by introducing a plate of metallic zinc, upon which the copper deposits. Iron is removed by heating the solution in the air for a considerable time, while stirring well, and then adding a small amount of zinc carbonate or oxide, to precipitate the ferric oxide.

Zinc sulphate forms colorless crystals containing 7 molecules of water, which effloresce in the air. It is very soluble in water. When heated, the crystals melt in their water of crystallization, and at 100° C., 6 molecules of water are expelled. The final molecule is driven off at 300° C., while at a red heat the anhydrous salt decomposes, leaving a residue of zinc oxide.

Zinc sulphate is used somewhat in dyeing and printing; as a disinfectant; for preserving and clarifying glue solutions; in medicine as an astringent, and in lotions; in the preparation of dryers

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* Bruno Kerl, Mineral Industry, **1895**, 83.

for "boiled oils"; and to some extent as a preservative for hides and timber.

Aluminum sulphate, $Al_2(SO_4)_3$, 18 H_2O, is extensively employed in the arts, under the name "concentrated alum." It is usually prepared from pure kaolin, or from bauxite [$Al_2O(OH)_4$, or $Al_2O_3 \cdot 2\ H_2O$], or from the hydrated alumina obtained in the cryolite soda process (p. 113) or Bayer's process (p. 283). Aluminum hydroxide, prepared from bauxite or cryolite, is almost entirely free from iron, since it is precipitated from an alkaline solution of sodium aluminate, in which the iron of the mineral is not soluble. When this hydroxide is dissolved in pure sulphuric acid, a very pure aluminum sulphate is formed.

(a). Aluminum sulphate from **clay**: — China clay, free from calcium carbonate, is calcined at a moderate heat, until nearly all of its water is expelled; then it is powdered and sifted through very fine sieves, and mixed with a little less than the theoretical quantity of sulphuric acid of 1.45 to 1.50 sp. gr., and heated with free steam to start the reaction, which soon becomes very violent. The mass swells, and quantities of steam escape, but when the reaction ceases, the swelling subsides. If it is now allowed to cool, a stonelike substance is obtained, which is employed in the arts as "alum cake." It contains all the silica and iron impurities of the clay, and usually from 2 to 3 per cent of free acid. But if the thick pasty mass is diluted with warm water while still hot, and decanted or filtered from the insoluble impurity, a solution of the sulphate is obtained, which on evaporation yields a salt containing about 0.2 per cent iron, and a trace of free acid. It is often customary to convert this solution directly into alum (p. 285), by adding the necessary alkaline sulphate.

(b). Aluminum sulphate from **bauxite**: — Bauxite is more easily decomposed by acid than is clay, but if dissolved directly, the product contains a large amount of iron. However, considerable bauxite is decomposed with acid to form a hard cake which is known in trade as "alumino-ferric cake," and is used for many purposes where iron and free acid do no harm, and a cheap source of soluble alumina is desired, *e.g.* in precipitating sewage and waste liquors from dyeworks.

But a pure sulphate is obtained by the following processes: The bauxite is roasted, powdered very fine, and mixed with calcined and finely powdered soda-ash, in the proportion of 1 molecule of Al_2O_3 to 1.1 molecules of Na_2O. If the bauxite contains much silica, more soda may be used, but the amount should not be sufficient to leave free carbonate in the product after calcination, otherwise the mass may fuse, and the solution of sodium aluminate obtained by lixiviating will be unstable. The mixture is calcined at a white heat, until all carbon dioxide and water are expelled; this requires 3 or 4 hours. The product is a porous, pale green or blue mass, which is ground and lixiviated with hot water, in a wooden tank, while stirring actively. A little caustic soda is added to the water, to prevent precipitation of alumina (see Bayer's process, below). The lixiviation must be rapid, not occupying more than 10 minutes, after which the solution of aluminate is decanted. According to Jurisch,* the liquor should be at least 35° Bé. density, and contain 170 grams Al_2O_3, and 182 grams Na_2O, per litre. Weaker solutions are said to yield a slimy precipitate of alumina, when decomposed in the next stage of the process. The liquor is quickly filtered (in a filter press), heated to 90° C., and decomposed by passing carbon dioxide into it, by which hydrated alumina is precipitated in a granular form, which is readily washed free from soda. The silica remains dissolved in the mother-liquor. The carbon dioxide may be derived from limekiln gases, or from the calcination of sodium bicarbonate.

The pure aluminum hydroxide thus made is added slowly to hot, pure, concentrated sulphuric acid, until the frothing ceases; the solution, cooled in flat lead pans, forms a crystalline mass. If an excess of alumina is used in neutralizing, basic salt results. Sulphate made thus is nearly free from iron and silica, but may contain small quantities of soda. It is used in the arts under the name of "concentrated alum." From analysis, the formula appears to be $Al_2(SO_4)_3 \cdot 20\,H_2O$, but the excess of water may be hygroscopic and not combined.

The process of J. K. Bayer † yields very pure alumina. A caustic soda liquor of 1.48 sp. gr. (47° Bé.) is digested for six hours under 4 atmospheres' pressure, at 170° C., with finely powdered bauxite, while actively stirred. The aluminum hydroxide of the bauxite dissolves to form sodium aluminate solution, having about 1 Al_2O_3 to 1.8 Na_2O. The solution is diluted to 1.20 sp. gr. (24° Bé.), filter-pressed rapidly, and then decomposed in tanks by agitating for about 72 hours, with a large excess of aluminum hydroxide. The hydroxide precipitates in crystalline form, until the proportions are about 1 Al_2O_3 to 6 Na_2O; silica and impurities remain in solution. A sufficient quantity of the milky liquid, carrying in suspension as much aluminum

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* Fabrikation von Schwefelsäure Thonerde, 52.

† Jurisch, *Ibid.*, 17–18. German patents, 43,977 (1887) and 65,604 (1892). J. Soc. of Chem. Ind., **1888**, 625.

hydroxide as was dissolved from the bauxite, is withdrawn and filter-pressed. The caustic soda liquor is again concentrated to 1.48 sp. gr. and the cycle repeated. The silica dissolved in the aluminate solution is precipitated during the digestion as an insoluble double silicate of sodium and aluminum ($Na_2Al_2Si_3O_{10} + 9\ H_2O$), and remains with the residue, together with the iron. The hydrated alumina precipitated is washed free from sodium salts, and dissolved in acid as described. It is also used for metallic aluminium (p. 638).

Another process for sulphate consists in dissolving bauxite in dilute acid, at a temperature of 90° C., with the addition of a little sodium nitrate to oxidize all the iron to the ferric state; then more bauxite, together with a little potash alum, is added. After stirring thoroughly, the whole is left for several weeks. The iron combines with some of the alumina to form a precipitate: —

$$2\ Al_2(SO_4)_3 + 2\ Fe(OH)_3.$$

(c). Sulphate from **cryolite**: — The hydrated alumina obtained in the cryolite soda process (p. 113) may be dissolved to make aluminum sulphate in the usual way. The product may contain some soda.

Another method of utilizing cryolite depends on the following reactions: —

1) $6\ NaF,\ 2\ AlF_3 + 6\ Ca(OH)_2 = 6\ CaF_2 + 2\ Al(NaO)_3 + 6\ H_2O.$
2) $2\ Al(NaO)_3 + 6\ NaF,\ 2\ AlF_3 = 2\ Al_2O_3 + 12\ NaF.$
3) $Al_2O_3 + 3\ H_2SO_4 = Al_2(SO_4)_3 + 3\ H_2O.$

Powdered cryolite is boiled with milk of lime, and the solution of sodium aluminate decanted. By boiling the aluminate liquor for a long time, with more powdered cryolite, while stirring thoroughly, the second reaction takes place; the residue is chiefly hydrated aluminum oxide, while sodium fluoride goes into solution. By boiling the latter with milk of lime, caustic soda may be obtained as a by-product.

$$2\ NaF + Ca(OH)_2 = CaF_2 + 2\ NaOH.$$

By evaporating an aluminum sulphate solution until very concentrated, and then cooling, a solid cake of the salt having a crystalline structure is obtained; its composition corresponds to

$$Al_2(SO_4)_3 \cdot 20\ H_2O.$$

It is difficult to obtain single crystals, but the usual formula assigned to them is $Al_2(SO_4)_3 \cdot 18\ H_2O$. The commercial product, however, never corresponds exactly to this formula. As now prepared, it contains but little free acid, or excess of alumina (basic salt), and only a minute trace of iron. It should contain 14 to 14.5 per cent Al_2O_3, and dissolve readily in water to form a clear solution, *i.e.* no basic salt should be present. About 0.5 per cent free acid and 0.01 to 0.1 per cent Fe_2O_3 are the average content of commercial samples. Since it may now be had of great purity, aluminum sulphate has largely replaced alum in the arts. It is extensively used as a mordant in dyeing; in preparing size for paper; for making alum and aluminum salts (red liquor, etc.); in tawing skins; for precipitating sewage or coloring matter from water; and, in general, for all purposes where alum was formerly used.

ALUM

An **alum** is a double sulphate of a univalent alkali metal and a hexad metallic radical of the form $(R_2)\overset{=}{\underset{=}{=}}$, crystallized with 24 molecules of water. The general formula is therefore

$$\cdot\, M_2SO_4,\ R_2(SO_4)_3 \cdot 24\ H_2O,$$

or, as it is more frequently written, $MR(SO_4)_2 \cdot 12\ H_2O$. The alkali metal may be sodium, potassium, ammonium, lithium, cæsium, or rubidium. The hexad radical contains aluminum, chromium, iron, or manganese. In the majority of alums the essential part is aluminum sulphate, but since this does not crystallize well alone, it has, until recently, been difficult to obtain it pure enough for some purposes. But the addition of an alkali sulphate forms alum, which crystallizes beautifully and is very pure, while the alkali sulphate itself has no injurious action in most cases where aluminum sulphate is used. But since "concentrated alum" (p. 283) can now be had very pure, it is generally preferred, because of its greater strength and solubility.

All alums crystallize, with the same number of molecules of water, in the regular system, either as octahedrons, or as cubes. They are all isomorphous, and a crystal of one kind of alum will continue to grow by accretion, if placed in a solution of another alum. Alum crystallizes from solution very perfectly, and forms exceedingly pure crystals, even from impure solutions.

Alum occurs in nature in small quantities, produced by the action of volcanic gases on rocks consisting of potash-aluminum silicates; also in combination with iron and aluminum hydroxides in the mineral **alunite**, or alum stone, K_2SO_4, $Al_2(SO_4)_3$, $4\ Al(OH)_3$, also formed by volcanic action. Other sources are alum slates and shales, clay, bauxite, and cryolite.

Alunite, or alum stone, is insoluble in water. It is calcined in heaps, or in small shaft kilns, at about 500° C., and the mass is then exposed to the weather for several months, being moistened from time to time. The calcination converts the iron and aluminum hydroxide into insoluble oxides, and the weathering forms alum in the mass, which is dissolved by lixiviation, and recrystallized. The alum thus obtained is basic, and crystallizes in cubes; owing to imperfect settling of the liquors before crystallization, some iron oxide is enclosed, giving the crystals a red color. This iron is, however, quite insoluble, and, no free acid being present, the alum yields a pure, neutral solution, and is especially desired for some purposes. It is made at Tolfa, near Rome, and so is called *Roman alum.* An imitation is made by coloring alum crystals derived in other ways, with brick dust, or with iron oxide (Venetian red). For further references on alunite see p. 158.

Alum slates or shales are mixtures of iron pyrites, aluminum silicates, and bituminous matter. By exposure to the weather, the pyrites is oxidized to ferrous sulphate and sulphuric acid, and these react with the aluminum silicate to form aluminum sulphate. Basic ferric sulphate is also formed. The oxidation can be greatly hastened by roasting the shale before weathering it, but the temperature must not be high enough to drive off the sulphur. After weathering, the mass is systematically lixiviated, and a solution of aluminum sulphate, having a specific gravity of about 1.16, containing some calcium and iron sulphates, comes from the leach tanks. This is clarified by settling, and some of the calcium and basic ferric sulphates deposit. The solution is evaporated in lead or iron pans by surface heating with direct flame, until ferrous sulphate crystallizes on cooling, and then the mother-liquor containing the aluminum sulphate is further concentrated to 1.40 sp. gr. During this evaporation, more calcium sulphate and a basic ferric sulphate separate. Scrap iron is generally placed in the vessel during concentration, to convert the ferric sulphate into the basic salt, and to reduce the destructive action on the pan. The hot solution is decanted from the sediment, and mixed with potassium or ammonium sulphate in exact amount to form the alum. By agitating the liquid during the cooling, very fine crystals of alum, called "alum meal," separate.

If the aluminum sulphate solution contains much iron, as is generally the case when working on a large scale, it is often the practice to add potassium chloride to form the alum. By decomposing the iron sulphates, this forms potassium sulphate in the solution, and, at the same time, converts the iron into the very soluble ferric and ferrous chlorides, which remain in the solution when the alum separates. But with a pure solution of aluminum sulphate, this causes loss by converting part of the aluminum into the very soluble aluminum chloride: —

$$4\ Al_2(SO_4)_3 + 6\ KCl = 3\ \{K_2SO_4,\ Al_2(SO_4)_3\} + 2\ AlCl_3.$$

The alum meal is washed with cold water in a centrifugal machine and recrystallized. It is sold both in the crystallized and in the powdered form.

The manufacture of alum from clay, bauxite, or cryolite involves the preparation of a pure solution of aluminum sulphate by methods already given, and the addition of the exact quantity of alkali sulphate to form the alum.

Blast furnace slag has been proposed as a source of alum. It is decomposed with hydrochloric acid, and the aluminum chloride solution is decomposed with calcium carbonate; the aluminum hydroxide so obtained is dissolved in sulphuric acid. The process is not successful, however.

"**Neutral alum**" is made by adding sodium or potassium carbonate, or caustic soda to an alum solution, until a slight precipitate remains, even after vigorous agitation. After filtering, cubical crystals of the neutral alum can be obtained, but, as a rule, the neutral solution is made by the user, and is not crystallized. Neutral alum is much used in mordanting, because of the great readiness with which it deposits alumina on the fibre.

The most important alums of commerce are **potassium alum,** $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$, and **ammonium alum**

$$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O.$$

The latter is less soluble than the potash salt, but in all other respects they are quite similar. Both are stable in the air.

Sodium alum, $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$, is very soluble in water and difficult to purify. Moreover, the crystals effloresce on exposure to the air; in this condition, they are sometimes sold as "porous alum."

When heated, alum loses water and some sulphuric acid, and falls to a white powder, "burnt alum," which is difficultly soluble in water. This is used occasionally as a caustic in medicine.

The chief uses of common alum are as a mordant in dyeing; in preparing size for paper-making; in tawing skins; in making pigment lakes; for clarifying turbid liquids, and precipitating sewage; and for hardening plaster of Paris casts, and other articles.

Besides the common alums of trade, containing aluminum sulphate as a basis, two others, iron alum and chrome alum, are also employed in the arts to some extent.

Iron alum, which may be either $(NH_4)_2SO_4, Fe_2(SO_4)_3 \cdot 24\ H_2O$, or $K_2SO_4, Fe_2(SO_4)_3 \cdot 24\ H_2O$, is made by oxidizing a copperas solution to form ferric sulphate, adding the proper quantity of alkali sulphate, and cooling below 10° C. It forms pale violet crystals, which are rather unstable, efflorescing and oxidizing in the air, forming basic ferric salt. Iron alum is chiefly used as a mordant.

Chrome alum, $K_2SO_4, Cr_2(SO_4)_3 \cdot 24\ H_2O$, is largely produced as a by-product in the manufacture of alizarine. A mixture of potassium bichromate and sulphuric acid is employed to oxidize anthracene ($C_{14}H_{10}$) to anthraquinone ($C_{14}H_8O_2$), from which the alizarine is produced. The effect of the reducing action of the organic body on the bichromate mixture is to form potassium and chromium sulphates in the solution in proper proportion to unite in chrome alum: —

$$C_{14}H_{10} + K_2Cr_2O_7 + 4\ H_2SO_4 = C_{14}H_8O_2 + K_2SO_4, Cr_2(SO_4)_3 + 5\ H_2O.$$

Chrome alum forms deep violet crystals, which effloresce on exposure to the air. It is used as a mordant; and in tawing skins, especially in certain chrome tannage processes.

REFERENCES

Die Fabrikation des Alauns, des Bleiweisses und des Bleizuckers. Dr. F. Jünemann, Leipzig, 1882. (Hartleben.)
Die Fabrikation von schwefelsäure Thonerde. K. W. Jurisch, Berlin, 1894.
Journal of the Society of Chemical Industry: —
  1882, 124. Newlands. **1883**, 482. Kynaston. **1886**, 16. Beveridge. **1888**, 625. (Bayer's Patent for Alumina Hydrate.) **1892**, 4 and 321.
Chemical News, **42**, 191 and 202.
Mineral Resources of the United States. **1893**, 159; **1903**, 265; **1904**, 285.
Bulletin No. 315, U. S. Geological Survey, **1906**, 215.

CYANIDES

Cyanides are produced on a commercial scale by several methods, and a large number of patents which have been put into practice are described in chemical literature. Much energy and money have been expended in fruitless search for processes of cheap production of cyanides. In 1843 Langlois * showed that by passing ammonia gas over white-hot coke or charcoal, some ammonium cyanide is formed. This reaction has been the base of a patent to Lange and Emanuel,† in which the yield is improved by mixing hydrogen and nitrogen or deoxidized air with the ammonia: —

$$2\ NH_3 + 2\ C + 2\ H = C_2(NH_4)_2.$$
$$C_2(NH_4)_2 + 2\ N = 2\ CN(NH_4).$$

Cyanogen is present in crude coal gas and in some large gas works it is recovered by Bueb's process.‡ The gas is led direct from the tar extractor into a scrubber machine containing a ferrous sulphate solution. The hydrogen sulphide and ammonia in the gas react with the iron salt to form ferrous sulphide, which in turn precipitates the cyanogen as an insoluble salt of iron-ammonium cyanides; this is drawn from the machine as a black mud suspended in the liquor, and is filter-pressed. The reactions are: —

$$FeSO_4 + H_2S + 2\ NH_3 = 2\ FeS + (NH_4)_2SO_4.$$
$$2\ FeS + 6\ NH_3 + 6\ CN + 3\ H_2O + 5\ O = (NH_4)_2Fe_2(CN)_6 + 2(NH_4)_2SO_4.$$

The solid cake is then decomposed with lime to form calcium ferrocyanide, which, in solution, is drawn off from the sludge and decomposed with potassium carbonate to yield potassium ferrocyanide. The ammonia is also recovered by distillation. If the ammonia is first removed from the crude gas by scrubbing, it is necessary to add alkali (Na_2CO_3) to the copperas liquor in the cyanogen scrubber. Foulis § process is based on this, a sodium ferrocyanide being formed.

The recovery of cyanides from the spent oxide from the purifiers is described on page 291.

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* Berzelius Jahresbericht, **22**, 84.

† German Pat. No. 100,775.

‡ German Pat. No. 122,280.

§ J. Soc. Chem. Ind., **1893**, 511.

Bunsen and Playfair's process * for making cyanides by heating barium carbonate with powdered charcoal in an atmosphere of dry nitrogen was not a commercial success. It involved the reaction: —

$$BaCO_3 + 4\ C + 2\ N = Ba(CN)_2 + 3\ CO.$$

They also showed that the injection of heated air into a furnace containing carbon, alkaline earth oxides, and heavy metals produces cyanide; thus the gases from blast furnaces contain these materials, and considerable attention has been given to recovering cyanides from the gases; but as yet there has been no general introduction of these methods.

Raschen's process † is based on the oxidation of sulphocyanide by means of nitric acid and atmospheric air. It is a continuous process, involving the following reactions: —

$$NaCNS + 2\ HNO_3 = HCN + NaHSO_4 + 2\ NO.$$
$$2\ NO + H_2O + 3\ O = 2\ HNO_3.$$

The apparatus consists of a series of earthenware jars, connected by earthenware pipes and so arranged that the liquor flows from near the middle of each jar, and passes to the bottom of the next. The gases from the decomposition contain prussic acid and much nitric oxide; they are scrubbed with water to remove the nitrogen oxides, and then the prussic acid is absorbed by caustic alkali and the solution evaporated in vacuum pans to prevent decomposition.

Ammonium sulphocyanide (thiocyanate), NH_4SCN, is sometimes prepared by Tscherniak and Günzburg's modification of Gelis' process.‡ This depends on the following reactions: —

1) $CS_2 + 2\ NH_3 = NH_4S_2CNH_2$. (Ammonium dithiocarbamate.)
2) $NH_4S_2CNH_2 = NH_4SCN + H_2S$.

Carbon disulphide and ammonium hydroxide (0.91 sp. gr.), in proper proportion for reaction (1), are heated in an autoclave to 125° C., while stirring actively. The steam is then cut off, but the stirring continued until the pressure rises to 15 atmospheres. This completes the first reaction, and the contents of the autoclave are

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* Rep. British Assoc., **1845**. J. pr. Chem., **42** (1847), 397.

† U. S. Pat. No. 567,552. Eng. Pat. No. 21,678 (1895).

‡ Dingler's Polytechnisches Journal, **245**, 214.

blown off into a still, which is heated to 110° C., at which point the ammonium dithiocarbamate is decomposed. The products of distillation are passed through condensers and scrubbers to collect volatile ammonium salts and carbon disulphide, while the hydrogen sulphide is conducted into a gasometer. The liquid in the still contains ammonium sulphocyanide, and is evaporated in tin vessels, and crystallized.

Sometimes lime and manganese peroxide are added to assist the reaction in the autoclave, in which case calcium sulphocyanide is formed: —

$$2\,CS_2 + 2\,NH_3 + MnO_2 + CaO = Ca(SCN)_2 + MnS + S + 3\,H_2O.$$

Ammonium sulphocyanide and potassium ferrocyanide are now largely obtained from the spent iron oxide from the purification of illuminating gas. The spent oxide is first lixiviated with warm water (60° C.), until the liquor has a density of from 1.07 to 1.085. The solution, containing ammonium sulphocyanide and other ammonium salts, is evaporated to 1.2 sp. gr., and cooled, when the associated salts (ammonium sulphate, etc.) crystallize. The mother-liquor is further concentrated, and impure crystals of the sulphocyanide separate, which are purified by recrystallization. Ammonium sulphocyanide is also obtained from gas-liquor by treating the non-volatile residue from the steam distillation (see Ammonia) with copper and iron sulphates, whereby cuprous sulphocyanide is formed. This is washed, and treated with ammonium sulphide, forming cuprous sulphide and ammonium sulphocyanide. The latter is then extracted with water.

Ammonium sulphocyanide is very soluble in water and in alcohol. It is used as a source of other sulphocyanides, and in dyeing, to prevent the injurious action of iron on the color.

The residue from the lixiviation is mixed with quicklime (which is slaked by the moisture in the damp mass), and heated by steam in closed vessels to 100° C. The lime decomposes the ferric ferrocyanide and the double iron-ammonium cyanides, setting free ammonia gas, which is absorbed in scrubbers, and forming calcium ferrocyanide, which is obtained by lixiviating the mass. The solution of calcium ferrocyanide is evaporated, and treated with the calculated amount of potassium chloride to form the difficultly soluble calcium-potassium ferrocyanide, $CaK_2Fe(CN)_6$. This is separated from the mother-liquor, washed, and decomposed with potassium carbonate to form potassium ferrocyanide.

The reactions are: —

1) $Fe_4\{Fe(CN)_6\}_3 + 6\ Ca(OH)_2 = 3\ Ca_2Fe(CN)_6 + 4\ Fe(OH)_3$.

2) $(NH_4)_3Fe_3\{Fe(CN)_6\}_3 + 6\ Ca(OH)_2 =$
$3\ Ca_2Fe(CN)_6 + 3\ Fe(OH)_3 + 3\ NH_3 + 3\ H_2O$.

3) $Ca_2Fe(CN)_6 + 2\ KCl = CaK_2Fe(CN)_6 + CaCl_2$.

4) $CaK_2Fe(CN)_6 + K_2CO_3 = K_4Fe(CN)_6 + CaCO_3$.

Potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3\ H_2O$, also called **yellow prussiate of potash**, is made by fusing together potassium carbonate, iron borings, and nitrogenous organic matter of any kind (horn, hair, blood, wool waste, and leather scraps).* The potash is fused in a shallow cast-iron pan, set in a reverberatory furnace, and the organic matter, mixed with from 6 to 8 per cent of iron borings, is stirred in, in small portions at a time, until about $1\frac{1}{4}$ parts of the mixture for each part of potash have been added. The temperature must be kept high enough to keep the mass perfectly liquid, but not hot enough to volatilize the cyanogen salts. The reaction is violent at first, and when the liquid remains in quiet fusion the process is ended, and the melt is ladled into iron pans to cool. The mass, containing a number of substances (KCN, K_2CO_3, K_2S, FeS, metallic iron, carbon, etc.), is broken up into lumps the size of an egg, and digested with water at 85° C. for several hours. During this process reactions take place between the potassium cyanide and iron sulphide, by which the ferrocyanide is formed: —

$$6\ KCN + FeS = K_2S + K_4Fe(CN)_6.$$

Liebig explained the reactions during the fusion as follows: part of the carbon and nitrogen of the organic matter combine to form cyanogen $(CN)_2$, while some of the potash is reduced by the excess of carbon to metallic potassium, which at once unites with the cyanogen to form potassium cyanide. The sulphur in the organic matter combines with the iron, forming ferrous sulphide. Finally, on lixiviating, the formation of the ferrocyanide takes place. The solution is evaporated in iron pans by the waste heat of the furnace, and clarified while hot; on cooling, the crude ferrocyanide crystallizes, and is purified by recrystallization. The mother-liquors yield more impure salt on further evaporation.

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* The organic refuse is sometimes partially charred in retorts, by which much ammonia is driven off and saved. But the yield of ferrocyanide is then less, since the nitrogen content of the char is small.

The calcium ferrocyanide liquor from gas purification (p. 289) yields potassium ferrocyanide by treatment with potassium carbonate, filtering, and evaporation to crystallization.

Potassium ferrocyanide forms splendid large lemon-yellow crystals, having 3 molecules of crystal water, which it gives off at 100° C., and is converted to a white powder. It is not poisonous. It is largely used for making Prussian blue; in calico printing, and in dyeing; for case-hardening iron; for making potassium cyanide and ferricyanide; and to a small extent in explosives, and as a chemical reagent.

Barium sulphocyanide, $Ba(SCN)_2$, is made by heating ammonium sulphocyanide with barium hydroxide solution, under slight pressure. Ammonia distils off, and the liquid is evaporated to yield the barium salt, $Ba(SCN)_2 \cdot 2\ H_2O$. This is generally used for making potassium and aluminum sulphocyanides, KSCN and $Al(CSN)_3$, which are used in textile dyeing and printing.

Potassium ferricyanide, red prussiate of potash, $K_3Fe(CN)_6$, is usually made by passing chlorine gas into a solution of the ferrocyanide, until ferric chloride no longer forms a precipitate, only producing a brown color in the liquid. It may also be made by exposing the dry powdered ferrocyanide to chlorine until a test portion, dissolved in water, gives nothing but a brown color with ferric chloride.

$$2\ K_4Fe(CN)_6 + 2\ Cl = 2\ KCl + 2\ K_3Fe(CN)_6.$$

Excess of chlorine must be avoided, since this forms a dirty green precipitate (Berlin green) in the solution, which cannot be removed by filtering.

Lunge * recommends boiling the solution of ferrocyanide with lead peroxide, while passing a stream of carbon dioxide through the liquor: —

$$2\ K_4Fe(CN)_6 + H_2O + O = 2\ K_3Fe(CN)_6 + 2\ KOH;$$

but the final reaction may be written: —

$$2\ K_4Fe(CN)_6 + PbO_2 + 2\ CO_2 = 2\ K_3Fe(CN)_6 + PbCO_3 + K_2CO_3.$$

An excess of carbon dioxide is necessary to prevent decomposition of the ferricyanide by the lead oxide and alkali.

A very good product is obtained by the action of potassium per-

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* Dingler's Polytechnisches Journal, **238**, 75.

manganate on a mixture of calcium and potassium ferrocyanide solutions: —

$$3\ Ca_2Fe(CN)_6 + 7\ K_4Fe(CN)_6 + 2\ KMnO_4 = 10\ K_3Fe(CN)_6 + 6\ CaO + 2\ MnO.$$

The calcium and manganese hydroxides formed are removed from the solution by carbon dioxide, and the ferricyanide purified by crystallization.

Recently, anodic oxidation of a ferrocyanide solution, to form the ferricyanide, has been introduced.

Potassium ferricyanide crystallizes in blood-red prisms, without crystal water, and is very soluble, forming a solution of an intense yellow color. With ferrous salts, it gives the blue pigment, *Turnbull's blue*. With ferric salt, it gives a brown coloration, but no precipitate. Its solution, with caustic potash, is a powerful oxidizing liquid, and as such is used in calico printing for a "discharge" on indigo and other dyes. It also forms part of the sensitive coating for "blue print" papers. It has been recommended for use with the potassium cyanide solution in gold extraction.

Potassium cyanide, KCN, is generally made by fusing the ferrocyanide with potassium carbonate, until the evolution of gas ceases. The following is the reaction: —

$$K_4Fe(CN)_6 + K_2CO_3 = 5\ KCN + KCNO + CO_2 + Fe.$$

The metallic iron separated sinks to the bottom of the crucible, and the fused mixture of cyanide and cyanate is run off. The addition of powdered charcoal reduces part of the cyanate to cyanide. The product is pure enough for many purposes. The cyanate, which is sometimes injurious, may be reduced by the action of metallic zinc or sodium, or the cyanide may be extracted with alcohol, acetone, or carbon disulphide.

By fusing the ferrocyanide with metallic sodium, a mixture of sodium and potassium cyanides is obtained, which is extensively employed in the arts as "potassium cyanide." The so-called "cyansalt" is made by fusing the ferrocyanide with sodium carbonate; this is cheaper than the pure potassium salt.

Potassium cyanide is also made by fusing the dry ferrocyanide in closed crucibles, until nitrogen ceases to be given off. Carbide of iron is formed, and sinks to the bottom of the crucible, if the fusion is allowed to stand for a considerable time. But the separation is imperfect, and the product is usually dissolved in alcohol or acetone, and the clarified solution heated in a still to recover the solvent. The product is then heated until it fuses, and when cold, it forms a white, transparent mass. Air must be carefully excluded during the whole process, to prevent the formation of cyanate. The reaction is · —

$$K_4Fe(CN)_6 = 4\ KCN + FeC_2 + N_2.$$

But the product is not entirely free from potassium carbonate, since it is practically impossible to evaporate a cyanide solution without some decomposition and escape of the weak hydrocyanic acid. The caustic potash thus formed then combines with carbon dioxide from the air. Water cannot be used to leach the iron carbide residue, since the potassium cyanide in solution at once recombines with the iron to form ferrocyanide again.

Potassium cyanide is made from the sulphocyanide, by extracting the sulphur with zinc or lead.* The zinc is melted in a graphite vessel, and charcoal powder is spread over its surface. The sulphocyanide is stirred into the fused metal until the mass becomes a thick paste, when it is allowed to cool. It is then systematically lixiviated in tanks similar to Shank's apparatus (p. 97.) Any alkali sulphide is precipitated by adding lead cyanide. The solution is evaporated in vacuum, and yields an impure product, containing cyanate and double zinc-potassium cyanide.

Beilby's process † consists in passing dry ammonia gas through a fused mixture of potassium carbonate and carbon. A little potassium cyanide is added to increase the fusibility of the charge. The process is conducted in a covered cast-iron pot, or in a vertical retort having revolving rakes to stir the charge, and the fumes pass to a dust chamber. When the desired percentage of potassium cyanide has been reached in the fused mass, the charge is tapped off through a strainer to retain suspended carbon and run direct into drums. A similar method by Siepermann is worked in Germany.

Castner's process involves the passing of dry ammonia gas over metallic sodium at a temperature of 350° C., and immediately running the sodamide thus formed through layers of red-hot charcoal; or a fusion of sodium cyanide and metallic sodium is mixed with powdered charcoal, and ammonia is passed through it.

$$NH_3 + Na = NaNH_2 + H.$$

$$NaNH_2 + C = NaCN + 2\ H.$$

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* J. Soc. Chem. Ind., **1892**, 14.

† *Ibid.*, **1892**, 747, 1004. Eng. Pat. No. 4820, **1891**.

Potassium cyanide comes in commerce as white lumps or powder, very soluble in water and having alkaline reaction. It smells somewhat like bitter almond oil, owing to the prussic acid liberated from it by the action of carbon dioxide and moisture in the air. On standing, or when warmed, its aqueous solution decomposes, yielding ammonia and potassium formate: $KCN + 2\ H_2O = NH_3 + HCOOK$. When heated with reducible substances, it has strong reducing properties; hence its use as a flux in assaying and metallurgy. It is extensively used in electroplating solutions, forming soluble double cyanides with gold, silver, copper, and other metals, in which the metal-ion concentration is very small, thus giving favorable conditions for a good deposit. Its largest use is for the recovery of gold from low-grade ores, and tailings of other reduction processes (p. 631). A weak solution is used to dissolve the gold, forming aurous potassium cyanide, $AuCN \cdot KCN$. Formerly it was employed in photography to "fix" the image of negatives and prints, but has now been displaced by sodium thiosulphate ("hypo"). Potassium cyanide is extremely poisonous, both when taken internally and when introduced into the blood directly.

The commercial salt usually contains cyanate and carbonate, and is sold in several grades; the pure potassium salt contains about 40 per cent of cyanogen, while sodium cyanide contains about 53 per cent cyanogen, thus an impure potassium cyanide containing sodium cyanide may, by analysis based on the cyanogen content, appear to be 100 per cent pure, or even higher, if estimated as KCN. Commercial grades may assay as low as 65 per cent, but 95 to 98 per cent is customary.

REFERENCES

The Cyanide Industry. R. Robine and M. Lenglen. Trans. by J. A. LeClerc, New York, 1906.
Coal Gas Residuals. Frederick Wagner, New York, 1914. (McGraw-Hill Co.)

Carbon disulphide, CS_2, may be made by passing sulphur vapor over coke or charcoal, at a red heat (higher temperatures are not necessary). This was formerly done in iron or fire-clay retorts * heated from without, but destruction of the retorts was rapid. An improved apparatus (Fig. 92), devised by Taylor,† makes use of electrical heating, which localizes the heat within the retort and makes it possible to keep the walls relatively cool, thus decreasing the wear and tear. Sulphur is put into the chamber (Z) and partly surrounds the carbon electrodes (E). Fragments of coke (J) fill the space between the electrodes and are fed to the furnace through (K, K), thus maintaining the continuity of electrodes. The shaft of the furnace is filled through (X) with charcoal ‡ (Y). Crushed sulphur is fed through (V, V) and (R), filling the chambers (O) and (U). An alternating current is applied through the electrodes, the sulphur in (Z) melts, and rising around the electrodes cuts off the contact more or less, and the furnace is partly self-regulating. The heat zone is at the top of the melted sulphur layer, and the vapor rises through the charcoal (Y), which has become sufficiently hot to form carbon disulphide, the vapor passing through (P) to the condensers. The furnaces are 41 feet high by 16 feet in diameter.

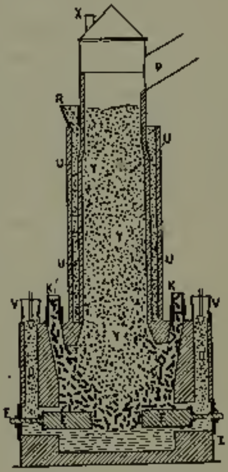

Fig. 92.

The crude carbon disulphide is impure and has a very offensive odor. It is purified to remove hydrogen sulphide, free sulphur, etc., by redistillation in a steam-heated still with a little caustic soda, or anhydrous copper sulphate, in the still; or by washing with limewater, followed by redistillation over a solution of lead acetate.

Carbon disulphide is a pale yellow, or colorless, heavy, mobile liquid, having a fetid odor when impure, boiling at 46° C., and ex-

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* J. Soc. Chem. Ind., **1889**, 93.

† Trans. Am. Electro. Chem. Soc., **1** (**1902**), 115; **2** (**1902**), 185. J. Soc. Chem. Ind., **1902**, 353, 979, 1236.

‡ Necessary to secure rapid reaction with the sulphur.

tremely volatile at ordinary temperatures. Its vapors inflame at 149° C., are very heavy, and are poisonous when breathed. It is sent to market in sheet iron cans, or drums, and is regarded as dangerous freight because of its extreme volatility, and the explosive nature of its vapor when mixed with air. When burned, it produces large quantities of suffocating gases (CO_2, SO_2). It is only slightly soluble in water, but mixes well in all proportions with ether, benzene, alcohol, and many oils. It dissolves sulphur, phosphorus, iodine, camphor, wax, tar, resins, rubber, and nearly all oils and fats. Hence its use as a solvent and extractive agent is extensive. It is also used as a disinfectant; as a germicide and insecticide in agriculture, and in museums and herbariums; in refrigerating machines; for exterminating moles, rats, woodchucks, and other burrowing animals; in the manufacture of rubber cement; in making cyanides and carbon tetrachloride; and in organic preparation work.

CARBON TETRACHLORIDE

Carbon tetrachloride is made by passing a mixture of carbon disulphide vapor and chlorine through a red-hot porcelain tube.* A mixture of sulphur chloride, S_2Cl_2, and carbon tetrachloride results, which is treated with milk of lime, and digested with potash, and the tetrachloride distilled. Or dry chlorine may be led into carbon disulphide containing a little iodine in solution.† The tetrachloride is distilled off, and washed with alkali, to remove iodine and sulphur chloride.

$$CS_2 + 6\,Cl = CCl_4 + S_2Cl_2.$$

Carbon tetrachloride is a heavy, colorless liquid, boiling at 76° C. It is a good solvent for many substances, and may be used instead of chloroform or carbon disulphide for extractions and is less poisonous than the latter. At temperatures but little above its boiling-point, it dissociates and hydrolyzes in the presence of water, forming chlorine and hydrochloric acid. This limits its uses as a solvent. It is not inflammable and is used in some types of fire-extinguishers.

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* Kolbe, Annalen der Chemie und Pharmacie, **45**, 41; **54**, 145.

† Lever and Scott, English Patent No. 18,990, **1889**.

MANGANATES AND PERMANGANATES

Sodium manganate, Na_2MnO_4, is made by mixing sodium nitrate or caustic soda solution with powdered pyrolusite, or manganese oxides, evaporating to dryness, and calcining the mass at a red heat, with access of air, in shallow vessels. The following is the reaction involved: —

$$MnO_2 + 2\ NaOH + O = Na_2MnO_4 + H_2O.$$

The product of the fusion is a dull green, porous mass, which, if lixiviated, yields a green solution of the manganate. But this is unstable, and if exposed to the air, or treated with an acid, or boiled, the manganate is converted into permanganate: —

$$3\ Na_2MnO_4 + 2\ H_2O = 2\ NaMnO_4 + 4\ NaOH + MnO_2.$$

In alkaline solution, however, the manganate is more stable.

Sodium manganate is a powerful oxidizing agent, and is used as a disinfectant. It is also converted to the permanganate, and sold in solution as " Condy's liquid " for disinfecting purposes. Sodium permanganate does not crystallize well.

Potassium manganate, K_2MnO_4, is very similar to the sodium salt, and is made in the same way. It is chiefly used in preparing the **permanganate,** $KMnO_4$, which crystallizes very well. This, being easily purified, and stable when crystallized, is the most important permanganate of commerce. It was formerly made by decomposing potassium manganate with sulphuric acid, carbon dioxide, or chlorine, followed by recrystallization.

$$3\ K_2MnO_4 + 2\ H_2SO_4 = 2\ KMnO_4 + 2\ K_2SO_4 + MnO_2 + 2\ H_2O.$$

$$3\ K_2MnO_4 + 2\ CO_2 = 2\ KMnO_4 + 2\ K_2CO_3 + MnO_2.$$

$$2\ K_2MnO_4 + Cl_2 = 2\ KMnO_4 + 2\ KCl.$$

It is now made by anodic oxidation of the manganate (made as above) in alkaline solution, the cell having a porous diaphragm: —

$$2\ K_2MnO_4 + O + H_2O = 2\ KOH + 2\ KMnO_4.$$

The permanganate crystallizes and settles to the bottom of the anode compartment, from which it is " fished " out at intervals. The caustic potash formed migrates to the cathode, whence it is continuously removed and returned to the manganate fusion. By this process no foreign substances are introduced, and the conversion of the manganate to permanganate is complete.

Potassium permanganate forms deep purple, prismatic crystals, which dissolve in 16 parts of cold water. The solution has a powerful oxidizing action, and can only be filtered on glass-wool or asbestos. When mixed with organic matter, the dry powder is subject to spontaneous combustion, and forms explosive mixtures with easily oxidizable substances. It is used as a disinfectant; in bleaching and dyeing; for coloring wood a deep brown; for purifying ammonia and carbon dioxide gases; and in medicine.

PART II

ORGANIC INDUSTRIES

DESTRUCTIVE DISTILLATION OF WOOD

Wood consists mainly of cellulose $(C_6H_{10}O_5)_n$, with its incrusting layer of *lignin*, and of sap, containing water, resins, tannins, coloring matter, and mineral salts. Air-dried wood contains 15 to 20 per cent of moisture. When heated in closed retorts, away from the air, the cellulose and ligneous matter decompose, after the moisture is expelled, and a complex series of reactions occurs,* by which a great number of substances are formed. The crude products are gases, thin liquids, viscous liquids or tar, and charcoal. When wood is carbonized in pits (p. 35), the volatile products go to waste; by the use of retorts, the valuable liquid distillates and tar are saved; the gases evolved are mainly hydrogen, methane, ethane, ethylene, carbon monoxide, and carbon dioxide; they have no value for illuminating, and are burned under the retorts, thus economizing fuel.

When wood is heated in retorts, the moisture is driven out, but no decomposition occurs until the temperature approaches 160° C.; between 160° and 175° C., a thin, watery distillate, called "**pyroligneous acid,**" is formed; above 275° C., the yield of gaseous products becomes marked, and between 350° and 450° C., liquid and solid hydrocarbons are principally formed. Above this last temperature, little change occurs, and charcoal, containing the mineral ash, remains in the retort.

The pyroligneous acid contains the important distillates, methyl alcohol and acetic acid, together with acetone, methyl acetate, phenols, ketones, and other substances. The tar contains aromatic hydrocarbons and paraffines. Its most valuable constituent is the creosote oil, containing guaiacol, creosol, and other phenols of high molecular

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* Zeit. angew. Chem., **1909** (**22**), 1205.

weight. A comparatively small amount of phenol or carbolic acid is present, however.

The proportion of gaseous products to liquid distillate and charcoal is affected by the method of heating; rapid heating to a high temperature increases the quantity of gas; by distillation at a low temperature, the yield of pyroligneous acid, tar, and charcoal is larger. The variety of wood used affects the amount of acid and tar; deciduous trees, especially birch, oak, and beech, are preferred; coniferous woods yield less acid, but afford a tar containing much resin and turpentine. The yield of acid and tar is increased by the rapid removal of the vapors from the retort.

Wood is distilled in various kinds of kilns or retorts. If charcoal is the only product in view, the carbonization may be done in "pits" or kilns (p. 35), and the volatile products go to waste. Masonry kilns of large capacity (15 to 90 cords at a charge) are often used; the necessary heat may be derived from combustion of part of the charge itself, or from an external fire whose combustion gases pass into the kiln, or through flues in its walls.

When the volatile products are to be saved boiler-plate iron retorts, externally heated, are employed; these may be either stationary or movable, and of large or small capacity. Small horizontal cylinders (Fig. 93,* A), holding about 1 or 1½ cords at a charge, are usually set two in a bench, over a common furnace. Each retort connects with a separate condenser (C) by the copper pipe (B); a pipe (D) carries the uncondensed gases to the grate where they are burned under the retorts. The wood, cut to proper length, is rapidly filled into the retort, which is still hot from the previous charge, the door is closed and luted and distillation begins at once. After some 12 hours, the hot charcoal is rapidly drawn into an iron box to cool out of contact with the air, and the retort at once recharged.

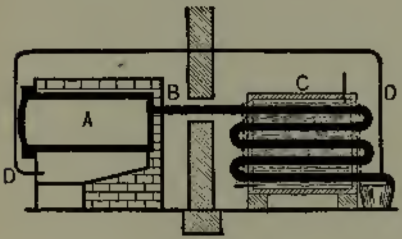

FIG. 93.

For larger output, horizontal **oven-retorts** (Fig. 94) are used. These are rectangular iron boxes, into which several steel cars, each loaded with 2 to 4 cords of wood, are run at one time, and the carbonization carried on for 24 hours. Thus charges of 10 to 20 cords of wood at a time are expeditiously handled. When carbonization is finished,

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* J. Soc. Chem. Ind., **1897**, 667 and 722 (M. Klar).

the doors at each end of the retort are opened, and a string of newly loaded cars pushed in, which also shoves out the cars carrying the hot charcoal from the previous charge, into a large iron box or cooler, placed directly opposite, where they cool out of contact with the air. This transfer and introduction of a new charge requires only a few minutes, so these retorts are practically continuous in action and the loss of charcoal by combustion is small. This system consumes less fuel, and has lower labor and repair costs for a given output than the small retorts.

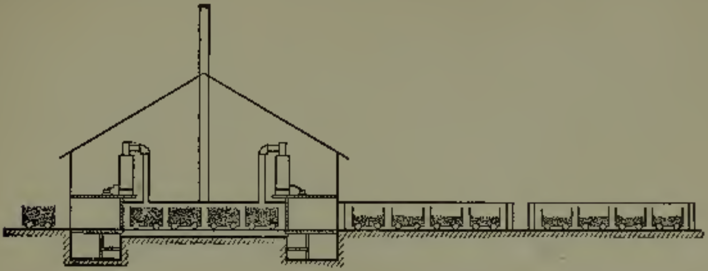

Fig. 94.

Movable retorts are vertical boiler-plate cylinders (Fig. 95 *) so arranged that the retort (A), filled with wood and with cover luted on, is lowered by a crane into the furnace; when carbonization is finished, the retort containing the charcoal is lifted out to cool *unopened*, while another charged with wood is put into its place. Connection with the condenser is made by a copper swing-pipe (B), clamped to the vent on the top of the retort. Each cylinder holds one cord of wood, and as it is packed cold, a complete filling of the space is possible. The labor cost for this type is less than for small horizontal retorts, but the wear and tear on the furnace and retorts from the frequent moving and cooling is great; the original cost of plant is also higher.

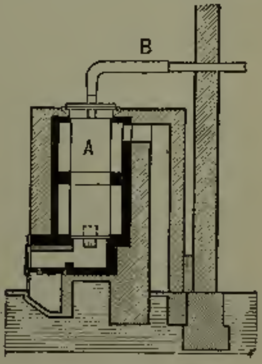

Fig. 95.

Coniferous woods are often distilled in retorts into which superheated or free steam is introduced, preliminary to the distillation proper. Thus the turpentine and much rosin are driven out at tem-

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* J. Soc. Chem. Ind., **1897**, 668.

peratures below that at which the cellulose is decomposed. Then by raising the heat of the retort, true destructive distillation follows, yielding wood vinegar, tar, and charcoal. Many plants for distilling fat pine, "light wood," have been erected in this country, but not always with satisfactory results. Considerable wood turpentine is produced, the yield being 10 to 20 gallons of crude turpentine per cord of "light wood," but the odor and color are often not satisfactory.

Extraction processes, depending on the use of solvents for both turpentine and rosin, such as carbon disulphide or carbon tetrachloride or turpentine itself, have been patented. The extracted chips are steamed to recover the solvent, but the losses are so large that the future of these methods is uncertain. The extracted chips are suitable for wood pulp, or they may be distilled for pyroligneous acid and tar. By treating the chipped wood with caustic soda liquor and steaming, the turpentine can be distilled off, while the rosin dissolves in the alkaline liquor. When drawn off and acidified, the rosin is precipitated.

Pyroligneous acid or crude "wood vinegar" is a reddish brown liquid with strong acid reaction and empyreumatic odor due to furfurol in part. It averages 5 to 10 per cent acetic acid, 1.5 to 3 per cent methyl alcohol, and 0.1 to 0.2 per cent acetone; its specific gravity varies from 1.020 to 1.050. A small amount is used directly for making an impure iron acetate, sold as "pyrolignite of iron"; but it is usually worked for methyl alcohol and acetic acid.

By neutralizing pyroligneous acid directly with milk of lime and distilling, a raw wood spirit is collected as distillate, while calcium acetate solution remains in the still, which on evaporation to dryness yields so-called "**brown acetate of lime**," averaging about 67 per cent of calcium acetate. During the evaporation, tar separates as a scum, which is skimmed off. The method is not much used at present.

By distilling pyroligneous acid in a copper still, the tar is left and a purified "**wood vinegar**" obtained, containing acetic acid, methyl alcohol (wood spirit), methyl acetate, acetone, acetaldehyde, etc., and traces of tar, empyreumatic matter, etc. This is neutralized with lime, precipitating many of the impurities; the clarified solution is then rectified in a column still, yielding wood alcohol of about 82 per cent. The solution in the still yields on evaporation to dryness "**gray acetate of lime**," averaging 80 per cent calcium acetate. The tarry matter decomposes during the drying.

The raw wood alcohol is further purified by diluting with water until the oily matters (ketones, aldehydes, etc.) precipitate, as shown by the milky appearance. On standing several days, the oils rise to the top and are skimmed off; then the alcoholic solution is again distilled in a fractionating still, until the concentration is about 95 per cent alcohol; the product is known as **wood spirit** or **methyl alcohol.** By filtering through charcoal, the color and unpleasant odor can be largely removed. Treatment with caustic lime and redistillation yields alcohol of 99 per cent, or higher, concentration; but this does not remove the acetone.

The wood spirit may be purified from acetone by treatment with caustic soda and iodine, producing a precipitate of iodoform with the acetone. Or calcium chloride is added to combine with the methyl alcohol and form a crystallized solid, stable at 100° C., from which the acetone is distilled off; then by adding hot water and heating to 100° C., or over, the alcohol is distilled off and rectified.

Commercial methyl alcohol is often slightly yellowish in color and frequently has a disagreeable odor. It is much used as a solvent in varnish making, for which purpose the presence of acetone is desirable; for making formaldehyde; for mixing with ethyl alcohol to prepare "denatured ethyl alcohol" or "methylated spirit" (p. 460).

Acetone, when recovered from wood spirit, is generally distilled from the calcium chloride compound with the methyl alcohol. It is, however, more commonly made by the dry distillation at 290° to 300° C., of calcium acetate: —

$\begin{matrix} CH_3 \searrow \\ CH_3 \nearrow \end{matrix} C = O$

$$Ca(C_2H_3O_2)_2 = CaCO_3 + CH_3 - CO - CH_3.$$

The product obtained by either of the above methods is crude; sodium bisulphite is added, and forms a double salt with the acetone, which is purified by recrystallization from aqueous solution. This salt is decomposed by heating with sodium carbonate solution, liberating the acetone, which distils off pure. Or the crude acetone is neutralized with lime, settled, and the supernatant liquid diluted with water and rectified in a column still, yielding a pure acetone distillate and an oily residuum called acetone oil which finds some use for solvent and denaturizing purposes.

A method for making acetone devised by Dr. E. R. Squibb * consists in passing acetic acid *vapor* through a rotating iron cylinder, heated to about 500°–600° C., and containing pumice stone with precipitated barium carbonate: —

$$2\,C_2H_4O_2 = H_2O + CH_3 - CO - CH_3 + CO_2.$$

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* J. Am. Chem. Soc., **17**, 187.

The barium carbonate acts as a contact body, since the temperature is always above that at which barium acetate decomposes. The vapors from the still pass to a fractional condenser to remove water and acetic acid; the acetone condenses in a second condenser.

Acetone is a colorless mobile liquid, having a peculiar odor and unpleasant taste; its specific gravity is 0.797 at 15° C. and should not exceed 0.802 in the commercial product. It boils at 56.3° C., and mixes with water in all proportions; is an excellent solvent for many resins, gums, fats, nitrated cellulose, and other substances. It is used in the manufacture of celluloid, smokeless powders, chloroform, iodoform, sulphonal, for extracting resin from crude rubber, and for denaturizing ethyl alcohol.

Commercial **acetic acid** is prepared from gray or brown acetate of lime * (p. 304) by distilling with strong hydrochloric or sulphuric acid. In the hydrochloric acid process, copper stills heated by steam coils are used; free steam can also be blown into the charge. The acetic acid distils over, leaving calcium chloride in the still. The acid is a slightly colored liquid containing from 30 to 50 per cent of anhydrous acid, according to the strength of the hydrochloric acid used. It may be further purified by distilling again over a little potassium permanganate, and filtering through fresh charcoal.

The sulphuric acid process is more commonly used at present; the still is made of cast-iron (Fig. 96 †) with a scraping device inside to break up the solid mass which forms in the still, and facilitate the escape of the acetic acid. The stills are heated by direct fire. A dust chamber should be placed between the still and the copper worm condenser. Owing to secondary reactions, some sulphuric acid is reduced, contaminating the product with sulphur dioxide, and necessitating the use of some excess of sulphuric acid in the still. Von Linde employs vacuum in the still, whereby the temperature is lowered sufficiently to permit steam heat to be used for the distillation, and secondary reactions are much reduced.

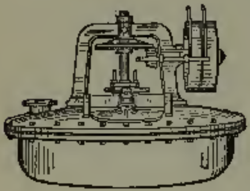

Fig. 96.

Behrens' process consists in dissolving the calcium acetate in acetic acid, and then decomposing the solution with sulphuric acid, whereby the reaction takes place at lower temperature.

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* Brown acetate is calcined at 230° C., to destroy tarry matter before use in this way.

† After Klar, Technologie der Holzverkohlung.

The distillate contains about 75 per cent anhydrous acetic acid and usually a little sulphur dioxide. This acid is then rectified in a large copper column still, heated by a steam coil. The plates in the column are often porcelain or earthenware; the condensers are usually copper worms. If air is excluded from the apparatus, there is little attack on the copper by the acid; but this necessitates the immediate refilling of the still after each charge has been worked off. If the operation is to be discontinued, the still and condensers should be thoroughly washed out with water. When starting each distillation, the heating should be slow, to allow the sulphur dioxide to pass off before the acetic acid begins to distil.

According to the amount of cooling water admitted to the fractional condenser, a clear colorless liquid containing from 80 to 99 per cent of anhydrous acid can be obtained; it contains traces of empyreumatic matter, which can be removed by gentle heating with potassium permanganate in an earthenware vessel, and redistilling in a copper still, with an earthenware, or pure silver, worm condenser. The residues from the several distillations are collected together and redistilled to recover as much as possible of the acetic acid in them. The final tarry residues are burned.

By distilling the pyroligneous acid, without neutralization, in a copper still, most of the methyl alcohol passes over before the acetic acid; by collecting the distillate until its specific gravity is about 1.000, a crude " wood spirit " is separated. If the acetic acid vapors following are passed into a solution of soda, a solution of sodium acetate is obtained. This is evaporated until only a fused mass of sodium acetate remains, which is heated to nearly 300° C., at which point the sodium acetate is stable but the impurities are decomposed. The fused salt is dissolved in water, the solution filtered and evaporated to crystallize. The process may be repeated for further purification.

If the distillation of the pyroligneous acid be continued after the methyl alcohol has passed over, the distillate, collected between 100° and 120° C., is called " **wood vinegar** "; it is dilute and still retains some empyreumatic matter, but is somewhat employed technically. It is generally neutralized with lime or soda to yield acetates.

Glacial acetic acid is the nearly anhydrous, 99 to 100 per cent acid, which crystallizes if cooled to 16.5° C. It may be made from fused sodium acetate, by distilling with strong sulphuric acid at 120° C. The residue from the still is sodium sulphate and may be used to decompose calcium acetate in solution, to prepare more sodium acetate.

Common acetic acid is found in commerce as a slightly colored liquid of various strengths: ordinary No. 8 has a specific gravity about 1.040 (8° Tw.) and contains approximately 30 per cent anhydrous acid; it is used in preparing acetates, in making white lead, in textile work, and in pharmacy. Stronger acid, containing 50 per cent or more of anhydrous acid, is used in preparing coal-tar colors and calico printers' pastes, for preparing organic acetates, and for solvent purposes. Pure acetic acid from wood distillate may be used for vinegar, but lacks the characteristic salts and flavoring substances present in true fermentation vinegar (p. 463).

Acetates. — **Aluminum acetate** in the pure state is not known, but a solution of it in acetic acid, called "**red liquor,**" is largely used in dyeing and in calico printing. It is made by dissolving aluminum hydroxide in acetic acid, or by decomposing lead or calcium acetates with aluminum sulphate or alum: —

$$Al_2(SO_4)_3 + 3\ Pb(C_2H_3O_2)_2 = 2\ Al(C_2H_3O_2)_3 + 3\ PbSO_4.$$

Calcium acetate yields the best red liquor; that made from lead acetate is not entirely free from lead, which dulls the shade of delicate colors; when made from alum, it contains sulphate of the alkali metal, and decomposes more readily than when made from aluminum sulphate. Several basic aluminum acetates are made by adding sodium carbonate to the normal acetate solution. These deposit alumina on the fibre very readily.

Chromium acetate finds some use as a mordant in calico printing. It is usually made by dissolving chromium hydroxide in acetic acid, or by decomposing a solution of chromium sulphate or chrome alum with lead or calcium acetate. The solution is violet, but becomes green if heated. It may be evaporated to dryness without rendering the salt insoluble. Alkalies and alkaline carbonates yield no precipitate in the cold solution, but when heated, a precipitate of chromium hydroxide forms.

Basic acetates are prepared by adding lead or calcium acetate to basic chromium sulphate solution. Sulphate-acetates are also made and used as mordants.

Calcium acetate has been mentioned as brown or gray acetate of lime (p. 304). The pure salt, occasionally used as a mordant, is made by neutralizing acetic acid with the theoretical quantity of lime. Litmus does not show the point of neutrality. The crystallized salt, $Ca(C_2H_3O_2)_2 \cdot H_2O$, is very soluble in water.

Cupric acetate, $Cu(C_2H_3O_2)_2 \cdot H_2O$, is best made by adding lead acetate to copper sulphate solution: —

$$CuSO_4 + Pb(C_2H_3O_2)_2 = Cu(C_2H_3O_2)_2 + PbSO_4.$$

It may be made by dissolving verdigris, or copper carbonate or oxide, in acetic acid. For basic acetates see p. 237.

Ferrous acetate, $Fe(C_2H_3O_2)_2 \cdot 4\ H_2O$, may be prepared from copperas and lead or calcium acetate; or by dissolving scrap iron in acetic acid. It is quickly oxidized in the air to basic ferric acetate. "**Pyrolignite of iron,**" **black liquor**, or **iron liquor**, is made by dissolving scrap iron in pyroligneous acid. It is sold as a dirty olive-brown or black liquid, having a density of about 25° Tw., and consists mainly of ferrous acetate, with some ferric acetate and tarry matter. It is used as a mordant in dyeing black silks and cottons, and in calico printing.

Ferric acetate, $Fe(C_2H_3O_2)_3$, made by adding lead acetate to ferric sulphate, is stable in cold solution. It forms basic salts when treated with caustic soda. It was formerly used in black silk dyeing.

Sodium acetate, $NaC_2H_3O_2 \cdot 3\ H_2O$, forms needle-like crystals which melt in their crystal water when heated; when anhydrous, it fuses without decomposition. It is chiefly used for making pure concentrated acetic acid, in making certain diazo bodies, and as a developer for the azo-dyes, in which the color is made on the fibre.

Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$, "**sugar of lead,**" is made by dissolving feathered lead by causing acetic acid to trickle over it in the presence of a current of air. Or litharge is dissolved directly in acetic acid. If wood vinegar is used, the product is "brown sugar of lead." With an excess of litharge, basic acetates are formed. The normal salt is very soluble in water, and is used for making other mordants and for chrome yellows. The salts are poisonous, and are affected by the carbon dioxide and hydrogen sulphide in the air.

Wood-tar varies somewhat in character with the kind of wood carbonized. It is washed with hot water, or treated with milk of lime, to remove acetic acid, and then washed with very dilute sulphuric acid. Excess of water is evaporated by warming in steam-jacketed vessels. The tar is then distilled in iron stills, provided with stirring apparatus, the temperature being raised very slowly. The distillate collected below 150° C. is called "**light oil,**" and is chiefly used as a substitute for oil of turpentine in varnish and paints. Between 150° and 250° C. the "**heavy oil**" is collected, containing creosote, toluene, and paraffine bodies. By stopping the distillation at 250° C., a thick, brownish liquid is obtained, which is used in making axle grease, shoemakers' wax, for lampblack, and for coating the interior of casks and barrels to render them impervious to liquids.

The **creosote oil** is washed with caustic soda, and boiled in the air to oxidize various substances which it contains. The alkaline solution is then acidified with sulphuric acid, to precipitate the creosote, which is treated with alkali and acid as before. It is then distilled again, and the distillate, collected between 200° and 220° C., is the commercial wood-tar creosote. It has a strong, smoky odor, is a good antiseptic, and is not poisonous.

Stockholm tar and **pine tar** are obtained by a crude distillation of pitch-pine or other coniferous wood, in heaps, covered with turf. These are of different composition from retort tar, and are mainly used for tarred ropes, with oakum for ship calking, and for preserving timber.

REFERENCES

Das Holz und seine Distillations-Producte. Dr. G. Thenius, Leipzig, 1880.
Die Meiler und Retorten Verkohlung. Dr. G. Thenius.
Das Chemische Technologie der Brennstoffe. F. Fischer, Braunschweig, 1880.
Die Verwerthung des Holzes auf chemischen Wege. J. Bersch, Leipzig, 1883.
Destructive Distillation. E. J. Mills, London, 1892. (Gurney and Jackson.)
Handbuch der Organischen Chemie. Victor Meyer and Paul Jacobson. Vol. I. Articles — "Essigsäure" and "Methylalkohol." Leipzig, 1893.
Technologie der Holzverkohlung. M. Klar, Berlin, 1910. (Springer.)
Handbuch der Organischen Chemie. F. Beilstein. Vol. 1, 3d ed. Purification of Wood Spirit. Leipzig, 1894. (L. Voss.)
Jahres-Bericht über die Leistungen der technischen Chemie: —
1892. **1893**, 14. (Distillation of Wood.)
Journal of the Society of Chemical Industry: —
1892, 395 and 872. **1897**, 667, 722. M. Klar. (Modern Distillation of Wood.)

DESTRUCTIVE DISTILLATION OF BONES

Bones are usually extracted with benzine or with carbon disulphide, and the fatty matter used for soap stock. They still contain nitrogenous organic substances, and are distilled in iron or clay retorts, similar to those used in coal-gas making (p. 315), yielding volatile products, consisting of gases, ammonium salts, and bone oil; these pass through condensers, where the water and bone oil condense; the gases pass into a receiver containing sulphuric acid, which takes up the ammonia and its volatile compounds; the inflammable gases are burned under the retort.

The **bone oil** (" **Dippel's oil** ") and aqueous liquor collected under the condensers are separated by gravity. The liquor contains ammonium carbonate, cyanide, sulphocyanide, and sulphide, and is treated in the same way as gas liquor (p. 151) for the recovery of the ammonia. The crude bone oil is a dark-colored, foul-smelling liquid, lighter than water. It is redistilled and divided into numerous fractions. At high temperatures it also yields ammonium carbonate and cyanide; the thick tar remaining in the still is the basis of commercial Brunswick black.

The constituents of bone oil are exceedingly numerous, but the more important are pyrrol, C_4H_4NH; pyridine, C_5H_5N; picoline, $C_5H_4(CH_3)N$; lutidine (dimethylpyridine); collidine, $C_5H_2(CH_3)_3N$; and quinoline, $C_6H_4 \cdot C_3H_3N$. These have but little technical use, but are employed in Europe for denaturating alcohol, and in the preparation of certain antiseptics. They are closely related to some of the alkaloids, but are not as yet used to prepare them.

The residue from the bone distillation is the **bone-black** or **bone-char** of commerce. It forms about 65 per cent of the original weight of the bones and consists largely of calcium phosphate and carbonate, impregnated with free carbon. While still hot, it is drawn from the retort into closed vessels and cooled out of contact with the air. It is largely used in decolorizing sugar solutions, glucose, glycerine, oils, paraffine, vaseline, etc., and in case-hardening iron. It loses its effectiveness after a time, and is then " revivified " (p. 418). When it becomes too finely powdered for successful filtration, it is used as a fertilizer (p. 165).

ILLUMINATING GAS

Illuminating gas may be made by enriching water gas with oil gas, or by the destructive distillation of coal, wood, or petroleum. Coal gas, such as is generally used at the present time, was first employed for house illuminating by William Murdock, in London, in 1792. It was introduced for street lighting in London in 1812, and in Paris in 1815. In this country, the so-called water gas, enriched with naphtha, has largely replaced coal gas in many of the large cities. This has greater illuminating power, requires a smaller plant and less labor, and ensures greater economy of working.

Water gas (p. 39) is produced by the action of steam on incandescent carbon, according to the reactions: —

$$C + 2\ H_2O = 2\ H_2 + CO_2.$$
$$C + CO_2 = 2\ CO.$$

It is composed chiefly of hydrogen and carbon monoxide, is non-luminous, and has a high heat value.

Luminosity depends on the presence of hydrocarbons, such as ethane, C_2H_6, ethylene (ethene), C_2H_4, acetylene, C_2H_2, and benzene, C_6H_6, and their homologues, the most important of these " illuminants " being ethylene and benzene. In order to render the water gas luminous, it is *carburetted* with gases derived from oil, which are rich in illuminants.

Illuminating water gas is now made by two general methods: (*a*) the carburetted gas is made in one operation; (*b*) non-luminous gas is prepared, and then carburetted by a second process. The first method is most successfully carried out by the Lowe process. The generator (Fig. 97) is filled with anthracite coal or coke, which is brought to incandescence by a blast of air. The gases from the generator, at this time consisting mainly of carbon monoxide and nitrogen, enter at the top of the carburettor, a circular chamber lined with firebrick, and containing a " checker-work," of the same material; while passing down through this, the producer gas (p. 41) is partly burned by an air blast which enters the apparatus near the top, and the checker-work is heated white hot. The gases pass on to the " superheater," a taller chamber, also filled with checker-work. At the bottom of this an air blast is introduced to complete the burning of the producer gas and to raise the temperature of the checker-work to a very bright red heat. From the top of the superheater, the waste gases escape into a hood leading into the open air. When both the carburettor and superheater have reached the desired temperature, the air blasts are cut off, and steam is introduced into the generator, where it is decomposed by the incandescent fuel, according to the reactions. The water gas thus formed passes into the carburettor, while a small stream of oil is being introduced through a pipe at the top. The oil is decomposed by contact with the hot checker-work, forming illuminating gases which mix with the water gas, and passing into the superheater, are completely fixed as non-condensable gases.

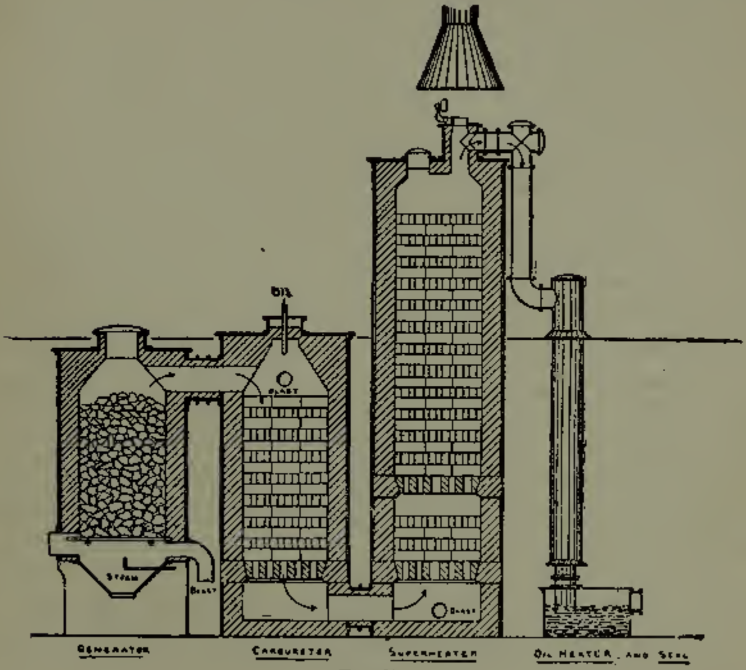

Fig. 97.

It is customary to run the air blast for some eight minutes, when the fuel reaches a temperature of about 1100° C. The steam, superheated before entering the generator, is run about six minutes, until the temperature of the generator and carburettor has fallen below the point at which decomposition occurs. In order to economize heat, the hot carburetted gas is passed through a pipe surrounded by a jacket, within which the oil is circulating, thus heating it before it enters the carburettor. The lower end of the pipe leading from the superheater is closed by a water seal, to prevent any backward rush of the gas during the operation of the air blast. It is customary to lead the gas from the superheater into a storage holder, from which it is drawn through the purifying apparatus.

In this process, the blowing of air and of steam are intermittent, but the actual formation of gas is accomplished in one operation.

The second method of preparing illuminating water gas is the Wilkinson process. Water gas is made by blowing steam into the hot coal in the generator, and is stored in the holder. A measured quantity of gas is then introduced into the carburettor, a closed iron box, containing slightly inclined plates, over which the exact amount of oil necessary to carburet the gas, is flowing in very thin layers. The carburettor is also provided with a steam jacket and coils to keep the temperature high enough to vaporize the oil. These vapors mix with the gas and pass at once into the fixing apparatus, which is a long, narrow, fire-clay retort, kept at a white heat by external fire. Here the oil vapors are " cracked " into hydrocarbons, which are non-condensable gases, and being mixed with water gas, render it luminous when burned. The mixed gases then go directly to the scrubbers and purifiers. For 1000 cubic feet of gas, about 50 pounds of anthracite and 4.2 to 5 gallons of naphtha are consumed.

The impurities in the water gas are essentially the same as those in coal gas, and the method of washing and purifying are the same.

The illuminating value of coal gas is frequently raised by mixing it with carburetted water gas. Owing to its high percentage of carbon monoxide, water gas is exceedingly poisonous when inhaled, and much care is necessary to prevent leakage into inhabited rooms (see table, p. 325).

Coal gas, prepared by the destructive distillation of bituminous coal, is generally made by the smaller gas companies in this country. In Europe scarcely any water gas is made for illuminating purposes. The composition and yield of coal gas depend upon the kind of coal used and the manner of distillation. A " fat " coal, moderately low in sulphur, and caking on distillation to a good coke (*e.g.* the Pennsylvania gas coals), is most desirable for illuminating gas. The temperature of the retort is a very important factor in the character of the distillation products. When it is low, the quantity of gas formed is small, but it contains a large percentage of illuminants, and hence is of a high candle power. When the temperature in the retort is high the effects are as follows: (*a*) the yield of gas is much increased, but the percentage of methane, ethane, and hydrogen is much greater, and since these have very little illuminating value, the gas is of low candle power; (*b*) the yield of tar is increased; (*c*) the vapors of the heavy hydrocarbons which constitute some of the tar are decomposed on coming in contact with the hot retort, forming gases of lower carbon content, and depositing free carbon on its walls. This "gas carbon" * adheres very firmly and if allowed to become thick causes much loss of heat. It is especially liable to deposit if there is undue pressure in the retort, which may be the case if the exhausters are not working properly; (*d*) there is a larger yield of organic bodies having ring nuclei in their composition, such as naphthalene, phenols, anthracene, etc. These not only cause loss, but also cause clogging in the service pipes and burners.

The products of the distillation are gas, ammoniacal liquor, tar, and coke. When coal is distilled for coke (p. 35), the ammoniacal liquor and tar are sometimes saved by the use of by-product ovens, but the gases are burned for fuel or go to waste. When distilled for illuminating gas, the process is carried on with a view to the best yield of high quality gas, but the ammoniacal liquor, tar, and coke are valuable by-products. The coke is too soft for metallurgical purposes, and is chiefly used to heat the retorts or sold for domestic fuel.

A diagram of a complete plant for coal gas making is shown in Fig. 98. The retorts (A) are ⌓-shaped, fire-clay vessels, about 8 feet long, 18 inches wide, and 15 inches high; they are set six or eight together in a furnace, the whole constituting what is called a "bench." Each retort has a cast-iron mouthpiece projecting out of the furnace, and carrying the door, closed by a screw clamp. Retorts may be "single," *i.e.* closed at one end and having but one door for charging and discharging; or they are "through" retorts, about 18 feet long, having a door at each end, so that they may be charged or emptied from either side of the furnace. A modified form of the latter is the "inclined" retort, set at an incline of about 32°, the coal being run in at the upper end, and the coke discharged by gravity, by opening the door at the lower end. Vertical retorts are also in use. Each bench is heated to 1000° or 1200° C. by a coke fire on a grate below the retorts, or, in more modern plants, by generator gas. A number of benches are built together, and constitute a "stack."

* Gas carbon is used for electric light carbons, battery plates, and other electrical appliances. It is denser and purer than most other forms of carbon.

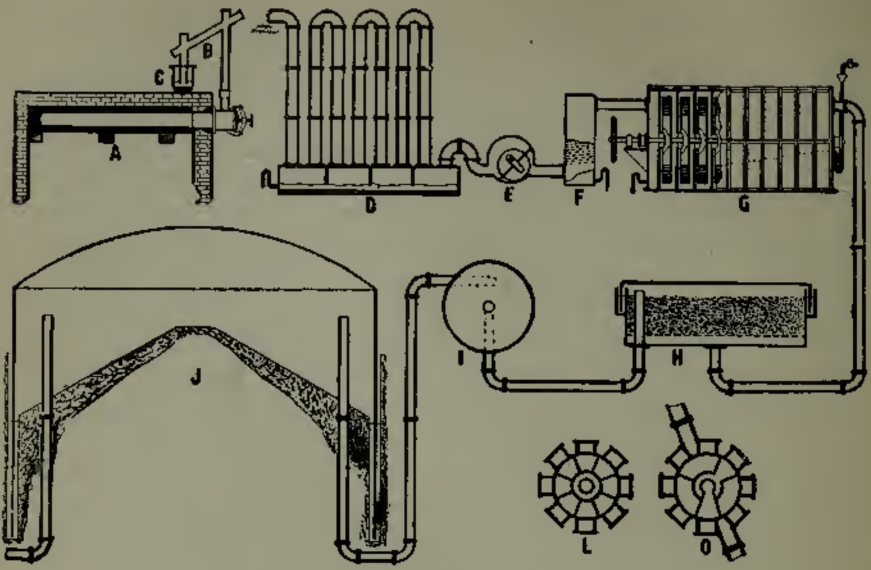

Fig. 98.

From the front of each retort a vertical cast-iron pipe (B) about 6 inches in diameter, and called the "**stand-pipe**," ascends to the top of the bench, where it joins the "bridge-" and "dip-pipes," which conduct the volatile products from the retort to the **hydraulic main** (C). This is a long covered trough, extending the entire length of the stack, and receiving the gas and distillate from each retort. In it the greater part of the tar and oily products condense and collect under the water which is kept in the main to act as a seal to the ends of the dip-pipes, to prevent the gas from passing back into the retort when the latter is opened. Ammonium salts, such as sulphate, sulphide, and carbonate, are washed from the gas as it bubbles through the water, and are afterwards recovered (p. 151). The ends of the dip-pipes must not extend more than 2 inches into the water; otherwise, there is pressure in the retort and consequent loss from leakage and from deposition of carbon in the retort and stand-pipe. If the gas is allowed to cool in contact with the tar, the latter absorbs some of the illuminants, thus reducing the candle power (p. 323). If the stand-pipes are too hot, the volatile constituents of the tar are driven out, and a very thick mass deposits, causing clogging.

From the hydraulic main a pipe (not shown) leads to the **condenser** (D), which consists of a series of vertical cast-iron pipes, connected by bends at the top, and opening at the bottom into an iron box.

This box is divided by transverse partitions which do not extend to the bottom, merely dipping into the ammoniacal liquor and tar contained in it. The liquor forms a seal, thus forcing the gas to pass through the pipes, while the condensed products flow along the bottom of the box to the tar well. These condensers are simply air cooled, but certain forms are constructed with water coolers. In those most frequently in use in this country the pipes are laid at a slight incline to the horizontal.

The **annular condenser** consists of a series of vertical pipes connected by diagonal pipes leading from the bottom of one to the top of the next. Through each of these vertical pipes a smaller tube passes parallel to the length of the pipe and opening to the air at both ends, thus forming an annular space in each pipe, through which the gas passes *downward,* and then through the diagonal pipe to the top of the next. In this way a very large air-cooled surface is obtained. At the bottom of each cooling pipe a small pipe carries away the condensed tar and liquor.

The **tubular condenser** consists of a rectangular box about 2 feet wide and 20 feet high, divided into narrow sections by partitions extending alternately to within a few inches of the top and of the bottom. Through each section, a number of narrow horizontal tubes, open to the air at each end, extend from one side of the box to the other. In this way the gas passing through the sections is exposed to a very large cooling surface.

Water condensers consist essentially of pipes surrounded by flowing water. Through these the gas is made to pass in a direction opposite to that in which the water flows. By regulating the supply of water, the temperature is easily controlled.

The object of the condenser is to cool the gas *slowly* to the temperature of the atmosphere, provided this in not under 50° C. Cooling below this causes condensation of some of the illuminants, with corresponding loss. If the cooling is very rapid, the tarry matter separates quickly, and drags some of the lighter hydrocarbons down with it.

The **exhauster** (E, Fig. 98) draws the gas from the retort, through the hydraulic main and condenser, and acts as a pump forcing it through the remaining parts of the plant. By drawing the gas out of the retort quickly there is less decomposition of the gas itself, and hence less carbon is deposited in the retort; a larger yield results and less fuel is necessary, while the retort lasts longer.

Another form of exhauster is a direct-acting pump, which draws the gas from the retort and condenser, and forces it to the purifiers.

Root's rotary exhauster is frequently employed, as is also Beal's (Fig. 99). This consists of an outer circular casing having inlet and outlet pipes, and an inner revolving drum (B), turning on an eccentric axis in such a way that the drum just touches the lowest point of the inner surface of the casing. Through slots cut in the drum, two blades or diaphragms (D) slide freely over one another, to form a double diaphragm, variable in width, according to the relative position of the blades to each other. In the outer end of each blade is a pin, which travels in a circular groove sunk in the ends of the casing. Thus as the drum revolves about its axis, the pins, travelling in the fixed groove, draw the blades in and out, across the axis of the drum. The outer ends of the blades are thus always kept in contact with the walls of the casing. The exhauster is driven by an engine, and the rotary blades and drum catch the gas which enters through the inlet, and force it out through the other pipe.

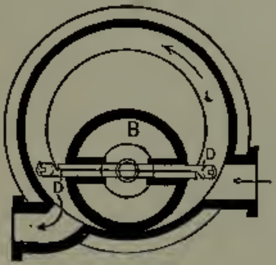

Fig. 99.

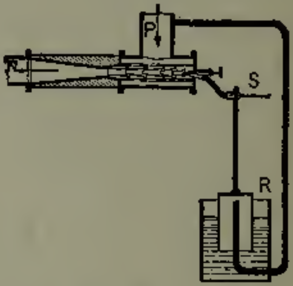

Fig. 100.

The **steam jet exhauster** (Fig. 100 *) is effective, but heats the gas, which is afterwards cooled in the washer. A jet of steam is blown through conical openings into a wide pipe, drawing the gas along with it into the cones.

The **tar extractor** (F, Fig. 98) is a short tower filled with numerous horizontal perforated plates. The friction of the gas in passing through the small holes in these plates removes the last traces of tar and prevents clogging in the scrubber. In Europe the apparatus of Pelouze and Audouin is much employed. This is a bell made up of three layers of wire netting, or of perforated plates, which is suspended in a water seal. The gas enters under the bell and passes through the meshes

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* After Ost, Lehrbuch d. tech. Chemie.

or perforations of the bell walls, to which the tar particles attach themselves and finally drop to the bottom and run off by a special pipe.

The **scrubber** and **washer** are intended to remove the ammonia and part of the carbon dioxide and hydrogen sulphide. In the former the gas is brought into contact with thin films or layers of ammoniacal liquor from the hydraulic main or condensers, which trickles over coke, twigs, wooden slats, or pebbles, in a tower. This liquor absorbs some of the carbon dioxide and hydrogen sulphide, which combine with the ammonia. In the washer the gas is brought in contact with pure water, trickling over twigs, coke, etc., and which removes the ammonia from the gas.

Tower scrubbers are tall cast-iron vessels built in segments, each of which has a "grid" or grating, upon which the filling material is supported. Two towers are always used in conjunction, the first fed with ammoniacal liquor and the second with water. The amount of liquor and water is carefully regulated, and the gas entering at the bottom of the first tower passes up and then to the bottom of the second, and is thus first brought into contact with the strongest liquor and finally with pure water. These tower scrubbers are now only used in old plants; in all modern establishments they have been replaced by scrubber-washer machines.

The **Standard scrubber-washer machine** (G, Fig. 98) is a ∩-shaped iron vessel divided into a series of narrow chambers by transverse partitions. In the upper half of the apparatus is a revolving shaft carrying a number of thin wooden grids, bolted together in parallel segments, with blocks making a space of about one-eighth of an inch between each pair of grids. A group of these slats revolve in each chamber. Water at about 60° F. is admitted to the last chamber of the series, at the rate of about one gallon for each 1000 cubic feet of gas, and, automatically regulated, flows from chamber to chamber in a direction opposite to that in which the gas is passed. Thus the fresh water comes in contact with the most nearly purified gas. The level of the water is lower in each succeeding chamber, until in the first chamber, where the gas enters the apparatus, the strong ammoniacal liquor is only a few inches deep.

By the revolution of the shaft, the grids are submerged in the liquor, and freshly wetted surfaces are brought into the upper part of the apparatus. By a suitable arrangement of baffle plates, the gas is made to enter each chamber at the centre, and find its way to the circumference by passing through the narrow spaces between the grids. The water, forming a thin film on them, absorbs the ammonia, carbon dioxide, etc.; and as the shaft revolves from 12 to 15 times per minute, the solution formed is at once mixed with the liquor in the bottom of the chamber. The machine works effectively, and in this country is rapidly replacing the tower scrubbers.

From the scrubbers the gas passes to the **purifiers** (H, Fig. 98), whose chief purpose is to remove sulphur compounds. They are shallow rectangular iron boxes, each having a false bottom, upon which the purifying material rests. The gas enters under this grating and leaves by a pipe opening just under the cover, which rests in a hydraulic seal, and is lifted by a travelling crane. Usually four purifiers are placed in a series, one of which is emptied and recharged at a time, without interrupting the purification process. The foul gas enters the most nearly exhausted purifier, and, passing through the others, leaves the apparatus through that most recently charged, connection being made between the purifiers by means of a complicated piece of apparatus (L and O, Fig. 98) called the **centre seal.**

The purifying materials may be slaked lime or hydrated ferric oxide. Lime is the oldest material used and is also the best, since it removes both the carbon dioxide and carbon disulphide. But it is expensive, and the spent lime, having a most offensive odor and considerable bulk, is difficult to dispose of. The lime should be thoroughly slaked several days before use, and should contain as much water as it will hold without becoming pasty or liquid. It is placed in the purifiers in layers about six inches deep. The reactions occurring with lime are: —

1) $Ca(OH)_2 + 2\ H_2S = Ca(SH)_2 + 2\ H_2O.$
2) $Ca(OH)_2 + H_2S = CaS + 2\ H_2O.$
3) $CaS + CS_2 = CaCS_3$ (calcium thiocarbonate).
4) $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$

Since carbon dioxide will decompose calcium sulphide, sulphydrate, or thiocarbonate, if gas containing it is passed through a foul purifier, the following is liable to take place: —

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S.$$
$$CaCS_3 + CO_2 + H_2O = CaCO_3 + CS_2 + H_2S.$$

The volatile sulphides thus liberated must be removed in a second purifier, into which no carbon dioxide enters. Carbon dioxide has a deleterious effect on the illuminating power of the gas.

When iron oxide is used, only the hydrogen sulphide is removed from the gas: —

$$1)\ Fe_2O_3 \cdot 3\,H_2O + 3\,H_2S = 2\,FeS + S + 6\,H_2O.$$
$$2)\ Fe_2O_3 \cdot 3\,H_2O + 3\,H_2S = Fe_2S_3 + 6\,H_2O.$$

The oxide is a natural bog iron ore, $Fe_2O_3 \cdot 3\,H_2O$. When fresh, it contains about 50 per cent water and a large amount of vegetable matter, but before use it is dried until about one-half of the moisture is expelled, and is then mixed with an equal bulk of sawdust to render it more porous. When it becomes inactive through absorption of sulphur, it is "revivified" by removing it from the purifier and spreading it in a layer a foot or more in depth, where the air can act upon it. Considerable heat is evolved by the action of the oxygen of the air on the iron sulphides: —

$$2\,FeS + 3\,O = Fe_2O_3 + 2\,S.$$
$$Fe_2S_3 + 3\,O = Fe_2O_3 + 3\,S.$$

Thus free sulphur is deposited in the oxide. The ore may be revivified repeatedly until the free sulphur accumulates in it to the amount of 50 or 55 per cent, when the proper action in the purifiers is hindered, and fresh oxide must be used. If some air is admitted along with the gas, the iron oxide is revivified in the purifiers, and need not be removed so often; but this dilutes the gas slightly with nitrogen. One ton of good iron oxide will purify ten to twelve million cubic feet of gas. Sometimes lime is used before the iron oxide, in order to remove carbon dioxide. Any sulphur compounds of the lime which may be formed are decomposed by the carbon dioxide in the foul gas (see above). Considerable carbon dioxide is present in unpurified water gas, and is generally thus removed before the gas enters the iron oxide purifiers.

The purified gas passes through the station meter (I, Fig. 98) and then to the holder (J), from which it is delivered to the street mains.

The **Feld process** of gas purification has found some favor in Europe. The gas, which has not been freed of ammonia, is washed in a scrubber with a dilute solution of ferrous sulphate; both ammonia and hydrogen sulphide are absorbed: —

$$FeSO_4 + 2\,NH_3 + H_2S = FeS + (NH_4)_2SO_4.$$

The exhausted wash-liquor is regenerated by blowing sulphur dioxide gas into it, forming soluble ferrous thiosulphate and precipitating sulphur: —

$$2\,FeS + 3\,SO_2 = 2\,FeS_2O_3 + S.$$

This liquid, with the sulphur in suspension, is used in the scrubber for more crude gas: —

$$FeS_2O_3 + 2\ NH_3 + H_2S = FeS + (NH_4)_2S_2O_3.$$

This liquor is in turn regenerated by blowing a mixture of air and sulphur dioxide into it, when the thiosulphate is oxidized to sulphate: —

$$2\ FeS + 2(NH_4)_2S_2O_3 + 3\ SO_2 + 2\ O_2 = 2\ FeSO_4 + 2(NH_4)_2SO_4 + 5\ S.$$

This is repeated until the ammonium sulphate reaches 30 to 40 per cent, when the sulphur is filtered off; the iron precipitated as ferrous sulphide is also filtered and the sludge returned to the process. The ammonium sulphate is recovered by evaporation.

Cyanides (p. 289) are recovered from the impure gas in some of the large works. When this is done by the use of iron salts,* without previous removal of the ammonia, a special arrangement of the apparatus is desirable. The tar extractor is put behind the air-cooled condenser; next is a standard scrubber, charged with heavy tar oils in the forward compartments to remove naphthalene, and the iron solution is in the later compartments to remove the cyanogen; following this is the water-cooled condenser, and then the ammonia scrubber. Thus the gas enters the ammonia scrubber nearly cold. This removal of cyanogen from the gas renders the activity of the iron oxide in the purifiers of greater duration, for only the hydrogen sulphide is to be removed, no sulphocyanide nor Prussian blue is formed, and the ultimate amount of sulphur in the mass readily reaches 50 per cent, when the material is suitable for making sulphuric acid.

The ammoniacal liquors from the hydraulic main, condensers, and scrubbers are mixed, forming "gas liquor" of approximately "10 ounce" strength, *i.e.* the ammonia gas which can be liberated from one gallon of the liquor will neutralize 10 ounces by weight of real sulphuric acid. It is used for the production of ammonia (p. 151). The tar from the tar well is shipped to the tar distiller (p. 327).

The usual impurities found in gas are ammonia, hydrogen sulphide, and carbon dioxide. Ammonia is detected by holding a strip of wet turmeric or litmus paper in a stream of the gas; the former becomes brown or red, and the latter blue. For hydrogen sulphide, paper wet in lead acetate or silver nitrate is used. Carbon dioxide is detected by shaking a small bottle of the gas, freed from hydrogen sulphide, with lime or baryta water.

* Journal für Gasbeleuchtung, **1899**, 470.

The yield from one ton of good gas coal is approximately: —

10,000 cu. ft. 16 candle power gas.
1400 pounds coke.
120 pounds tar.
20 gallons ammoniacal liquor (10 to 12 oz.).

The illuminating power of gas is expressed in "candles," by which is meant the ratio of its illuminating power to that of a "standard candle," as measured by a photometer. The English standard is the light of a sperm candle, weighing one-sixth of a pound, when burning 120 grains per hour. But this is subject to variation, and much ingenuity has been expended in devising a better standard. A burner designed for use with a mixture of air and pentane, C_5H_{12}, has found some favor in Europe. In Germany the light of a lamp burning amyl acetate, with a specified height of flame and size of wick, is the official standard. In this country standard candles are used. When testing gas, it is customary to burn it at the rate of 5 cu. ft. per hour, in a burner of the argand type. Ordinary coal gas is about 16 candle power, but it is sometimes "enriched" by putting into the retort, along with each charge of coal, an iron cylinder containing petroleum oil. This is closed with a cork, which burns out, and the escaping oil is decomposed, the vapors mixing with the coal gas, increasing its illuminating power.

Another method of enriching coal gas is the addition of benzol vapors, the gas having been previously scrubbed with heavy oil to remove naphthalene, phenols, and other constituents.

A modern improvement in gas lighting is the introduction of incandescent burners, in which the non-luminous flame of a Bunsen burner is made to heat a mantle or gauze composed of the oxides of various rare earths, especially thorium and cerium, which possess in high degree the property of selectively radiating light at relatively low temperatures. The mantle heated to incandescence glows with a powerful light, while very little heat is given out. These burners consume about three and one-half feet of gas per hour, and their efficiency is four times that of an ordinary argand burner. They are advantageous to use with a gas of low illuminating power, provided it has considerable heating value.

Oil gas is now largely made by "cracking" certain petroleum, tar, or shale oils in retorts. In Pintsch's process the retort is divided by a partition into an upper and lower chamber; the oil is cracked in the upper compartment, and the vapors pass into the lower one, which is heated to about 1000° C., where they are " fixed " and form permanent gases. In Peebles' process the retorts are not so hot, and the oil is partly cracked and partly distilled; the heavier fractions condense and return to the retort, and only very volatile hydrocarbons leave the apparatus. Purified oil gas has a high candle power, usually over 50, and is burned in special forms of burner, otherwise it is liable to smoke or deposit soot; it is rich in benzene and olefine hydrocarbons, and may be burned alone or used to enrich other gases. Burning with pure oxygen improves its combustion and illuminating power greatly. Pintsch gas is much used for lighting railroad cars; it is compressed into cylinders for carriage, but the pressure must be low or great loss of illuminating power occurs owing to the condensation of the heavy illuminants.

Blau gas * is made by " cracking " petroleum in a steel retort, at low red heat (500°–600° C.); both liquid and gaseous products result, which are cooled to condense the higher boiling constituents. The gas then passes a purifier (iron oxide and lime) to remove hydrogen sulphide and carbon dioxide; then it is compressed in a four-stage compressor to 100 atmospheres, whereby part of it liquefies, and under the heavy pressure, the liquid hydrocarbons dissolve much of the fixed gases and hold them in solution. The liquid is then charged into steel cylinders for use. The residual unabsorbed gas separated from the liquid is used in gas engines driving the compressors.

Blau gas is nearly free from carbon monoxide and consists essentially of methane and hydrogen dissolved in saturated and unsaturated hydrocarbons, which impart high calorific and illuminating value (50 c. p.). It is used in isolated buildings, factories, yachts, and railway cars; and with oxygen for autogenous welding and metal cutting.

Acetylene is made from calcium carbide (p. 266) by treating with water: —

$$CaC_2 + 2\ H_2O = Ca(OH)_2 + C_2H_2.$$

One ton of 80 per cent carbide yields about 9000 cu. ft. of acetylene gas. The crude gas is usually contaminated with hydrogen sulphide, phosphine, and ammonia; it is purified by passing over bleaching powder, chromic acid, or cuprous chloride. When burned under pressure, in a special form of burner, it yields a very brilliant light. It is not used to enrich coal- or water-gas, since its candle power is much lowered by mixing with other gases. With air in greatly varying proportions the gas forms explosive mixtures.

Heavily compressed acetylene gas is liable to explode; hence

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* Jour. Soc. Chem. Ind., **1908**, 550. Met. and Chem. Eng., **1914**, 153.

storage in the compressed state in gas tanks is dangerous. But enormous quantities of the gas dissolve in acetone under pressure, and the solution is not explosive; on releasing the pressure, the gas is evolved rapidly and steadily. By filling the cylinders completely full of some porous material, as asbestos, or charcoal embedded in cement, after thorough drying, a considerable quantity of the acetone-acetylene solution can be introduced at about 15 atmospheres pressure and safely stored or transported. Cylinders of the acetylene solution are much used for automobile and car lighting. Acetylene is considerably used for illuminating detached country houses and factories, and for the public supply of towns.

When burned with oxygen, acetylene yields an intensely hot flame (2500° C.) Oxy-acetylene blow pipes are much used for autogenous welding of iron, steel, and other metals; also for cutting and boring steel plates and beams, the metal being rapidly melted in a very narrow area at the point of the flame jet.

Air gas, so-called, is made by blowing a carefully regulated current of air through layers of the very volatile petroleum distillates, of from 80 to 90° Bé. The air, carrying sufficient vapor to form a combustible mixture, goes directly into the burner, since it cannot be piped very far without condensation of the illuminants. Air gas is much used where other gas is not available.

In some parts of Europe, where coal is expensive, gas is made by distilling dried peat. The gas contains more carbon dioxide than coal gas, and more lime is needed for purification; it is about 18 candle power, and considerable tar and ammoniacal liquor are obtained. The composition of typical kinds of gas is shown in the following table.*

ANALYSES

	Coal	Water (Carburetted)	Water (Fuel)	Oil
Candle power . . .	17.5	25.0	—	65.0
Illuminants	5.0	16.6	—	45.0
Marsh gas	34.5	19.8	1.0	38.8
Hydrogen	49.0	32.1	52.0	14.6 Ethane
Carbonic oxide . . .	7.2	26.1	38.0	—
Nitrogen	3.2	2.4	3.0	1.1
Oxygen	—	—	—	—
Carbonic acid . . .	1.1	3.0	6.0	—

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* C. D. Jenkins. Reports of the Mass. State Gas Inspector.

The gas produced in by-product coke ovens contains some **benzene** (C_6H_6), and if the gas is not to be used for illuminating purposes, this benzene may be washed out of the gas in counter-current scrubbers using mineral oil. The oil is then distilled with steam to recover the benzene, and the residual oil returned to the scrubber. Coal-gas intended to be used for illuminating may be scrubbed in the same way, but in this case other illuminants must later be added to the gas.

REFERENCES

Practical Treatise on the Manufacture and Distribution of Coal Ga Samuel Clegg, London, 1859.
Traité theoretique et pratique de la Fabrication du Gaz. E. Borias, Paris 1890.
Manufacture of Gas from Tar, Oil, etc. W. Burns, New York, 1887.
Fabrikation der Leuchtgase. G. Thenius, Leipzig, 1891.
The Chemistry of Illuminating Gas. N. H. Humphreys, London, 1891.
Handbuch für Gas-Beleuchtung. E. Schilling, 1892.
A Treatise on Gas Manufacture. W. King. (King.)
Gas Engineer's Handbook. T. Newbiggin, London, 1898. (King.)
Acetylen in der Technik. F. B. Ahrens, 1899.
Acetylene. V. B. Lewes, 1900.
A Textbook of Gas Manufacture. John Hornby, London, 1902. (Bell and Sons.)
Acetylene. F. H. Leeds and W. J. A. Butterfield. London, 1903.
The Chemistry of Gas Manufacture. W. J. A. Butterfield, 3d ed., London, 1904.
Chemistry of Gas Manufacture. H. M. Royle, 1907.
Handbook of American Gas Engineering Practice. M. N. Latta, 1907.
Modern Appliances in Gas Manufacture. F. W. Stevenson.
Practical Testing of Gas and Gas Meters. C. H. Stone, 1909.
Gasbeleuchtung und Gasindustrie. H. Strache, Braunschweig, 1913.
Journal of Gas Lighting. London. Vols. **59**, **60**, **61**, **62**, and others. (Coal Gas.)

COAL-TAR

The tar from the hydraulic main and condensers of the gas works is a black, oily, foul-smelling liquid averaging 1.15 sp. gr. Its composition is very complex, and it is mixed with some of the gas liquor, retains in solution some constituents of the gas, and carries fine carbon in suspension. In the early days of gas making, no use being known for tar, it became a great nuisance. But the discovery of important derivatives from it has given rise to great industries.

Coal-tar is used to some extent without treatment for preserving timber, as a protective paint and cement in chemical works; in forming certain furnace linings; and as liquid fuel. But much of the tar produced is fractionally distilled to separate the more important constituents. These consist of: (*a*) the hydrocarbons, the most valuable, bodies of a neutral character not affected by dilute acids nor alkali; (*b*) the phenols, bodies of a weak acid character, and containing oxygen; (*c*) the bases, containing nitrogen, and often present in such small amounts that they are not recovered. The method of distillation varies much as the market for the distillates fluctuates, and the composition of the tar from different gas works is variable. If benzenes are low in price, the light oils are collected together. Often the phenols are not separated, when the demand for them is not great. Some tars are distilled only until the light oils are removed, and the residue variously employed. But if anthracene is present, the heavy oils are distilled off, and the residue forms pitch.

When received from the gas works, the tar is run into a tank, or cistern, and allowed to stand until the ammoniacal liquor mixed with it separates by gravity. To facilitate this the tar may be warmed by a steam coil in the tank, especially in cold weather. Gas liquor causes frothing in the still, so is removed as completely as possible, and sent to the ammonia distiller.

Formerly, old boilers often served as stills, but in modern works the stills are constructed for the purpose.

In America tar distillation is conducted in a rougher and less perfect manner than in Europe. Horizontal stills of from 15 to 25 tons capacity, similar in construction to petroleum stills (p. 339) but smaller, are commonly used. The condenser worm is ordinarily wrought iron, electrically welded to avoid joints as far as possible. Perforated pipes within the still permit the use of steam or compressed air, to assist in distilling the heavy oils and prevent adhesion of coke to the plates.

In Europe vertical cylinders of wrought iron or steel plates from three-eighths to one-half inch thick are preferred; the diameter is equal to the height; the bottom is concave, and the top is a cast-iron dome, having a manhole, an inlet pipe for the tar, a broad, curved vapor pipe (" goose-neck "), and a small overflow pipe (" tell-tale "); also a thermometer tube and a safety-valve usually; if the latter is omitted, the manhole cover is not screwed down, but closes the opening by its own weight; should excessive pressure develop within the still, the cover is lifted and the vapors escape. The arched bottom rises to a considerable height, thus distributing the heat into the interior of the mass of tar, and the outlet pipe being placed at the lowest point, it is also of assistance in emptying the still. The bottom is sometimes protected from direct contact with the flame by a brick arch (curtain arch). There is usually a coil in the still, through which superheated steam is blown, towards the end of the process, to assist in the distillation of the heavy oils.

These upright stills are set in furnaces so that the flames play under the bottoms, and about half-way up the height, through side flues in the brick setting. They vary much in size; in England they are from 10 to 20 tons capacity; in Germany larger ones are used.

The condenser consists of a cast- or wrought-iron or lead worm, placed in a tank of water. A steam pipe is arranged to warm the water, if necessary.

While the still is yet hot from the previous distillation, the tar is run in. Since the large mass of cold tar requires some time for heating, the fire is started when the still is half full. When the tar runs from the tell-tale pipe, the manhole and valves are closed, and the heat raised until the contents begin to froth. The overflow pipe is then opened, and any ammoniacal liquor which has separated is drawn off. The heating is continued carefully until the still-head gets warm, and puffs of vapor, and finally drops of liquid, begin to come from the condenser. The fire is then moderated, in order to prevent boiling over. A closed receiver is placed at the end of the condenser, and the distillation is continued very slowly, until the temperature reaches 105° C., when, as a rule, the first receiver is changed. The distillate is commonly separated as follows: —

First runnings, or " first light oil," to 105° C.
Light oil to 210° C.
Carbolic oil, to 240° C.

Creosote oil, to 270° C.
Anthracene oil " green oil," above 270° C.

Sometimes the first runnings and light oil are collected together until the temperature reaches 170° C.; and the distillate between 170° C. and 230° C. is taken as carbolic oil. The temperature at which the distillation is stopped depends upon the quantity of anthracene in the distillate and upon whether it is desired to produce hard or soft pitch.

The first runnings, or first light oil, contain water, ammonium salts, the very volatile oils, and a small quantity of heavier oils carried over mechanically. After this distillate has run for some time, it nearly ceases, although the fire is now increased. This is known as the " break," and is the point where the receiver is generally changed. During the interval a peculiar sputtering noise (" rattles ") is heard in the still, caused by drops of condensed water falling into the tar, which is now considerably above 110° C.

When the liquid begins to run from the condenser again, the " second light oil " is collected until the temperature of the tar reaches 210° C., or until the distillate equals 1.000 sp. gr. This is shown by catching some of it in a glass of water; if it forms spherical drops which neither sink nor rise in the water, but float at whatever point they happen to fall, the receiver should be changed. During this period very little cooling water is admitted to the condenser, so that it is warmed to 40°–50° C.; the water is then cut off entirely.

The carbolic oil is distilled until the temperature of the tar reaches 240° C., or until a few drops of the distillate cooled on an iron plate show crystals of naphthalene. This oil contains phenols, and as the naphthalene is less soluble in the heavy oils than in the phenols, its crystallization indicates that all the latter have distilled off. The warm water in the condenser prevents crystallization in the worm; towards the end of this period it is sometimes necessary to heat the water by a steam coil.

The receiver is again changed, and the " creosote oil " collected until the temperature reaches 270° C. The first runnings of this contain much naphthalene, but later the quantity present is small, and remains dissolved in the heavy oil. This distillate is the least valuable and is often not purified further.

The anthracene oil, or " green oil," collected over 270° C., contains anthracene, the most valuable constituent of the tar. The water in the condenser is now brought to the boiling point. Superheated steam is injected into the hot tar in the still to aid in carrying over the heavy vapors. The process is generally stopped when the distillate becomes "gummy"; on cooling it has about the consistency of butter.

The pitch left in the still is a thick, viscous mass while hot, and if run out immediately will take fire in the air. After cooling a few hours, it is run out through the pitch cock, and, when cold, hardens and is sold as "hard pitch." But the still must be emptied while the pitch is warm enough to drain out completely, for if any is left in the still the heat radiating from the brickwork will convert it into coke, which fastens very firmly to the still bottom and does not dissolve when a fresh charge of tar is run in. To facilitate emptying and also to supply a demand for "soft pitch," it is often the practice after the anthracene oil is distilled, to pump into the still a certain amount of creosote or carbolic oil, or the "dead oils" from which the anthracene has been extracted. This mixes with the hot tar and produces a pitch of any desired consistency, according to the quantity of oil used.

Stills are sometimes provided with mechanical stirring apparatus to prevent the pitch from burning on the bottom, and to assist in mixing it with the oils used for softening it.

The crude distillates obtained directly from the tar are further purified and separated into commercial products. The **first runnings** contain ammoniacal liquor and naphtha, which are usually separated by gravity. The former is put with the gas liquor from the tar; the latter is usually refined with the light oil distillate.

The **light oil** contains benzene, toluene, and xylene, with some thiophene, phenols, pyridine bases, and heavy oils. It is distilled in stills much like those used for tar, but smaller. Two fractions are made, naphtha, which distils under 170° C., being further purified; and the last runnings, which are put with the carbolic oil.

The **naphtha** is put into a lead-lined vessel provided with an agitator, and thoroughly mixed with dilute caustic soda solution. This combines with the phenols, which are thus removed when the soda solution is drawn off. After washing the oil with water, about 5 per cent of sulphuric acid (sp. gr. 1.83) is added and agitated with the oil, the temperature being kept low. This dissolves thiophene, unsaturated hydrocarbons and pyridines, and chars and destroys other matter. The acid tar thus formed is drawn off and the oil washed several times with water, and finally with caustic soda to remove all the acid. The washed oil is then redistilled. When collected up to 110° C., the distillate is called "**90 per cent benzol**," since that amount by volume distils below 100° C. It contains about 70 per cent pure benzene, 24 per cent toluene, and some xylene. If collected up to 140° C., the distillate is known as "**50 per cent benzol,**" and contains about 46 per cent pure benzene. Between 140° C. and 170° C. a distillate called "**solvent naphtha**" or "**benzine**" is obtained. This consists mainly of xylenes, cumenes, etc., and is used as a solvent for resins and rubber, for thinning paints, and to wash the crude anthracene obtained from the anthracene oil. It is also employed to enrich illuminating gas, and as a cleansing agent for grease-stained fabrics. It must not be confused with petroleum benzine (p. 340), which is of different composition.

The crude 50 or 90 per cent benzol is chiefly employed in the coal-tar dye industry. By careful distillation in a rectifying still, such as Coupier's or Sevalle's (p. 12), it yields pure benzene, boiling at 80–82° C., toluene at 110–112° C., and xylene, 137–143° C.

The **carbolic oil** contains phenols and naphthalene; after cooling, the oil is pressed or filtered out of the magma of crude naphthalene crystals, which are purified by treating with sulphuric acid and heating to destroy the phenol left in them. After separating the acid tar and washing, the naphthalene is distilled or sublimed.

The oil pressed from the naphthalene crystals may be treated by either of the following processes to recover the phenols: (*a*) The oil is agitated with *dilute* caustic soda, which dissolves the phenols, forming solution of "sodium carbolate." This separates by gravity from the undissolved neutral oils and is drawn off and decomposed with sulphuric acid, or carbon dioxide, or furnace gases, whereby crude carbolic acid (phenol) separates as an oily liquid, from which crude phenol crystallizes on chilling. (*b*) The oil may be heated with a mixture of lime and sodium sulphate, sodium carbolate being formed and calcium sulphate precipitating. After the impurities have settled, the solution of phenols (tar acids) is decanted and sold as crude carbolic acid. This is purified by repeated distillation in a column apparatus of iron or copper, with zinc condensers. Sometimes potassium bichromate and sulphuric acid are put into the still to oxidize the impurities. Crystals of phenol separate from the distillate on cooling, while the cresols remain liquid. The phenol is separated from all liquid matter by a centrifugal machine. By treating the alkaline solution of phenols with an insufficient quantity of acid, the cresols are precipitated first and may be separated, the phenol being separated afterwards with more acid.

Crystallized phenol, C_6H_5OH, melts at 42° C., but the presence of a very little water causes the whole mass to liquefy. It boils at 184° C., and can be distilled unchanged. Carbolic acid is a violent poison and has a penetrating odor. It is a powerful antiseptic, germicide, and disinfectant. It is the source from which many dyes, explosives, and medicinal chemicals are prepared. When dissolved in soap, the crude tar acids are often used as antiseptics under the names lysol and kreolin; these are soluble in water or emulsify with it.

The **creosote oil** also furnishes naphthalene, which crystallizes on cooling. It is filtered, or pressed in presses which have steam-heated plates; the crude naphthalene is washed with caustic soda solution and with concentrated acid, and is distilled or sublimed; the oil contains cresols and higher phenols, naphthol, and liquid paraffine, which have but little value and are not separated. It is chiefly used for preserving ("pickling") timber and railroad sleepers; the timber is thoroughly dried, placed in tanks from which the air is exhausted, and the hot creosote oil pumped in under heavy pressure. A small amount is used for lubricant, and as an illuminant for outdoor work where smoke is of no consequence. It is also used as fuel, and extensively in the preparation of "sheep dips," liquids used for destroying ticks and vermin on sheep and cattle.

Naphthalene is one of the most important constituents of coal-tar, forming over 5 per cent of it. It forms shining white platelike crystals, which melt at 79° C., and boil at 218° C. It has a peculiar penetrating odor, and is much used instead of camphor to protect woolen goods and furs from moths; it is also used to prepare naphthols, naphtylamines, and phthalic acids as "intermediates" for the manufacture of dyes. Nitronaphthalene is employed to remove the "bloom" from mineral oils (p. 342).

The **anthracene oil**, or "**green oil**," contains about 10 per cent anthracene, $C_{14}H_{10}$, together with other solid hydrocarbons, such as phenanthrene, chrysen, carbazol, paraffine, and liquid oils of high boiling points. The mass is cooled until the solid matter has crystallized, when the liquid oils are removed by bag filtering or by a filter press or centrifugal machine. The crystalline mass so obtained is pressed in canvas bags in a hydraulic press at a temperature of 40° C. The oils expressed are then again chilled to a low temperature and pressed, or are redistilled to recover more anthracene; then they are mixed with the creosote oil or run back into the tar still to soften the pitch. The crude 30 per cent anthracene from the press is pulverized and washed with creosote oil or with solvent naphtha from the light oils, which dissolves much of the contaminating substances, but does not remove carbazol. The magma is "centriffed" or pressed; the liquid separated is distilled to recover the naphtha, and the residue of phenanthrene, having little value, is usually burned for lampblack.

By these washings, the anthracene is raised to about 50 per cent, when it is sold to the alizarine manufacturer. For further purification, it is washed with caustic potash to remove carbazol, and then it is sublimed in an atmosphere of superheated steam. It forms white plates of pearly lustre, melting at 213° C. and boiling at 360° C. It is employed chiefly in the preparation of artificial alizarine.

The **pitch** left in the still is either hard or soft, as described on page 330. If so soft that it remains liquid when cold, it is often used as a black varnish for painting metal work and wood, or for making tarred paper or roofing paper. Soft pitch is used as a binder in preparing fuel "briquettes" from coal dust. Pitch is also mixed with asphalt for making sidewalks and pavements. Soft pitch softens at about 38°–40° C. and melts at 60° C. When a small piece is chewed, it coheres together like gum. Hard pitch softens at 75°–80° C., and melts above 120° C. When chewed, it pulverizes into a non-cohesive powder in the mouth.

The yield of crude products from tars is about as follows: —

	Gas-Works Tar*	Coke-Oven Tar†
Ammoniacal liquor	1.81 %	2.3 %
Light oils	1.65	3.7
Middle oils (carbolic oil)	10.66	9.8
Heavy oil (creosote oil)	8.18	12.0
Anthracene oil	14.05	4.3
Pitch	61.16	67.0
Loss	2.48	0.9

The yield of purified products from tar is about as follows: ‡ —

Benzol and toluol	0.22 %	Cresols	1.13 %
Xylol and solvent naphtha	0.62	Naphthalene	6.40
Phenol	0.40	Anthracene (pure)	0.44

REFERENCES

Das Anthracene und seine Derivate. G. Auerbach, Braunschweig, 1880.
Die Chemie des Steinkohlentheers. Gustav Schultz, Braunschweig, 1890.
Die technische Verwerthung des Steinkohlentheers. G. Thenius, Vienna, 1887.
Coal-Tar and Ammonia. Geo. Lunge, 4th ed., London, 1909.
Die Industrie des Steinkohlentheers und des Ammoniaks. G. Lunge und H. Köhler. 2 vols. Braunschweig, 1912.
Coal Gas Residuals. Frederick Wagner. New York, 1914.

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* Schniewindt, Mineral Industry, **1902**, 152.

† Lunge, Coal-tar and Ammonia, I, 116.

‡ Heusler, Chem. Technologie, Leipzig, 1905, 188.

MINERAL OILS

THE PETROLEUM INDUSTRY

Petroleum is widely distributed, being found in many places in sufficient quantities for profitable working. The principal deposits in America are located in Pennsylvania, New York, Ohio, West Virginia, Indiana, Illinois, Kansas, Kentucky, Oklahoma, Louisiana, Texas, California, Colorado, Mexico, and Canada. The next in importance to the American oil fields are the Russian, in the Baku district around the Caspian Sea, in the Caucasus mountains, and along the northeast coast of the Black Sea. Less important deposits occur in Persia, Burmah, Borneo, Galicia, and Roumania. Small deposits are worked in Germany, Hungary, Algiers, Japan, Venezuela, New Zealand, and in some of the islands of the Pacific.

Petroleum occurs in all geological formations from the Silurian to the Tertiary, the New York and Pennsylvania deposits being in the Devonian and Upper Silurian, the Colorado fields in the Cretaceous, and those in California in the Miocene epoch or Middle Tertiary. The Russian, Galician, and Indian oils are chiefly in the Tertiary. In all cases, the strata in which it is found are horizontal or but slightly inclined, usually not over 30°. It is generally found in sandstones or conglomerates, called "oil sands," overlaid with an impervious shale or slate. Frequently several layers of sandstone are struck, lying between beds of the shale.

The origin of petroleum has been the subject of much study by many eminent chemists. Berthelot regarded it as the product of the action of steam and carbon dioxide on the alkali metals. Mendeleeff supposed it resulted from the decomposition of metallic carbides by water. This necessitates the acceptance of La Place's theory of the formation of the earth, and the assumption that heavy metals, such as iron, were among the first substances to condense into the liquid and solid state, thus forming the central portion of the earth; and that these metals then combined with the carbon from the surrounding atmosphere to form carbides, which were afterwards decomposed by water, from the cooled surface, which percolated down through cracks and fissures caused by the cooling and shrinkage of the earth's crust. Thus hydrocarbons were formed and metallic oxides left in the earth. This theory requires that all petroleums have approximately the same composition, in whatever formation they are found, but this is not the case.

Another hypothesis supposes petroleum to be of organic origin. Here again are several theories as to the formation of the oil from the vegetable or animal remains. One is that the organic matter, probably consisting of vegetable matter and mollusks, decomposed under salt water with exclusion of oxygen and at a rather low temperature.* Another, that only animal matter is the basis of the oil and that the nitrogen of the animal tissues escaped as ammonia or other nitrogen compounds, and that the remaining fat was subjected to a species of dry distillation under great pressure, yielding crude petroleum.† There is reason to believe that the New York, Pennsylvania, and Ohio petroleums are of vegetable origin,‡ but those of California,§ Texas, and some others contain nitrogen and are found in rocks filled with animal remains.

The crude oil usually consists of hydrocarbons, present in homologous series, though oils from different localities show differences in these series. The Pennsylvania oils contain members of the marsh gas series with the general formulas, C_nH_{2n+2}; all of these, from methane, CH_4, up to solid paraffines with $C_{27}H_{56}$, have been isolated from these oils. Also, small amounts of the olefine series, C_nH_{2n}, and the benzene series, C_nH_{2n-6}, and in some oils, sulphur and nitrogen have been found. Various crude oils from California, Texas, Oklahoma, and Kansas contain asphaltum, as well as paraffine. The Russian oils consist largely of the naphthene series, general formula C_nH_{2n}, isomeric with the olefines, but differing from them in their properties, so the refining is not the same as that of the American oils.

In many places crude oil comes to the surface in small quantities, mixed with the water from springs, the first discoveries having been reported as "oil springs." The explorers in central New York, as early as 1630, mentioned an Indian remedy containing petroleum. Later it was sold as "Seneca oil," by the Seneca Indians. Their method of collecting it was to spread blankets on the surface of the water on which the oil was floating, wringing it out when the blanket became saturated. If the layer of oil was thick enough, it was skimmed off with a flat board.

About the middle of the 19th century, petroleum from various parts

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* Phillips. Am. Chem. Jour., **16**, 409–429.

† Engler, Ber., **1888**, 1816; **1889**, 592.

‡ Orton. Report on Occurrence of Petroleum, Natural Gas, and Asphalt in Western Kentucky. 1891.

§ Peckham. Am. Jour. Science, **48**. (1894.)

of the world had begun to attract some attention, and crude methods of refining it had been devised; in some few instances this purified oil was being used for illuminating. But none of these efforts had been very successful, and it was not until 1859, when Mr. Drake drilled the first productive oil well near Titusville, Pa., that the real development of the petroleum industry began.* The Russian, Indian, and Galician oils were mentioned by explorers during and before the Middle Ages, but the industries have never been developed to any great extent, until within the last thirty years, when the Russian fields have become very important.

The crude oil is obtained by boring tube wells through the shale into the sand rock. There is no certainty beforehand that a well will yield oil, and, indeed, about one-fifth of those bored in this country produced none; these are called "dry holes."

The machinery used in oil-well drilling is very ingenious, and a great number of special devices have been invented to overcome the numerous obstacles encountered. Only the principal tools can be mentioned here. The chief one is the "**centre-bit**" (Fig. 101), a chisel-shaped piece of steel 4 feet long and weighing about 300 lbs., the cutting edge of which is nearly as wide as the diameter of the well. Above the centre-bit is the "**auger-stem,**" a rigid bar from 12 to 45 feet long, to which the bit is screwed. Its chief purpose is to guide the bit and keep the hole straight; it also adds weight to the drill. Next above the auger-stem is a peculiar piece of apparatus called the "**jars**" (Fig. 102). It consists of two links of steel which have a sliding motion, one within the other, of from 20 to 24 inches. The object of this is as follows: the centre-bit frequently becomes fastened in the hole, either by fragments of broken rock acting as wedges between it and the sides of the well, or through sinking into a seam in the rock. Any attempt to loosen it by a steady upward pull would break the rope, but a sudden upward shock is generally sufficient to loosen it. This is obtained by the movable links of the jars. But they are not allowed to close completely, and so give a downward stroke, unless the tools become fast in the well. Above the jars is a long, heavy steel bar called the "**sinker-bar.**" Through its momentum this gives greater effect to the action of the jars. To the top of the sinker-bar the rope


FIG. 101.


FIG. 102.

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* A period of wild excitement and speculation followed, the description of which by Peckham, Crew, and others, is very interesting reading.

is attached, by which the entire mass is lifted and dropped, just as a pile-driver is operated. The drop allowed for each stroke of the bit is about two feet. The rope is fastened to the "**temper-screw,**" which lowers the tools slightly as the rock is cut away by each blow of the bit, and turns them in the hole so that the next cut shall be at a slight angle to the last one. When all screwed together, the drilling tools form a rod about 60 feet long and weighing about a ton.

Over the spot where the well is to be drilled a timber or steel structure is built, called the "**derrick**"; this is from 35 to 80 feet high, and from 12 to 15 feet square at the bottom, tapering to about 5 feet square at the top. On the floor of the derrick is the windlass for handling the drilling tools, the rope passing over a small wheel at the top. During the drilling the rope passes through a clutch at the end of a large walking-beam, driven by the engine, imparting a rapid up-and-down motion to the tools.

An iron "**drive-pipe**" is sunk through the drift and clay to the solid bed-rock. If the latter is within 15 or 20 feet of the surface, a shaft 6 or 8 feet square is sometimes dug down to it. Then the drilling of the well proper begins, which is usually 7⅞ inches in diameter to the bottom of the water-bearing strata. Then the hole is decreased to 5¾ inches diameter, and a tube, called the "**casing,**" is put down; this is provided with a rubber or leather collar to fit closely against the shoulder formed where the diameter of the well decreases, making a water-tight joint. Then the hole is continued to the oil-bearing strata, by means of a 5½-inch bit.

At frequent intervals it is necessary to remove the mud and splinters of rock. This is done by the "**sand-pump,**" or "**bailer,**" which is a long metal tube, having a valve in the bottom. It is lowered until a pin on the under side of the valve strikes the bottom of the well. The water, which is always present, rushes into the bailer, drawing with it the débris; then the tool is at once raised and the valve closes.

It is customary to drill some distance into the oil-bearing stratum, and sometimes a cavity filled with gas, oil, and water is struck. The pressure is occasionally so great as to drive the oil to the surface, sometimes with great force. Such wells are called "gushers." They seldom continue to flow for more than a few days or weeks, when pumping must be employed. Some of these gushers have produced enormous quantities of oil, as much as 75,000 * barrels a day when at their height.

But most wells do not gush, and it is now customary to resort to "torpedoing," in order to increase the yield of oil. A tin

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* Mineral Resources of the United States, **1902**, 570.

shell, from 3 to 5 inches in diameter and from 5 to 20 feet long, is filled with nitroglycerine and lowered to the bottom of the well. On top of the can is a percussion cap, which is fired by dropping a piece of iron, called a "go-devil," weighing several pounds, into the well. The resulting explosion cracks and shivers the rock, giving the oil a better opportunity to flow into the well. Very often a well gushes after torpedoing, and measures are usually taken beforehand to dispose of the first heavy rush of oil and water.

The finished well is prepared for pumping by lowering a 2-inch pipe, at the bottom of which is the oil pump, worked by a wooden rod inside the pipe. Fig. 103 shows sections through a pumping and through a flowing well. In a flowing well no pump rod is introduced, but the space between the casing and tubing is tightly closed at the top, in order to force both gas and oil through the tubing.

Fig. 103.

The wells range in depth from 50 to 4000 feet, the average in New York and Pennsylvania being from 1200 to 1800 feet. The cost varies, but from 3000 to 4000 dollars is about the average. The ordinary production varies from one to several hundred barrels per day.

The crude oil is now generally carried from the wells to the refineries by pipe-lines, — six- or eight-inch pipe, through which the oil is pumped. At frequent intervals along the pipe-lines are tanks of from 30,000 to 40,000 barrels capacity, in which the oil is stored until wanted for refining. This system mixes all varieties of oils; hence, if a special kind is required, it must be transported in tank cars or in barrels.

Crude petroleum is an oily liquid varying in color from greenish brown to nearly black; some varieties are reddish brown or orange when viewed by transmitted light. Nearly all show some fluorescence, and have a rather unpleasant odor. The specific gravity varies from 0.782 to above 0.850, in oils from different localities. As it comes from the well, more or less gas is dissolved in it, consisting chiefly of marsh gas, CH_4; ethane, C_2H_6; propane, C_3H_8; and butane, C_4H_{10}. A very small amount of phosphorus is often present, but seldom more than 0.05 per cent. The oils from Ohio and Canada have an unpleasant odor, because they contain some sulphur compounds. Sand and water are also mixed with the crude oil, but these settle on standing in the storage tanks.

In order to separate the various products from the crude oil, it is subjected to fractional distillation. The higher the percentage of the lighter oils, the more profitable for the refiner; but many crude oils are distilled only for the lubricating oils. A few may be used as lubricants without distilling. Considerable petroleum is used for fuel, but this is being replaced by the residuum from which the more valuable light oils have been separated.

Refining consists in the separation and purification of the marketable products of the crude oil, which is usually separated into about five portions. These are naphthas, illuminating oils, lubricating oils, paraffines, and coke. The process is usually worked in two stages: the distillation and refining first of the light oils, and then of the heavy oils. It is only in the large refineries that both processes are carried out; usually one refiner produces the naphthas, burning oils, and "residuum," and another starts with the residuum and finishes the process.

For distilling the light oils, the **cylindrical or horizontal still** (Fig. 104) is used; this is 30 to 40 feet long by 12 or 15 feet in diameter, and is set in a brick furnace, with the upper half of the still exposed to the air. It holds 600 to 750 barrels, and is provided with steam coils and arrangements for blowing in free steam to carry on the process as a steam distillation if desired.

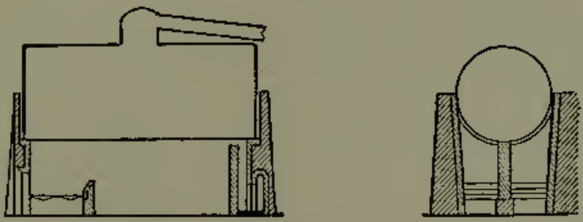
FIG. 104.

The **condensers** are long straight pipes set in troughs through which water flows, or they are coils set in tanks of cold water. They are so arranged that the distillates are delivered at some distance from the still, to diminish the fire risk. Each pipe is usually provided with a trap by which the gases (passing over with the oil vapors) are collected and then led under the still and burned, thus economizing fuel. Sometimes the very light oils are burned with the gases, but they are usually condensed, forming the "**benzine distillate**," or **crude naphtha**. This is stopped when the gravity reaches 62° Bé. (sp. gr. 0.729). Then comes the **kerosene, or burning oil distillate**, until the gravity equals 0.790, or for heavy illuminating oils, 0.820. Here the distillation is stopped and the residuum drawn off, to be distilled for lubricating oils, in the "tar stills."

*p340-f

At high temperatures oils undergo decomposition; the heavy oils tend to split off gas, hydrocarbons and carbon, forming lighter oils; these reactions are reversible. The process is called "**cracking**"* and the reactions are complex, the number of products formed being quite large. The heavy oils decompose into paraffines and olefines of lower boiling points and hydrocarbons of the aromatic series may also be produced. As an example of what *may, perhaps,* take place the hydrocarbon $C_{18}H_{38}$ (octadecane), boiling at 317° C, may be assumed to decompose into $C_{10}H_{22}$ (decane), boiling at 173°, and C_7H_{16} (heptane), boiling at 98°, and carbon; or it may form a paraffine and an olefine, *e.g.* C_8H_{18} (octane), boiling at 125°, and $C_{10}H_{20}$ (decylene), boiling at 172°. The lower boiling product would be put with the naphtha distillate, and the higher boiling would form a part of the burning oil.

During the course of the reactions certain amounts of the aromatic hydrocarbons are formed in the order, cymene, xylene, toluene, benzene, naphthalene, and anthracene; these substances are produced progressively each by the decomposition of the one preceding, the reactions progressing further in the direction indicated, the higher the temperature. Thus the formation of aromatic bodies in the distillation of coal is also explained, and the conditions indicated under which the formation of the individual hydrocarbons will be a maximum. Rittman has succeeded in so controlling the temperatures and pressures of the decompositions that the artificial manufacture of gasolines and benzenes becomes possible.

The still, as already shown, has its upper part exposed and thus cooled by the air; a column loosely packed with stones is set above the still and the vapors pass into it; often a dephlegmator is also used. The heavy oil vapors partly condense on these cooler surfaces and fall back into the boiling residuum, which is much hotter than their boiling points, the oils of high molecular weight decompose into into bodies of lower boiling points, while some carbon separates and forms a coke in the still. The several distillates from the crude oil are redistilled and divided into further subdivisions.

The benzine distillate yields†: —

Cymogene,	B. P. = 32° F. = 0°C	Sp. Gr. = 0.590–0.610	Petroleum ether. ?
Rhigolene,	B. P. = 60° F.	Sp. Gr. = 0.625–0.631	
Gasoline,	B. P. = 115° F.	Sp. Gr. = 0.635–0.666	
C Naphtha (Benzine)	B. P. = 122°–140° F.	Sp. Gr. = 0.678–0.700.	
B Naphtha,		Sp. Gr. = 0.714–0.718.	
A Naphtha (Petroleum naphtha),		Sp. Gr. = 0.741–0.745.	

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* The history of the discovery of this process is given in chap. iii of Petroleum Distillation, by A. N. Leet, New York, 1884.

† Boverton Redwood — Groves and Thorp's Chemical Technology, Vol. II.

The burning oil distillate yields: —

110° fire test burning oil (" Standard white "). } Export Oil.
120° fire test burning oil (" Prime white "). }
150° fire test burning oil (" Water white ").

The residuum from the above distillation is transferred to the tar still, or if the distillation has been carried on under vacuum, it is known as "**reduced oil,**" and is used to make fine lubricating oils or vaseline.

The **tar stills** are cylindrical, and are set in much the same way as those already described, but are encased in brickwork almost to the top. They are provided with pipes for introducing superheated steam, and are much smaller than the crude oil stills.

The first distillate is collected until the gravity is about 38° Bé. (0.834 sp. gr.), and is mixed with the next charge of crude oil, or washed with acid and soda and refined for burning oil. Then follow several distillates of increasing color and density, which are purified as described below, and treated to separate the paraffine wax and lubricating oils. The distillation is carried on until the still bottom is red-hot, when a gummy yellow distillate, called "yellow wax," is collected. This contains anthracene and other hydrocarbons of high molecular weight. The residue of coke is valuable for electric light carbons and other electrical purposes.

The fractions collected from the burning oil distillate are more or less yellow, colored by tarry matters, which would collect in the lamp-wick and soon choke it. To remove these impurities, the oil is put into an "**agitator,**" a large, lead-lined, iron tank, where it is mixed with from 1 to 2 per cent of concentrated sulphuric acid, and the mixture stirred by blowing in air at the bottom. The acid unites with the tarry matters, and when the blast is stopped, sinks to the bottom and is drawn off as "sludge acid." Water is added, and after the mixture is agitated, is drawn off. Next a solution of caustic soda is introduced (about 1 per cent), and the contents of the tank again agitated. Then the oil is again washed with water and drawn into the settling tanks, where the suspended water settles out, leaving a bright, clear oil. These tanks are very shallow, usually only about 1 foot or 15 inches deep, but may cover an area of 20 by 30 feet. They are exposed to the light and air, and usually contain steam coils for warming the oil in winter.

If the oil is now found to have too low a flash point (p. 344), it is run through a "**sprayer,**" an upright pipe with cross-arms of small perforated pipe, through which the oil is forced into the air in fine jets or spray; after falling some distance, it is collected in tanks. By this exposure to air, any light oils, such as benzine or naphtha, are volatilized, and the flash point thus raised. But spraying is less frequently necessary now, since more care is taken in the original distilling.

Instead of washing, some kerosenes are redistilled, but this generally fails to remove all the yellow color, though, when burned, they do not form a crust on the wick, due to traces of caustic soda or sodium sulphate.

A small amount of burning oil of very high fire test (about 300° F.) is made by treating a crude oil distillate (0.823 to 0.846 sp. gr.) with a very large proportion (5 to 7 per cent) of sulphuric acid, washing with caustic soda, and redistilling with caustic soda lye in the still. This oil is sold as **mineral colza**, **mineral seal**, and **mineral sperm** oil.

The **paraffine oils** are treated with acid in agitators which may be heated by steam pipes; they are washed and then chilled and left several hours until the paraffine crystallizes. The soft mass is then put into canvas bags and pressed at 40° F. in hydraulic presses. The crude paraffine cake is again melted, crystallized, and pressed. It is then washed with a little benzine and pressed once more. It is finally melted and filtered hot through bone-char, or fuller's earth and on cooling forms the white commercial paraffine. The oils expressed are lubricating oils of various grades.

After the paraffine is removed, some of the lighter lubricating oils are converted into "**neutral oils**" by bone-char or fuller's earth filtration and exposure to sunlight and air, to remove the "**bloom**," so that they may be used to adulterate certain animal and vegetable oils. It may also be removed chemically by adding about 1 per cent of nitronaphthalene, or dinitrobenzol, or nitric acid. Bloom has no injurious effect upon the oil or machinery.

Crude petroleums containing sulphur (*e.g.* those from Ohio and Canada) are more difficult to refine, and consequently were formerly only used for fuel. Successful methods for refining them are, however, now in use. The common process is to pass the vapors from the crude oil distillation over copper oxide; or to collect the distillates from the crude oil separately and redistil them with a large excess of copper oxide, or a mixture of lead and copper oxides in a still, which is provided with an agitator. The residue consists of a mixture of tar, copper sulphide, and oxide. This is pressed and calcined at a low temperature, the combustion of sulphur and tar furnishing sufficient heat. The final product is copper oxide, which is returned to the process. A solution of litharge in caustic soda is sometimes used in the agitator after the usual acid and alkali treatment, to remove the sulphur, but this is not always a success; though it destroys the offensive odor, traces of sulphur sometimes remain and become noticeable on burning.

The lighter lubricating oils are called "**spindle oils**" and are used on rapid-running bearings. "**Machinery oils**" form the middle grades, and "**cylinder oils**" are the heaviest. Paraffine in lubricating oils is said to reduce its viscosity and cause it to become gummy when in use.

"**Reduced oils**" are made from the residuum left after distilling the burning oils from some crude petroleums by the aid of vacuum or by simply exposing certain crude oils to the sun and air in shallow tanks which may be gently heated by steam-coils in winter. The very light oils soon evaporate and the suspended impurities settle. Another process is to let the crude oil flow in thin films over woollen blankets suspended in warm rooms; the very volatile oils evaporate and much of the suspended matter is retained by the cloth. By these methods, oils are obtained which are entirely free from any decomposition products due to heating, and from any chemicals such as are used in washing and bleaching ordinary lubricating oils. Crude oils of high gravity (below 32° Bé.) are usually selected for this purpose.

Reduced oils are valuable lubricators and command a good price. Sometimes they are char-filtered to improve their color and quality.

Vaseline or **petrolatum** is made from the residuum of vacuum distilled crude oils. It is treated with acid and soda, washed and char-filtered, and sometimes redistilled in vacuum.

The **Russian petroleums** are distilled in much the same way as the American, but less acid is used, as the naphthenes are somewhat soluble in it. It is found practicable to use continuous stills, as the residuum is more fluid than in the case of American oils. The stills are heated by separate furnaces and connected in such a manner that the overflow pipe from one is the supply pipe for the next, the residuum from the last passing through coils placed in the supply tank, so that the crude oil is warm when it enters the first still. By careful regulation of the heat and the flow of oil, each still can be made to yield a distillate of constant gravity.

Russian petroleum yields about 38 per cent illuminating oils, which is lower than the Pennsylvania oils. Since fuel is scarce, the residuum, called *astatki*, is burned in special burners and furnaces.

The yield of lubricating oils is large, being nearly 36 per cent. They are said to be superior to American lubricators for use in cold countries.

Oil-testing. — The usual test for kerosene is the flame test, *i.e.* the determination of the temperature at which the vapors take fire when mixed with air. The point usually taken is the "**flash point**," the temperature at which the oil gives off sufficient vapor to form a momentary flash when a small flame is brought near its surface. The "**fire test**" determines the temperature at which the oil gives off enough vapor to maintain a continuous flame if ignited; in other words, it shows the temperature at which the oil burns in the air, and is about 20° F. higher than the flash point. Both the flash point and the burning point are lower than the boiling point.

The flash point is determined in a special apparatus, and in many states and countries the particular instrument and its dimensions are specified by law. In this country, "open testers" are largely used, but Abel's "closed tester" has become very popular, and is now the legal instrument in some of the states and in England and Germany. There are many forms of apparatus for oil testing, but the two above mentioned cover the general principles involved in all. Open testers do not represent the conditions prevailing in an ordinary lamp; the closed tester more nearly approaches these, and its indication is usually about 20° F. *lower* than that shown by the open tester.

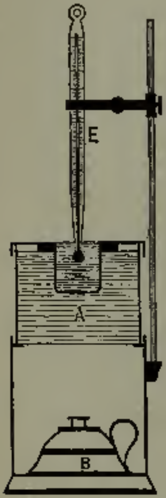

Fig. 105.

Tagliabue's **open tester** (Fig. 105) is very simple. A copper water bath (A), heated by the small lamp (B), contains the glass dish in which the oil to be tested is placed. A delicate thermometer (E) is hung to dip into the oil. Sometimes a stirring apparatus is provided for both the water bath and the oil. The water bath is slowly heated, and at regular intervals of temperature a lighted match or small gas flame is passed half an inch above the surface of the oil. The temperature at which a flame passes completely over the surface is noted as the flash point. The heating is usually continued until the oil catches fire on applying the light, when the temperature is taken as the burning point. The apparatus is rather crude and is open to errors.

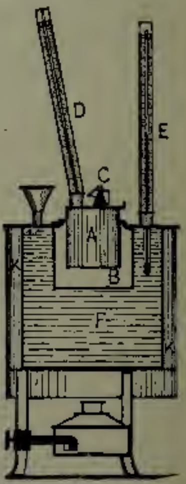

Fig. 106.

Abel's **closed tester** (Fig. 106) is more complicated, but obviates some of the errors of the open cup. It consists of a copper cylinder (K, K) in which is the water bath (F). In the upper part of the water bath is an air chamber (B) in which is suspended the copper vessel (A) carrying the oil. All these vessels are provided with close-fitting covers. The cover of (A) has three openings which may be opened or closed by a small lever. The cover also carries the thermometer (D), dipping into the oil, and a small lamp or gas flame set on an axis at (C), so that the flame may be brought directly over the middle opening in the cover. Usually the lever which moves the cover of the opening simultaneously turns the flame down to it. The thermometer (E) dips into the water bath, which is heated to 54° C. before the oil is introduced into (A). When the thermometer (D) registers 18°–19° C. the testing is begun, and repeated with each rise of a degree, until the flash is seen. This instrument is officially used in Germany, the lever being run by clock-work. It is also used in England, the law requiring a flash test of 73° F., which is rather low for safety; it should not be under 100° F. In this country, each state has its own standard. Some require 150° F. fire test in open cups, and others 110° F. Most states fix 110° F. flash test.

Lubricating oils are usually tested for viscosity, gravity, flash, and burning points, congealing point, and color. The gravity is usually determined with the hydrometer or Westphal balance. In this country, the Baumé instrument is almost always used.

Viscosity is determined by relative tests, *e.g.* the rate of flow of the oil through a capillary tube or narrow opening, as compared with the rate of flow of pure sperm oil through the same tube or opening. Temperature is here a very important factor.

The **congealing point**, or "cold test," determines the temperature at which the oil becomes pasty or solid through the crystallization of dissolved paraffine or other matter. This test is of great moment if the lubricators are to be used in cold climates.

Color tests are chiefly made on oils intended for export, by comparing a tube full of the oil with standard glass plates of various tints, in a colorimeter. For burning oils the colors range from pale yellow or straw to water white.

Certain animal and vegetable oils, when soaked up in waste, will take fire on standing. This is especially true of linseed, cotton-seed, corn, lard, and neatsfoot oils, and is caused by the rise in temperature due to the oxidation of the oil. If from 40 to 50 per cent of mineral oil be added to these oils, this spontaneous combustion is prevented to a great extent. This is one of the uses of the neutral oils (p. 342).

SHALE OIL INDUSTRY

In Scotland, Germany, and a few other countries, mineral oils are produced by the destructive distillation of certain bituminous shales. These are soft, light brown, or gray rocks, which do not contain oil as such, but are permeated with bitumen, a complex organic substance similar to pitch. When heated in retorts, this decomposes into gas, oily products, ammonia, and tar, leaving a carbonaceous residue. The temperature of the distillation greatly influences the character of the products, a low temperature affording an increased yield of oil.

The shale is broken to small size and heated to a low red heat in vertical retorts into which steam is injected to assist in the distillation. Both continuous and intermittent systems of distillation are in use, the former being generally employed in Scotland. The shale is charged at the top of the retort and when " spent " is drawn while still hot upon a grate beneath the retort, where its carbonaceous matter (amounting to 10–15 per cent) is burned, thus economizing fuel.

The products of the distillation pass through a series of pipes similar to the hydraulic main and condensers of the coal-gas manufacture. The light naphtha vapors and gas pass into a coke tower through which heavy paraffine oil trickles; this absorbs the naphtha, while the gas passes on and is burned under the retorts. In the hydraulic main and condensers the other distillates condense in two layers, the ammoniacal liquor below and the tar and oil above. These are separated by gravity. The ammonia liquor is treated in the same way as that from coal gas (p. 151). The oily tar (0.865 sp. gr.) is distilled in much the same way as crude petroleum until only solid coke remains in the still. The distillates are collected together as " once-run oil " and washed in agitators with sulphuric acid and caustic soda, and then fractionally distilled. These distillates are each purified, yielding commercial naphtha, burning oils, lubricator oils, and solid paraffine.

The acid tar from the washing yields some ammonium sulphate, and tarry matter which is used for fuel. The soda tar is treated with carbon dioxide, which liberates the creosote, used for the same purpose as that from coal-tar. The carbonate of soda solution is causticized and used again.

OZOKERITE

Ozokerite is a natural, paraffine-like substance containing a small quantity of oily matter. It was probably formed by the evaporation of petroleum until the more volatile oils had escaped. It occurs in irregular seams and masses in the earth in Galicia, in the Caucasus, in Utah, and in Colorado. In Galicia it is mined by sinking shafts and drifting, following the seams. The wax is separated from the earthy impurities by hand picking and by washing, the wax being lighter than water and rising to the surface. The residue is boiled with water to melt out the remaining wax, which is skimmed from the surface. Extraction with benzene is also employed.

The wax is sometimes distilled, by which light oils, illuminating oils, heavy oil, and paraffine are obtained. Or it is refined by treating with sulphuric acid and caustic soda, followed by a charcoal or bone-black filtration. The product, called **ceresine**, melts at 61° to 78° C.* and is similar to beeswax. It appears to belong among the olefines, having the general formula C_nH_{2n}. Its color ranges from pale yellow to white, according to the degree of refining.

It is used as candle stock; for preparing insulating compounds for electrical work; in making a black dressing for shoes and harness leather, and to adulterate beeswax.

ASPHALT

Asphalt or **mineral pitch** is probably an oxidized residue from the evaporation of petroleum. This name is usually applied only to the solid bitumens, the semi-solid or liquid bitumen being called **maltha,** or **mineral tar.** Asphalt generally contains sulphur and nitrogenous bodies, but is chiefly composed of hydrocarbons. The crude material consists of two chief ingredients, that soluble in petroleum spirit, called *petrolene,* and an insoluble black substance called *asphaltene.* Asphalt occurs in large quantities in and near the "pitch lake" on the island of Trinidad; also in Cuba, Venezuela, California, Utah, Texas, Canada, and in many European countries. The Utah deposit is particularly pure (gilsonite) and is much used for black varnish and for insulating material. It is also much used as a protective paint for the interior of chlorine stills, bleaching powder chambers, acid tanks, and for waterproofing purposes. Its chief use is for sidewalks and pavements, for which it is mixed with pulverized limestone or with the natural asphalt rock. The latter falls to a loose granular mass when heated until the asphalt softens, and is then rolled and stamped into place with hot irons. A certain proportion of purer asphalt, or of the heavy petroleum oils, is often added to the mixture to render it more plastic.

Crude asphalt contains much moisture and mineral matter. It is refined by heating until melted, whereby the moisture is expelled and some of the mineral matter separates by subsidence. Two varieties of Trinidad asphalt are in commerce,—"lake pitch" and "land pitch." The latter is harder, and has the higher melting point. Asphalt is soluble in carbon disulphide, acetone, and benzene, but not in alcohol nor water. When heated, it softens at from 80° to 100° C.

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* Redwood.

REFERENCES

Petroleum Distillation. A. N. Leet, New York, 1884.

Report on Petroleum; U. S. Census, 1880. S. F. Peckham, Washington, 1885.

Das Erdöl von Baku. C. Engler, Stuttgart, 1887. (Enke.)

A Practical Treatise on Petroleum. Benj. J. Crew, Phila., 1887. (Baird & Co.)

Die deutsche Erdöle. C. Engler, Stuttgart, 1888. (Enke.)

Le Petrole. Henry Deutsch, Paris.

Das Erdöl und seine Verarbeitung. A. Veith, Braunschweig, 1892.

Petroleum; Its History, Origin, etc. W. T. Brannt, Phila., 1895. (Baird & Co.)

Die Fabrikation der Mineralöle. W. Scheithauer, Braunschweig, 1895.

Treatise on Petroleum, 2 vols. B. Redwood and G. T. Holloway, London, 1896. (Griffin & Co.)

U. S. Geological Survey, 8th report. (Formation of Petroleum.)

Report of Experts on Asphalt Paving. Dept. Public Works, Philadelphia, **1894.**

L'Asphalte. Leon Malo, Paris, 1888. (Baudry et Cie.)

Mineral Oils and their By-Products. I. I. Redwood, London, 1897. (Spon.)

On the Nature and Origin of Asphalt. C. Richardson, New York, 1898.

Der Asphalt und seine Anwendung. W. Jeep, Leipzig, 1899.

The Oil Fields of Russia. A. Beeby Thompson, London, 1904.

Das Erdöl, seine Verarbeitung und Vervendung. R. Kissling, Halle, a. S., 1908.

Lubricating Oils, Fats and Greases. G. H. Hurst, 3rd ed., London, 1911.

A Short Handbook of Oil Analysis. A. H. Gill, 6th ed., Philadelphia, 1911.

American Chemical Journal, **16**, 406. The Origin of Petroleum and of Natural Gas. F. C. Phillips.

Proceedings of the American Academy of Arts and Sciences, Vol. **32**. Investigations on American Petroleum. Charles F. Mabery.

Proceedings of the American Philosophical Society, Vol. **36**, No. 154. Origin and Chemical Composition of Petroleum. S. P. Sadtler.

Journal of the Society of Chemical Industry: —
- **1890**, 359, The Oil Fields of India, Burmah, etc. B. Redwood.
- **1894**, 719, Removal of Sulphur from Petroleum.
- **1894**, 790, Origin of Petroleum. F. C. Phillips.
- **1894**, 794, Present State of the Petroleum Industry.
- **1894**, 872, American and Russian Petroleums.

Journal of the Association of Engineering Societies: —
- **1894**, On the Composition of the Ohio and Canadian Sulphur Petroleum. C. F. Mabery.

Mineral Resources of the United States, **1882** +.

VEGETABLE AND ANIMAL OILS, FATS, AND WAXES

These oils are usually called "fatty" oils, to distinguish them from the mineral and essential oils. They are very widely disseminated in nature, both in plants and in animals, and often form a large percentage of the weight of the substance in which they are found. They differ from the mineral oils in their chemical composition, being compounds of *organic acids*, with bodies belonging to the group called *alcohols*, *i.e.* they are esters or compound ethers of the organic acids. In the majority of cases, the alcohol from which these esters are derived is **glycerine**, or **glycerol**, $C_3H_5(OH)_3$, a triatomic alcohol; but occasionally, *e.g.* in the waxes, a monatomic alcohol is the base. The ethers formed from glycerine with the fatty acids are called *glycerides*, a name which is sometimes applied to the oils also. The glycerine radical C_3H_5 is called *glyceryl*.

The acids most commonly found in these glycerides are shown in the following tables:—

SATURATED ACIDS. (ACETIC SERIES.)

Acid.	Formula.	Melting Point.	Boiling Point.	Specific Gravity.
Butyric . .	$C_4H_8O_2$	− 3°	163° C.	0.958
Caproic . .	$C_6H_{12}O_2$	− 1.5°	205°	0.929
Caprylic . .	$C_8H_{16}O_2$	+ 15°	236°	0.935
Capric . .	$C_{10}H_{20}O_2$	+ 30°	269°	0.930
Lauric . .	$C_{12}H_{24}O_2$	+ 43.5°	225° at 100 mm. pressure.	
Myristic . .	$C_{14}H_{28}O_2$	+ 54°	250° at 100 mm. pressure.	
Palmitic . .	$C_{16}H_{32}O_2$	+ 62°	271.5° at 100 mm. pressure.	
Stearic . .	$C_{18}H_{36}O_2$	+ 70.9°	291° at 100 mm. pressure.	
Arachidic .	$C_{20}H_{40}O_2$	+ 75°		
Carnabuic .	$C_{24}H_{48}O_2$	+ 72.5°		
Cerotic . .	$C_{27}H_{54}O_2$	+ 78°		

UNSATURATED ACIDS. (ACRYLIC SERIES.)

Acid.	Formula.	Melting Point.	Boiling Point.
Acrylic	$C_3H_4O_2$	8° C.	140° C.
Crotonic	$C_4H_6O_2$	72°	180°
Hypogaeic	$C_{16}H_{30}O_2$	33°	
Physetoleic		30°	
Oleic	$C_{18}H_{34}O_2$	14°	
Erucic	$C_{22}H_{42}O_2$	34°	
Brassic		60°	

UNSATURATED ACIDS. (PROPIOLIC SERIES.)

Acid.	Formula.	Melting Point.	Specific Gravity.
Linoleic	$C_{18}H_{32}O_2$	Liquid at −18° C.	
Linolenic	$C_{18}H_{30}O_2$		
Ricinoleic	$C_{18}H_{34}O_3$	−10° C.	0.940

The acids containing ten or fewer carbon atoms in the molecule may be distilled under ordinary atmospheric pressure without decomposition; they are called *volatile fatty acids*. The others given in the tables are called *non-volatile acids;* some of them may be distilled undecomposed under reduced pressure or by superheated steam.

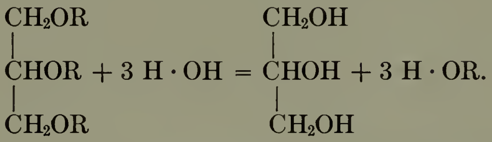
With the exception of a few of the less common oils and waxes, only acids having an even number of carbon atoms in the molecule occur in the fatty oils. The glycerides composing the greater part of the important commercial fats are those of butyric, lauric, palmitic, stearic, oleic, linoleic, and ricinoleic acids; to a less extent occur the esters of caproic, caprylic, crotonic, and myristic acids. The fats are always mixtures of several glycerides, and the proportion in which these are present determines the nature of the fat, whether hard, soft, or liquid; while certain peculiar properties of some fats are due to the presence of one or two particular glycerides.

The glycerides of palmitic and stearic acids are white crystalline solids, melting at 61° and 72° C. respectively; that of oleic acid is liquid at ordinary temperature.

The fatty acids are monobasic, and glycerine being a triatomic alcohol, the glycerides are composed of three acid radicals combined with one alcohol rest; thus the glyceride of palmitic acid has the formula $(C_{16}H_{31}O_2)_3 \equiv C_3H_5$, and is called tripalmitin, or, more often, simply *palmitin*. The glyceride of stearic acid is $(C_{18}H_{35}O_2)_3 \equiv C_3H_5$, called tristearin or *stearin*. That of oleic acid is $(C_{18}H_{33}O_2)_3 \equiv C_3H_5$, called triolein or *olein*.

The fats and oils are lighter than water. They cannot be boiled or distilled, even under reduced pressure, for when heated much above their melting point they decompose. Among other products of decomposition is a substance called **acrolein** $CH_2 = CH - CHO$. This is a low boiling liquid, having a very disagreeable odor, and whose vapors are very irritating to the eyes.

Fresh fats are nearly odorless and of neutral reaction, but when exposed to the air for some time many of them undergo a change by which the glycerides are decomposed and the fatty acids set free, while glycerine is formed and usually further decomposed at once. This breaking up of an organic ester into free acid and an alcohol is called **hydrolysis**, since the elements of water are taken up by the acid and alcohol. Thus if R represent the acid radical, hydrolysis of a fat may be represented by the general equation: —



$$\begin{array}{lcl} CH_2OR & & CH_2OH \\ | & & | \\ CHOR + 3\,H\cdot OH & = & CHOH + 3\,H\cdot OR. \\ | & & | \\ CH_2OR & & CH_2OH \end{array}$$

This change is often brought about by the fermentation or putrefaction of other substances of a gelatinous or albuminous character present in the oil, and is accompanied by numerous secondary reactions, which produce bodies of a very disagreeable odor and taste. The oil is then said to be "rancid."

Hydrolysis may be readily brought about by chemical means, and is then called "saponification"; in this case the reaction is much more complete, and these secondary reactions do not occur. The process is employed in soap and glycerine manufacture, as will appear later.

Certain oils are oxidized when exposed to the air, and are converted into thick gummy or resinous masses, or in thin layers form dry, hard, transparent, or translucent films. This change is called "**drying**," and is most noticeable in oils containing the glycerides of linoleic, linolenic, and ricinoleic acids, which, being unsaturated, oxidize very readily.

The unsaturated compounds of the fatty acid series unite directly with hydrogen in the presence of suitable catalyzers, to form saturated bodies;* thus oleic acid ($C_{18}H_{34}O_2$) is converted to stearic acid ($C_{18}H_{36}O_2$), and *olein* yields *stearin*, which have greater commercial value, owing to their higher melting points. Platinum, palladium, copper, nickel, and other metals have been tried as catalyzers, but nickel is found most suitable, since it is highly active and of moderate cost. The nickel is used as a finely divided, metallic deposit upon some kind of inert support, or carrier, as pumice-stone, kieselguhr, asbestos, or charcoal.

A solution of nickel salt is mixed with the pulverized carrier, an alkali added to precipitate the hydroxide, and the mass after filter-pressing is washed free from soluble matter, and dried. The product

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* Jour. Soc. Chem. Ind., **1912**, 1155.

is ground fine, and the nickel reduced by heating to 300° C., in an atmosphere of hydrogen; precautions to prevent reoxidation during cooling and subsequent handling must be taken.

The reduced nickel catalyzer is then mixed with the oil and introduced into a vessel where it can be treated at about 175° to 200° C., with hydrogen gas, under pressures ranging from atmospheric up to 25 pounds per square inch. The operation is continued until test-portions show that the fat has acquired a sufficiently high melting point, when the hot oil is filter-pressed to remove the catalyzer and carrier, and then cooled. Oils containing linoleic, linolenic, and other less saturated bodies are also converted to hard fats by this treatment, but require more prolonged exposure to the hydrogen.

These hardened fats now find extensive use in the preparation of lard substitutes and other food products, and for soaps, and in making lubricants. "Thickened" cotton-seed, peanut, sesame, or other edible oils have largely replaced the oleo-stearin from tallow in lard compounds.

Oils and fats are found in every part of plants and animals, certain parts being richer than others. In plants, the seeds or fruit generally contain the most oil, but the quantity varies, even in the same variety of plant, according to the soil, cultivation, climate, and the maturity of the fruit. Usually it is in inverse ratio to the amount of sugar and starch present. In animals, most of the fat is found in the abdominal cavity, surrounding the kidneys, or in a layer just beneath the skin. The latter is especially true in the case of marine animals (whales, etc.) and those living in cold climates.

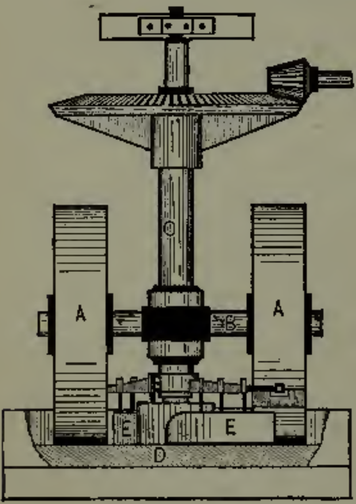

Fig. 107.

The **vegetable oils** are obtained by crushing or grinding that part of the plant richest in oil, and then pressing the crushed material, or extracting it with some solvent, such as benzine or carbon disulphide. Mills for crushing olives are of great antiquity, the oldest form being light edge-runners of wood or stone, that did not break the kernels. Heavy **edge-runners** of stone or iron (Fig. 107) are used at the present time, but steel rolls and buhr-stone mills are more generally employed. The edge-runner consists of two heavy rollers (A, A), fixed on a common axle (B), and travelling in a circle around a vertical shaft (C). The rollers rest on a solid stone or metal bed (D), on which the material to be ground is spread. Scrapers (E) are fixed on the shaft so that they bring the material directly into the path of the rollers.

The ground pulp is pressed in strong canvas or camel's-hair cloths. Sometimes part of the oil is expressed cold, and the meal is then heated and pressed a second time while hot. Cold-pressed oils are of lighter color and of better quality, but hot pressing gives a larger yield. Wedge-presses and screw-presses were used in ancient times, but the invention of the hydraulic press by Bramah in 1795 revolutionized oil pressing. Knuckle-joint and eccentric presses are later inventions, but are not so extensively used.

The **hydraulic press** (Fig. 108) consists of a large piston or ram (R), which is forced out of its cylinder (C) by the hydrostatic pressure of a liquid pumped into the cylinder in a small stream. The bags of pulp (B) are placed between the ram and a fixed top plate (P), and the oil expressed is caught in troughs placed around the ram head.

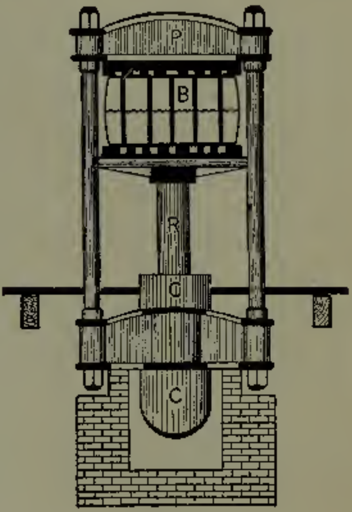

Fig. 108.

In 1850 Jesse Fisher of Birmingham, England, invented the **extraction process**, using a volatile solvent such as carbon disulphide, or better, petroleum naphtha. The solvent is pumped into a closed vessel containing the pulp. After extraction, the solution of oil in the solvent is drawn off and the latter recovered by distilling it off from the oil. This method gives a larger yield of oil, comparatively free from gelatinous matter, but some resins and coloring matter may be dissolved, thus contaminating it, and up to the present time edible oils are not prepared by this process, owing to the persistence of the odor and taste of the solvent. A complicated and expensive recovery plant which is also costly to operate is required. Moreover, if the extraction is carried too far, the residue of crushed seed pulp has less value as animal food and is chiefly used as fertilizer or fuel. Pressing involves less fire risk and yields a lighter colored oil, especially if done cold, while the press-cake from many vegetable oils has a high value as cattle food, owing to the oil and proteids remaining in it.

Animal oils are contained in cells composed of membranous tissue which putrefies soon after the animal is killed, causing the fat to become rancid and have a bad odor. Consequently it must be rendered immediately. These oils are obtained by: (*a*) melting, "trying out," or **rendering** in open kettles. The fat is chopped into small bits and heated over a fire with a very little water. The tissue shrivels together forming "cracklings," which float on the oil and are removed by straining and are pressed to obtain all the oil. Much care is required to prevent overheating, and this process has been generally abandoned in favor of steam rendering (see below); (*b*) by boiling with water to which sulphuric acid is sometimes added to decompose the cell walls, thus liberating the oil; (*c*) by heating with direct steam under pressure in large digesters or autoclaves (Fig. 109), breaking down the cell walls. The fat is introduced through the manhole (B) which is closed when the digester is nearly filled to the top, and steam at about 50 pounds pressure is admitted by the pipe (C) entering near the bottom. Before closing the digester, the fat is sometimes washed by flushing with water which runs off by the cocks (D) and (E). The foul-smelling gases given off during the rendering are conducted away by the pipe (H), and after cooling to condense steam they are discharged into the chimney or into a closed sewer. After several hours heating, the steam is cut off, the pressure relieved, and the digester allowed to remain quiet until the oil has risen to the top, leaving the cracklings and condensed water in the bottom of the tank. The progress of the separation may be followed by trials at the test-cocks (F, F). The water is then drawn off through (E), until the oil reaches the level of (G), through which it is then drawn off. The cracklings are discharged by dropping the lower manhole cover (J).

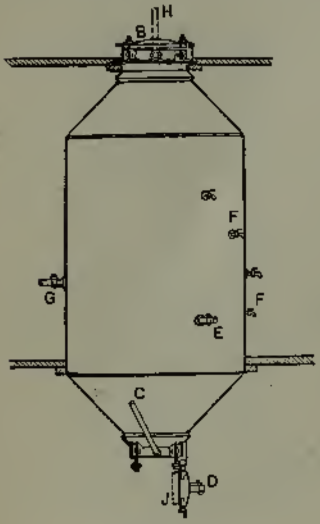

Fig. 109.

In testing fatty oils, certain distinguishing properties and reactions are sought. The **specific gravity** is an important indication as to the purity of the sample. It is determined by the Westphal balance, Sprengel tube, or specific gravity bottle.

The **saponification value** * represents the number of milligrams of potassium hydroxide needed to saponify one gram of the oil. It is determined by saponifying one or two grams of the oil with 25 cubic centimeters of $\frac{N}{2}$ alcoholic potassium hydroxide and titrating the excess alkali with $\frac{N}{2}$ hydrochloric acid, using phenolphthalein as indicator.

The **iodine** (or bromine) **value** * represents the percentage of iodine (or bromine) absorbed by the oil, forming addition, or to a smaller extent, substitution products. The saturated fatty acids and their glycerides do not combine with the halogens to any appreciable extent; but those of the oleic or ricinoleic series combine with two atoms of iodine (or bromine); those of the linoleic unite with four, and of the linolenic with six, atoms of the halogen. Thus the determination of this value affords a method of determining the percentage of *unsaturated* fatty acids (or glycerides) present in the oil. The weighed amount of oil (0.2 gram) dissolved in 10 cc. of chloroform is mixed with 30 cc. of a standard solution of iodine in mercuric chloride and shaken occasionally during fifteen minutes; 15 cc. of potassium iodide solution is added and the excess iodine titrated with $\frac{N}{10}$ sodium thiosulphate. † The number of cc. of thiosulphate used, multiplied by its value in terms of iodine, gives the number of grams of iodine not absorbed by the oil; the difference between this quantity and the amount of iodine added to the oil gives the weight absorbed by the oil; this divided by the weight of oil used and multiplied by 100 gives the iodine value.

The **Maumené test** ‡ shows the amount of heat developed when oil is mixed with sulphuric acid. Fifty grams of the oil are treated with ten cubic centimeters of strong acid under exact conditions, and the "rise in temperature" observed.

The **elaidin test** depends upon the fact that nitrous anhydride (N_2O_3), when brought into contact with olein, converts it into the isomeric solid elaidin, but the glycerides of linoleic, linolenic, and isolinolenic acids are not affected by this treatment. Thus the non-drying oils become solid, while the semi-drying and drying oils remain liquid, or at most, become buttery. Five grams of oil are mixed with seven grams of nitric acid (1.34 sp. gr.), about one gram of copper wire added, and the glass placed in cold water (15° C.) and the oil well stirred. After standing two or three hours the solidity of the elaidin cake is examined.

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* Oils, Fats, and Waxes. Benedikt-Lewkowitsch.

† Oil Analysis. A. H. Gill.

‡ Compte Rendu, **35** (1852), 572.

For convenience in study, the fatty oils are generally classified according to certain similarities in their properties and sources. A convenient classification is as follows*: —

- **Oils and Fats. Glycerides.**
  - Oils or Liquid Fats
    - *Vegetable Oils.*
      - Drying Oils. (1)
      - Semi-Drying Oils. (2)
      - Non-Drying Oils. (3)
    - *Animal Oils.*
      - Marine
        - Fish Oils. (4)
        - Liver Oils. (5)
        - Blubber Oils. (6)
      - Terrestrial. (7)
  - Solid Fats.
    - *Vegetable Fats.* (8)
    - *Animal Fats.* (9)
- **Waxes. Non-Glycerides.**
  - Liquid Waxes. (10)
  - Solid Waxes.
    - *Animal Waxes.* (11)
    - *Vegetable Waxes.* (12)

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* Oils, Fats, and Waxes. Benedikt-Lewkowitsch.

OILS AND FATS

(1) VEGETABLE DRYING OILS

Linseed oil is derived from the seeds of the flax plant, *Linum usitatissimum*, L., which is extensively cultivated in northern Europe, Italy, Turkey (near the Black Sea), India, Argentina, and in the United States. When the plants are raised for their fibre (p. 490), they are pulled up before the seeds are ripe; such seed must be aged several months before pressing, but the best oil is obtained from ripe seed. The yield is from 25 to 32 per cent, according as the seeds are pressed or extracted. The cold-pressed cake is often heated and pressed again. Cold-pressed oil is a clear golden yellow, while the hot-pressed product is amber or brown. The latter may be "bleached" by treating with a solution of ferrous sulphate and exposing it to the sunlight. The crude oil is stored until the mucilaginous matter and water settle; the product is called "tanked oil." Or the crude oil is refined by agitation with sulphuric acid, followed by washing with water. The "tanked" or purified product is called "raw oil."

Press-cake from raw oil is one of the most valuable cattle foods.

Linseed oil is the most important of the drying oils. It contains* about 65 per cent of the glycerides of isolinolenic acid, $C_{18}H_{30}O_2$, and 15 per cent each of the glycerides of linoleic, $C_{18}H_{32}O_2$, and linolenic, $C_{18}H_{30}O_2$, acids and 5 per cent of olein. These glycerides absorb oxygen, and are converted into an elastic mass, *linoxyn*, of doubtful composition, which has been thought to be insoluble anhydrides of the acids. The oil becomes thicker and darker colored, and, when in thin films, forms a dry, hard varnish. This drying may be hastened by the so-called "boiling" of the raw oil. The latter is heated with certain salts (such as litharge, lead acetate, or the peroxide or borate of manganese), called "driers." A slight decompositon of the glycerides occurs, and some acrolein is set free; also a slight polymerization takes place. Possibly the driers form metallic salts with the fatty acids to a small extent, the glycerides being partly saponified in the process; the metallic salts remain dissolved in the oil and act as oxygen carriers in the drying, when they are exposed to the air. The boiling is carried on in open kettles heated by direct fire or by

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* K. Hazura. Zeit. für angew. Chem., **1888**, 312.

high-pressure steam, and is sometimes aided by blowing air into the hot oil. When the latter has lost from 8 to 10 per cent of its weight, the process is stopped. The temperature employed varies with the kind of drier used, being highest (250° C.) with litharge; but this gives a dark-colored product. The lower the temperature the lighter colored the product, and the longer the oil must be heated. By heating the oil for several days with borate of manganese at 60° C. to 125° C., a very light-colored boiled oil is produced. All boiled oil should stand several months, or even a year, before use, in order that the impurities may settle. Very little of the drier is dissolved by the oil, and the clarified boiled oil is decanted from the residue. It dries very readily, and is much used for paint mixing. If the boiling is continued for ten or twelve hours, at a high temperature, the oil becomes a thick, sticky, viscid mass, used as the basis of printers' ink.

If a small quantity of oil is brought to a high heat with the metallic salt, a dark-colored liquid " drier " or " japan " is formed, which may be mixed with a greater amount of raw oil at a moderate temperature (100° to 125° C.). This forms a so-called " **bung-hole** " **boiled oil**, which is lighter colored than if the whole mass of oil had been heated to a high temperature. The product is claimed to have as good drying properties as the genuine kettle-boiled oil.

Several grades of linseed oil are in the market, the Calcutta being considered the best in this country, while the Western and La Plata oils are often of poorer quality. In Europe the Baltic oil * is held in high esteem, while the Indian oils are regarded as low grade. Linseed oil is sometimes adulterated with mineral oil, or with rosin, corn, menhaden, or cotton-seed oil.

Raw linseed oil has a specific gravity of 0.9316 to 0.9354; saponification value of 189 to 195, and an iodine value of 170 to 188. (Boiling lowers the iodine number.) It does not yield solid elaidin. It is used as a soap stock for soft soap, in some kinds of paint, for varnish making, and for rubber substitute. Boiled oil is used for paint, for printing inks, for oilcloth making, and in the preparation of linoleum. For this last, the partially boiled oil is exposed to the air at a moderate temperature (20° to 22° C.), until oxidized to a translucent jelly. It is then thoroughly incorporated with ground cork, and is rolled into sheets and dried.

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* Lewkowitsch, Oils, Fats, and Waxes. Allen, Commercial Organic Analysis, Vol. II. McIlhiney, Report upon Linseed Oil and its Adulterants, to Commissioner of Agriculture of New York State, Albany, 1901.

By the oxidation of certain oils, as in "drying," considerable heat is generated, and if they are exposed in thin layers, on porous, inflammable material (*e.g.* when absorbed in cotton rags or waste), spontaneous combustion frequently takes place. This is particularly liable to occur with linseed oil; it may be prevented by the addition of mineral oils.

Hemp oil is obtained from the seeds of the common hemp, *Cannabis sativa*, L. The yield is about 30 per cent. It is a greenish yellow oil of 0.925 to 0.930 sp. gr. Its saponification value is 190 to 191.1, and its iodine value 143 to 148. It is a poor drying oil, but is used in paint and as an adulterant for linseed oil; also as stock for soft soap.

Soja (or soya) bean oil, obtained from the seeds of *Soja hispida*, cultivated in China and Formosa, furnishes an important edible oil, and soap stock. Its sp. gr. is 0.9255; saponification value, 193.2; iodine number, 137 to 141; Maumené test, 86 to 87; index of refraction, 1.4750 at 20° C. The press-cake is a valuable cattle food.

Poppy oil is a good drying oil, from the seeds of the poppy, *Papaver somniferum*, L. The yield is about 45 per cent of a thin, yellow, odorless oil of 0.924 to 0.937 sp. gr.; its saponification value is 190 to 197; iodine value, 134 to 143. It is used as a salad oil and to adulterate olive oil; and in the preparation of colors for artists' use.

Tung oil, or **Chinese wood oil**, from the seeds of *Aleurites cordata*, a tree native to China and Japan, is chiefly used for paints, varnishes, and in making oilcloth. It is a pale yellow to dark brown in color, and dries rapidly, forming a hard film. Its sp. gr. is 0.941 at 15° C.; saponification value, 190 to 197; iodine number, 155 to 170. It contains glycerides of oleic and elæomargaric ($C_{18}H_{32}O_2$) acids.

Sunflower oil is a pale yellow, palatable, odorless oil, from the seeds of the common sunflower, *Helianthus annuus*, L. The yield is about 30 per cent, and the press-cake is a valuable cattle food. The oil contains the glycerides of oleic, palmitic, arachidic, and linoleic acids. Its sp. gr. is 0.924 to 0.926; saponification value, 190 to 194; iodine value, 120 to 133. It is used as a soap stock, for wool oiling, and to adulterate olive oil.

(2) VEGETABLE SEMI-DRYING OILS

These oils have an intermediate position between the true drying and the non-drying oils, some of them showing distinct drying properties, while others do not, as is indicated in their iodine values.

Corn oil or **maize oil** is derived from the germ of the common corn, *Zea Mays*, L. The germ (removed from the grain in starch making), when pressed, yields a yellow oil of 0.920 to 0.927 sp. gr. Its saponification value is 188 to 193; iodine value, 111 to 123; Maumené test, 56° to 88° C. It is used as an edible oil; in making soap and lubricants; and for rubber substitutes; the press-cake is an excellent cattle food.

Cotton-seed oil is derived from the seeds of the cotton plant, *Gossypium herbaceum*, L. After the husks are removed in cylinders containing rotary knives, the seeds are crushed in a roller mill.

The meal, heated in iron kettles at 75° to 90° C., is pressed under 3000 to 4000 lbs. per square inch. The yield is about 18 per cent. The press-cake is a valuable cattle food, but is mixed before feeding with two parts of the seed hulls, straw, or other fodder.

The crude oil is red or reddish brown in color, and must be refined for most purposes. After settling, it is pumped into large iron tanks having stirring apparatus, and steam coils for heating; here the heated oil is agitated for a few minutes with a solution of caustic soda of 12° to 18° Bé. The alkali combines with the free fatty acid of the oil to form a soap, insoluble in the oil. This soap is an effective adsorption agent for the coloring and albuminous matter, and separates together with the excess lye as "foots." The agitator is then stopped, the "foots" settle to the bottom, and the clear oil is drawn off. The amount of lye, temperature of the oil, and time of agitation varies according to the judgment of the operator. The "foots" are used for soap stock. The clarified oil is still yellow and for some uses is further bleached by treatment with fuller's earth, at a temperature of about 100° C., and with active stirring for a few minutes; the earth is then filtered out of the oil, leaving it water white or yellowish color, according to the quality of the oil. On standing or by chilling below 12° C., the palmitin and stearin in part crystallize, and may be removed by pressing. This solid fat, called "**cotton-seed stearin**," is used in making oleomargarine. The oil expressed is clear and light-colored, and is extensively used as a salad oil and to adulterate olive oil. It is also used in the manufacture of "compound lard," "cottolene," etc., for which it is mixed with about one and one-half times its weight of beef stearin; and in butterine and oleomargarine, to soften them in cold weather. Cotton-seed oil, hardened by hydrogenation, is much used as a substitute for lard as a food product.

Refined cotton-seed oil has a pale straw color and a specific gravity of 0.922 to 0.930. Its saponification value is 191 to 196; iodine value, 101 to 116; the elaidin test gives a soft buttery mass; Maumené test, 70° to 90° C. It is usually free from acids and has a pleasant taste. The poorer grades are used for soap making. It is not often adulterated.

Sesame or Gingili oil is obtained from the seeds of an East Indian plant, *Sesamum Indicum*, L., which is also grown largely in Egypt and Asia Minor. The crushed seeds are first pressed cold and then hot. The yield is 30 to 50 per cent of thin, yellow, odorless oil of pleasant taste, which does not become rancid on exposure. It consists of 76 per cent olein, the remainder being glycerides of palmitic, stearic, and myristic acids. Its specific gravity is 0.921 to 0.924; saponification value, 190 to 194; it yields a soft elaidin; the iodine number is 103 to 110; and the Maumené test, 65° to 68° C. The best quality is used as a table oil or to adulterate olive oil; the common grades are good burning oils or soap stock.

Rape-seed or **colza oil** is obtained from the seeds of several varieties of *Brassica campestris*, L. The seeds are crushed and heated by steam before pressing; this coagulates the albumin and improves the quality of the oil. The yield is about 36 per cent of crude oil which is refined by agitation with one per cent of strong sulphuric acid and washing with alkali; this removes traces of sulphuric acid and the free fatty acids formed by its action. The lighter colored and best grades are generally called colza oil, rape oil being applied to the commoner grades. Both contain the glycerides of oleic, stearic, and erucic or brassic acids. The specific gravity ranges from 0.922 to 0.930 at 15.5° C.; the iodine value is 101 to 117; saponification value, 191 to 196; by the elaidin test, solidification takes place very slowly, frequently requiring 50 to 60 hours, and the elaidin is very soft; Maumené test, 70° to 90° C.

The purified colza oil is a pale yellow and is odorless; it is chiefly used as a condiment and as a burning oil. It is often adulterated with hemp, cotton-seed, or fish oils or with rosin oil. Common rape oil is used as a lubricant, and being very viscid, is frequently employed as a standard for measuring viscosity. When exposed to the air, it becomes thick and gummy, but does not really "dry."

Castor oil is obtained from the seeds of *Ricinus communis*, L. They are cold pressed for the first grade of medicinal oil, and hot pressed for the common qualities, about 40 per cent of oil being obtained. It is very viscid, of 0.960 to 0.970 sp. gr., and contains the glycerides of stearic and ricinoleic acids. Its saponification value is 176 to 186; iodine value, 81 to 90; Maumené test, 47° C. It is apt to become rancid, and is soluble in alcohol and glacial acetic acid, and insoluble in petroleum spirit. Its purgative action is probably due to an alkaloid present in it. Large quantities are used in making "**Turkey-red oil,**" which is prepared by treating the castor oil with sulphuric acid at less than 40° C., and washing with a strong brine to remove the excess of acid. The oil is decanted from the brine and carefully neutralized with ammonia or soda, by which Turkey-red oil, the alkali salt of ricinoleo-sulphuric acid, $C_{18}H_{33}(HSO_3)O_3$, is formed. Oil thus prepared has largely replaced that made from olive oil for use in dyeing cotton with alizarine. Its exact composition is as yet uncertain, various views having been advanced.*

Castor oil is also used for making transparent soaps and common soap; its viscosity being greater than that of any other oil at the ordinary temperature, it is largely used as a lubricant for heavy machinery.

By blowing air through hot cotton-seed, linseed, lard, or rape oil, it is partially oxidized and converted into a thick viscous oil of very high gravity (0.942 to 0.970). Mixed with mineral lubricating oils, these "**blown oils**" are used as substitutes for castor oil for heavy machinery.

(3) VEGETABLE NON-DRYING OILS

These usually contain a high percentage of olein, absorb little or no oxygen, and do not dry in the air, yield solid elaidin, and have lower iodine values than the drying oils.

Peanut or **earthnut oil** is obtained from the fruit of *Arachis hypogæa*, L. The oil is a light greenish yellow, with a peculiar odor and taste, but when refined the best quality oil is colorless and has a very faint nutty taste. It contains glycerides of arachidic and hypogæic acids, besides olein, palmitin, and others. Its specific gravity is 0.916 to 0.922; saponification value, 190 to 196; and iodine value, 85 to 105; Maumené test, 45° to 75° C. It is employed as an adulterant for olive oil (formerly also in lard oil), as a salad oil, in butterine, for oiling wool, and for soap making.

Olive oil is obtained from the fruit of the olive tree, *Olea Europæa*, L. Both the fruit pulp and the kernel contain oil, but the former yields the better quality. The fruit is crushed in mortars or edge-runners (care being taken not to break the kernels) and cold pressed. A small quantity of "virgin oil" is thus obtained, which is used as a condiment. The residue is stirred up with hot water and pressed harder than before; then it is ground a second time, crushing the

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* J. Soc. Chem. Ind., **1883**, 537. Liechti and Suida. J. Soc. Chem. Ind., **1884**, 412. Mueller and Jacobs. Dingler's polytechnisches Jour., **254**, 346. Schmid. J. Soc. Dyers and Colorists, **1891**, 69. Scheurer-Kestner.

seeds, stirred up with hot water, and pressed as hard as possible. The final press-cake is extracted with carbon disulphide, or is put into pits with water and allowed to ferment for some weeks. The oil rises to the top and is skimmed off.

The several grades of oil obtained are purified by heating to coagulate the albuminous matter, and settling. A dark-colored, mucilaginous substance, called "foots," deposits, and is used for soap stock. The lighter colored oils are used for the table and the others for lubricators, illuminants, and soap stock. Considerable of the grade called "Gallipoli" is used for making "Turkey-red oil" and for oiling wool after scouring.

Olive oils vary in color from pale yellow with a greenish tinge (due to traces of chlorophyl) to greenish or brownish yellow in the poorer qualities. First-grade oils are odorless and palatable, but the lower grades are strong-smelling and usually have a disagreeable taste. On exposure to the air olive oil is apt to become rancid. The specific gravity varies from 0.914 to 0.918; its saponification value is 185 to 203; iodine value, 78 to 91.5; the elaidin test shows a solid mass within two hours, which is not displaced by inverting the vessel; Maumené test, 41° to 47° C. The oil contains about 72 per cent of olein and linolein, and about 28 per cent mixed palmitin and stearin. Being very expensive, it is frequently adulterated with cotton-seed, sesame, or rape-seed oil, while poppy, lard, and peanut oils are less commonly used.

MARINE ANIMAL OILS

These oils are glycerides, and are liquid at ordinary temperatures. They absorb oxygen, do not yield solid elaidin, and have high iodine values. The varieties of sperm oil do not belong with this group, since they are liquid waxes, although obtained from blubber.

(4) FISH OILS

Fish oils are obtained by rendering and pressing the entire body of the fish. The press-cake, consisting of the scales, meat, and bones, is ground and utilized as "fish scrap" (p. 166), for fertilizer or for feeding swine.

Menhaden or **pogy oil**, derived from a small fish, *Alosa Menhaden*, is brownish color, has a fishy odor, and dries in the air. Its specific gravity is 0.927 to 0.933; saponification value, 189 to 192; iodine value, 148 to 160; Maumené test, 123° to 128° C. It is much used in currying (p. 579); to adulterate whale oils and linseed oil and as a substitute for them. It is itself adulterated with mineral oils.

(5) LIVER OILS

These oils contain cholesterol and other biliary ingredients which are unsaponifiable.

Cod-liver oil is obtained from the liver of the codfish, *Gadus morrhua*. The livers are rendered by steam heat, and the oil separated, is chilled until the stearin solidifies, when it is pressed and the clear oil collected. Three grades are made, — pale, light brown, and dark brown. The pale oil, used in medicine, is limpid, light yellow, having little taste or smell; its value here may be due to traces of biliary substances, making it readily digested and assimilated. The darker, less pure grades are used for leather dressing. The oil contains glycerides of oleic, myristic, palmitic, and stearic acids, some volatile fatty acids, and cholesterol; also traces of iodine and phosphorus. The specific gravity is 0.922 to 0.930 at 15° C.; saponification value, 182 to 189; iodine value, 141 to 159; Maumené test, 102° to 113° C. It is often adulterated with shark-liver oil, seal oil, and other fish oils.

Shark-liver oil is chiefly obtained from the livers of the sunfish, *Squalus maximus.* Its specific gravity is 0.911 to 0.928. It is a clear yellow oil, containing a large amount of cholesterol, and is mostly used for leather dressing and for adulterating cod-liver oil.

(6) BLUBBER OILS

Whale oil or **train oil** is obtained from the blubber of the Greenland or "right" whale, *Balæna mysticetus,* and other animals of the whale tribe. By boiling the blubber in water, the oil rises to the surface and is skimmed off. It is yellowish brown in color and has a strong fishy odor. Its composition is variable and but little is known about it; glycerides of some of the lower members of the acetic series are often present. The glyceride of valeric acid, $C_5H_{10}O_2$, is characteristic of some whale oils. The specific gravity is 0.925 to 0.930; saponification value, 188 to 193; iodine value, 120; Maumené test, 85° to 91° C. Some varieties dry on exposure to the air. Whale oil is used for leather dressing, in tempering steel, and as an illuminating oil.

Porpoise oil, derived from the porpoise, *Phocæna brachycium,* is very similar to whale oil, and is obtained in the same way. Its density is 0.920 to 0.930; saponification value, 216; it yields a small amount of elaidin. The best grades (jaw oil) are used for lubricating clocks and watches, the commoner qualities for soap stock, for leather dressing, and as illuminating oil.

Blackfish oil is obtained from the blubber of the blackfish, *Globicephalus melas.* It is a pale yellow oil, which separates spermaceti (cetyl palmitate) on standing. That from the head and jaw is the finest quality, and is used for lubricating clocks and fine machinery.

(7) TERRESTRIAL ANIMAL OILS

These oils have low iodine value and yield solid elaidin. They are derived from the feet of cattle, horses, and sheep, or are expressed from lard and tallow.

Neat's-foot oil is made by boiling the feet and shin bones of cattle in water. It is a pale yellow, limpid oil of 0.916 sp. gr. at 15° C., is nearly odorless, and deposits stearin on standing. Its saponification value is 194; iodine value, 70; it yields a solid or semi-solid elaidin; Maumené test, 47° to 48.5° C. It is nearly pure olein, and does not readily become rancid nor gummy when used on machinery. It is used for a fine lubricator and for leather dressing. It is often adulterated with fish, rape, cotton-seed, and mineral oils, and other hoof oils. Bleached tallow oil is often sold as "neat's-foot."

Lard oil is prepared by cold pressing lard (p. 367). The best quality is limpid and colorless, and consists of olein, with some palmitin and stearin, the quantity of these latter depending upon the temperature of the pressing; poor grades have a brown color and offensive odor. It has a specific gravity of 0.915 at 15.5° C.; a saponification value of 195 to 196; iodine value, 56 to 74; it yields solid elaidin. It is used as an illuminant, as a lubricant, and for oiling wool. It is frequently adulterated with cotton-seed oil, cocoanut olein, "neutral mineral oil," or rape oil.

Tallow oil consists mainly of olein, and is obtained by pressing tallow (p. 367). It is chiefly mixed with mineral oil for use as a lubricant. If selected, fresh tallow is rendered at 65° C., and the clear oil kept for twenty-four hours in a graining vat, the stearin and part of the palmitin crystallize. By pressing, the liquid olein and some palmitin is obtained as "**oleo oil**," which is used for artificial butter making. The press-cake (oleo-stearin) is used in making "compound lard" (p. 360), and sometimes as a soap or candle stock. Low grades of tallow oil are not white, and are called "red oil" in trade; these must not be confounded with the red oil which consists of oleic acid (p. 382).

(8) SOLID VEGETABLE FATS

Palm oil is obtained from the fruit of several varieties of palm, *Elæis Guineensis*, Jacq., native to the west coast of Africa. It is a mixture of palmitic acid, palmitin, and olein, and is semi-solid in this climate. When fresh, it is red or orange yellow, but on standing, especially if exposed to the sunlight, it becomes brownish yellow or drab. It may be bleached by heating and blowing in air; or by treating with potassium bichromate and hydrochloric acid. Fresh oil has a pleasant odor, but is liable to become rancid, when it contains a large percentage of fatty acids and has a disagreeable odor. Its specific gravity at 99° C. is 0.859; the saponification value is 196 to 202; iodine value, 53 to 56. It is used as a candle and soap stock, and in making lubricants.

Palm kernel or **palm nut oil** is derived from the kernels of the fruit of *Elæis Guineensis*, Jacq. It is similar to and used in the same way as cocoanut oil.

Cocoanut oil is derived from the cocoanut, *Cocos nucifera*, L. (or *butyracea*, L. f.), the chief commercial supply coming from India, Ceylon, and the South Sea Islands. The dried meat ("copra") of the nut is pressed or boiled in water. The oil, which is a solid fat in this climate, contains the glycerides of myristic, palmitic, stearic, lauric, capric, caprylic, and caproic acids. It melts at 20° to 28° C.; its saponification value is 250 to 268; its iodine value, 8.9. It is very liable to become rancid. It is much used for soap stock, especially for the "cold-process" soaps, and since it is not readily precipitated by salt, for marine soaps; but it needs a strong lye for its saponification. It is also said to be used for artificial butter and as a substitute for lard. By cold pressing, a solid stearin is obtained which is used in making candles.

Cacao-butter is obtained from the cacao bean, the seeds of *Theobroma Cacao*, L., and is a solid fat having a pleasant odor and the flavor of chocolate. It consists of the glycerides of palmitic, stearic, and lauric acids, with traces of linoleic and arachidic acids. It is used for ointments and salves in pharmacy, and in the manufacture of "chocolate creams," and for toilet soaps. It is often adulterated with tallow, vegetable oils, beeswax, or paraffine wax. Its specific gravity is 0.890 to 0.900 at 15° C.; saponification value, 192 to 202; iodine value, 32 to 37.7.

Japan wax is obtained from a species of *Rhus* by boiling the fruit in water. It is a pale yellow or white, has a greasy feel, and can be kneaded in the fingers. It consists of palmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, with some stearin, and is easily saponified. It is not a true wax. It melts at 53° to 54° C., and its specific gravity is 0.970 to 0.980 at 15° C. It is soluble in benzene, petroleum spirit, and in boiling 97 per cent alcohol. It is used for candles, for wax matches, as a furniture polish, and for adulterating beeswax.

(9) SOLID ANIMAL FATS

Lard is prepared from the fat of the hog. It is rendered at a low temperature, and is a softer grease than tallow. It is a mixture of palmitin, stearin, and olein. It melts at 28° to 45° C., forming a clear liquid. Its specific gravity is about 0.932; saponification value, 195 to 196; iodine value, 59; Maumené test, 24° to 27° C. When pure, it is white, nearly odorless and tasteless. By pressing it yields lard oil (p. 365). It is often adulterated with water, 25 per cent or even more being worked into it; or with cotton-seed oil and oleo-stearin; or with beef fat and cotton-seed oil. The chief uses of lard are for culinary purposes, for soap stock, for butterine, and in ointments and salves. "Compound lard" is a mixture of oleo-stearin and white cotton-seed oil.

Tallow is the solid fat of the sheep or ox. Before rendering, it is customary to break up the tissues by grinding with hollow rolls having a rough surface and heated by steam. The rendered tallow solidifies at about 34° to 45° C., and is graded according to its appearance, hardness, odor, and rancidity. It consists of about two-thirds palmitin and stearin, and one-third olein. Its density at 99° C. is 0.860 to 0.862; saponification value, 195 to 198; iodine value, 40. It is extensively used for soap and candle stock, for lubricating, and as a leather dressing.

Bone tallow is a soft grease obtained by boiling fresh bones in water to extract the marrow and fat. It is dark-colored and foul-smelling and usually contains calcium phosphate. It is mainly used for cheap colored soaps.

Butter fat is derived from cows' milk. It is very complex, containing glycerides of a number of acids of which oleic (60 per cent), palmitic, stearic, and butyric (5 per cent) are the most important; small quantities of the glycerides of capric and caproic acids are also present. Butter fat has a specific gravity of 0.870 at 99° C.; its saponification value is 221 to 227; iodine value, 26 to 35. It is the basis of butter, of which it forms about 90 per cent, the remainder being water, salt, curds, and coloring matter. It is made by churning cream to cause the agglomeration of the fat globules into a solid mass. Sour cream churns more easily than sweet cream. The latter is removed from the milk by a separator * or by skimming before the milk sours. Butter from sour cream will not keep unless well salted, since it contains sufficient casein to increase its liability to become rancid, by which a considerable amount of butyric acid is formed. Butter is usually colored with carrot juice, saffron, turmeric, or annato; or sometimes with certain coal-tar colors.

Butterine, oleomargarine, and **margarine** are butter substitutes made from mixtures of animal and vegetable oils, flavored with some butter, and colored to imitate it. Oleo oil from tallow, and neutral lard are much used. These are mixed with cotton-seed oil in cold weather (or with peanut or sesame oil abroad) to increase the percentage of olein.

WAXES

(10) LIQUID WAXES

Sperm oil is obtained from the blubber and head cavity ("case") of the cachalot, or sperm whale, *Physeter macrocephalus*, the case alone sometimes yielding several barrels of free oil. The composition of sperm oil is not definitely known, but it differs materially from most oils. It contains no glycerides, consisting mainly of esters of monatomic alcohols. Some authorities hold that dodecatyl alcohol, $C_{12}H_{25}OH$, and its allied homologues, such as cetyl alcohol, $C_{16}H_{33} \cdot OH$, are present, but this is denied by Lewkowitsch. The oil holds in solution a considerable amount of spermaceti (below), which is usually filtered out of the cold oil before it is sold. Sperm oil is a limpid, golden yellow liquid, having a slight fishy odor; its specific gravity is 0.875 to 0.884 at 15.5° C.; saponification value, 123 to 147; iodine value, 81.3 to 85; it yields a solid elaidin; Maumené test, 45° to 47° C. It is a valuable lubricator, especially for rapid-running machinery, since its viscosity is less than other non-drying fatty oils, and varies

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* Before churning, sweet cream is always allowed to "ripen"; *i.e.* to stand a few hours undisturbed after separating. Usually a "starter" is added to set up lactic fermentation; by using pure cultures of acid-forming bacteria, the quality and flavor of the butter can be much better controlled than when the ripening is spontaneous.

but little with changes of temperature; and because it does not become gummy nor rancid. It is also used for illuminating, for leather dressing, and in tempering steel. Because of its high price, it is often adulterated with mineral oils or with other fish oils.

The related **Doegling** or **Bottlenose oil** is also a liquid wax.

(11) SOLID ANIMAL WAXES

Spermaceti is a crystalline wax found in the head of the sperm whale and which separates from sperm oil when chilled; it is obtained by expressing the oil. The brown or yellow scales of crude spermaceti are treated with a little caustic potash to remove adhering oil, and are thus rendered white and translucent while they retain their crystalline structure. Spermaceti consists mainly of cetyl palmitate, $C_{16}H_{33}O \cdot C_{16}H_{31}O$. It is odorless and tasteless and melts at about 45° C. Its specific gravity is 0.943 at 15° C.; saponification value, 108 to 128; it burns with a large clear flame. Its chief uses are in candle making, in confectionery, and in pharmacy.

Beeswax is obtained from the honey-comb of bees by melting it in hot water; the floating layer of tough brown or yellow wax is drawn off into moulds. It may be bleached by exposure in thin films to the sun and moist air, or by the moderate action of chromic or nitric acid, or hydrogen peroxide. Bleached wax is white, and has neither taste nor smell. It consists mainly of myricyl palmitate, $C_{30}H_{61}O \cdot C_{16}H_{31}O$, and some cerotic acid, $C_{27}H_{54}O_2$. It melts at 63° to 64° C., and has a specific gravity of 0.965 to 0.969 at 15° C. It is often adulterated with water or white mineral powders to increase its weight. Stearin, paraffine, cerasin, tallow, and vegetable wax are often added as adulterants. It is used in candle making, in pharmacy, and for many other purposes in the arts.

Chinese wax, or **insect wax**, is secreted by an insect, *Coccus ceriferus,* Fabr. The wax is deposited on the branches of certain trees, which are cut off and the wax removed by hand. It is melted in boiling water to separate the dirt, bark, etc. It is white, crystalline, and very hard, without taste or smell. It is soluble in benzine, and slightly so in alcohol and ether. It consists of ceryl cerotate, $C_{27}H_{55}O \cdot C_{27}H_{53}O$. Its specific gravity is 0.970 at 15° C., and it melts at 82° to 83° C. It is used for fine candles, in medicine, as size for paper, and as a furniture polish.

Wool grease is the greasy substance exuded with the perspiration from sheep. It is a complex mixture of alcohols and esters, especially of cholesterol and isocholesterol, and palmitic, stearic, myristic, carnaubic, and other acids; also potassium salts of these acids. It does not contain glycerides and the alcohols appear on analysis along with the unsaponifiable matter.

The grease may be obtained by extracting the raw wool with naphtha or other solvent; or the alkaline wash-waters in which the wool has been washed may be treated with sulphuric acid, in which case the grease also contains fatty acids from the soap used (p. 500). It is yellow or brown in color, has an unpleasant odor, and emulsifies with water. It is used for leather dressing, and in making axle grease and other lubricants. Purified wool grease has a specific gravity of 0.973 at 15° C.; iodine value, 25 to 28; saponification value, 98 to 102.

Lanolin is made by washing wool grease with water until all the soluble matter is removed, melting by heating in water, skimming and allowing it to cool and solidify. Lanolin is much used in pharmacy as a basis for salves, ointments, and emulsions. It contains about 25 per cent of water, and forms a very soft ointment.

(12) SOLID VEGETABLE WAX

Carnauba wax is derived from a species of palm, *Copernicia cerifera*, Mart., native in Brazil. It forms a coating on the leaves, and is removed by shaking or pounding. The raw wax is of a grayish or greenish yellow and is very hard, though readily powdered. When purified, it has no odor nor taste, melts at 83° to 88° C., and has a specific gravity of 0.990 to 0.999 at 15° C. Its constitution is complex, but it contains myricyl cerotate, $C_{30}H_{61}O \cdot C_{27}H_{53}O$, myricyl alcohol, $C_{30}H_{61}OH$, cerotic acid, $C_{27}H_{54}O_2$, and other bodies. It is used for candle making and for adulterating beeswax, and in varnish.

REFERENCES

Die Chemie der Austrocknenden Oele. G. J. Mulder, Berlin, 1867.
Die Fettwaaren und fetten Oele. C. Lichtenberg, Weimar, 1880.
Die Trocknenden Oelen. L. E. Andes, Braunschweig, 1882. (Vieweg.)
Technologie der Fette und Oele. C. Schaedler, Berlin, 1883.
Commercial Organic Analysis. A. H. Allen. Vol. II. London, 1886.
Das Wachs und seine technische Verwendung. S. Sedna, Wein, 1886.
Die Fetten Oele des Pflanzen und Thierreiches. G. Bornemann, Weimar, 1889.
Die Untersuchung der Fette, Oele, Wachsarten. C. Schaedler, Leipzig, 1890.
Les Corps Gras. A. M. Villon, Paris, 1890.
Les Matières Grasses. G. Beauvisage, Paris, 1891.
Painters' Colours, Oils, and Varnishes. G. H. Hurst, London, 1892.
Die Schmiermittel. J. Grossmann, Wiesbaden, 1894.
Chemical Analysis of Oils, Fats, and Waxes. R. Benedikt. Translated by J. Lewkowitsch. London, 1895.

Chemical Technology. C. E. Groves and Wm. Thorp. Vol. II. Lighting. Philadelphia, 1895. (P. Blakeston, Son & Co.)
Animal and Vegetable Fats and Oils. W. T. Brannt, Philadelphia, 1896.
Oils and Varnishes. J. Cameron, London, 1896. (J. and A. Churchill.)
Analyse der Fette und Wachsarten. Benedikt u. Ulzer, 3$^{\text{te}}$ Auf., Berlin, 1897.
Lubricants, Oils, and Greases. I. Redwood, 1898.
Oil Chemist's Handbook. E. Hopkins, 1900.
Vegetable Fats and Oils. L. E. Andes, 2d ed., 1902.
Oils, Fats, and Waxes. C. R. Alder Wright, 2d ed., London, 1903.
Cottonseed Products. L. L. Lamborn, New York, 1904. (Van Nostrand.)
Technologie der Fette, Oele, und Wachsarten des Pflanzen und Tierreichs. G. Hefter, 4 vols., 1906+.
Chemie, Analyse und Gewinnung der Oele, Fette, und Wachse. L. Ubbelohde, 4 vols., 1908+.
Handbuch der Chemie und Technologie der Oele und Fette. L. Ubbelohde und F. Goldschmidt, Leipzig.
A Short Handbook of Oil Analysis. A. H. Gill, 6th ed., Philadelphia, 1911. (Lippincott Co.)
Lubricating Oils, Fats, and Greases. G. H. Hurst, 3d ed., London, 1911.
Chemical Technology and Analysis of Oils, Fats, and Waxes. J. Lewkowitsch, 5th ed., 3 vols., London, 1914. (Macmillan & Co., Ltd.)

SOAP

Soaps are metallic salts of certain non-volatile fatty acids, the commercial article usually containing a mixture of several of these salts. Soaps intended for washing purposes should contain only *soluble salts* of the acids; *i.e.* those of sodium, potassium, or ammonium; the calcium, magnesium, lead, and other heavy metal soaps are insoluble in water.

As already explained, the common fats and oils contain the fatty acids in combination with glycerine, forming glycerides, and it is from these that soaps are generally made. The process of decomposing the glycerides and forming soap is called saponification, although this term is generally used to denote the decomposition of any organic ester into its basic alcohol and free acid. Saponification is effected in several ways: —

(1) By the action of water or steam at high temperature or pressure: —

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3\ H_2O = C_3H_5(OH)_3 + 3\ C_{18}H_{36}O_2.$$

This hydrolysis may be accomplished at a much lower temperature if the water is acidulated with a dilute mineral acid, which serves as a catalyzer and accelerates the reaction between the water and the glycerides of the fat. The amount needed is small, and it is all found unchanged, mixed with the products of the reaction. This method is chiefly employed for the preparation of glycerine and to obtain the free fatty acid.

(2) By the action of caustic alkalies: —

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3\ NaOH = C_3H_5(OH)_3 + 3\ C_{18}H_{35}O_2 \cdot Na.$$

This is the reaction employed in ordinary soap making, the caustic uniting with the fatty acid radical to form the soap, *i.e.* an alkali salt of the acid. The glycerine formed is a by-product, and progressive soap makers have a glycerine recovery plant or sell the lye to a glycerine manufacturer.

(3) By the action of lime; (Milly's process, p. 381).

The chemistry of saponification was first explained by Chevreul, who attributed the cleansing action of soap to free alkali formed by the decomposition of the soap when brought into solution. The fatty acids are weak and soap solutions are therefore strongly alkaline by hydrolysis; the insoluble fatty acids produced by this hydrolysis make the solution turbid. Soap removes the dirt by adsorbing on the surface of the dirt particles and thus emulsifying it; in this the soap acts as a protective colloid.

The alkalies commonly used for soap making are caustic potash and soda. The former yields a "soft soap," which is liquid under ordinary conditions, because of the lower melting point, greater solubility, and possible deliquescence of potassium soaps. The glycerine formed remains mixed in the soft soap.

Previous to Leblanc's invention of the soda process, soap was made with caustic potash derived from wood ashes and lime. Common salt was added after the saponification of the fat was complete, forming hard sodium soap, according to the reaction: —

$$KC_{18}H_{35}O_2 + NaCl = KCl + NaC_{18}H_{35}O_2.$$

But now most soft soaps are made from soda soaps by adding a large quantity of water.

The fatty material (soap stock) varies according to the kind of soap desired and the facility with which certain stocks may be obtained. For white soaps, the best grades of tallow, tallow-oil, palm oil, or cocoanut oil are chiefly used in this country. Cotton-seed oil may become rancid and cause yellow or brown spots in the product, besides giving it a bad odor and greasy appearance. Corn oil is also subject to rancidity. In Europe, Castile soap is made from second-quality olive oil, to which some cocoanut oil is usually added.

Laundry soaps are made from tallow, bone grease, and house grease, and often palm and cotton-seed oils. Yellow soaps are made from these materials, with the addition of a certain proportion of rosin. The latter combines readily with alkali, but forms a rather soft soap, with good lathering properties; rosin is cheaper than most of the fats, and when used in proper quantities, adds certain valuable properties to the soap, and is not an adulterant.

The non-drying oils, with caustic soda, generally yield the hardest soaps, while the semi-drying and drying oils form products of butter-like consistency.

Cocoanut oil saponifies readily with strong lye, without boiling; hence is used for "cold-process" soaps. "German mottled," or "olein soaps," are made from crude oleic acid ("red oil"), obtained in the candle industry (p. 382). The spent lyes from white or yellow soaps are often used in making red-oil soap, in order to save all the alkali, since the oleic acid will combine with the carbonate as well as with the caustic.

Toilet soaps should be made from the best material, but many cheap grades are made from poorer stock than laundry soap, and the defects covered by high color and perfume. Some toilet soaps are made by melting together two or more kinds of soap.

Good soap cannot be made from poor material. The lye must be a caustic liquor, free from other salts, sulphides and sulphites being especially injurious, since they cause discoloration of the soap. In many large works the lye is prepared by causticizing soda-ash with lime. When caustic is purchased, it is simply dissolved to form a solution of the desired strength, varying from 18° to 30° Bé.

Soap kettles are square or round, and vary in size from 10 feet in diameter by 15 feet deep, to 25 by 35 feet, and capable of holding 300,000 pounds of soap. In modern factories they are always heated by steam; very small ones, used for remelting toilet soaps, etc., being steam-jacketed, and the larger ones having both open and closed coils. A modern form (Fig. 110) has a conical bottom, in which the steam coils (A, B) are arranged. Such a kettle, calculated to hold 100,000 pounds of soap, is about 15 feet in diameter and 21 feet high, the cone bottom being about 5 feet deep, and the cylindrical walls about 16 feet high. It is made of $\frac{3}{8}$-inch boiler plate, and is sheathed with 2-inch pine staves. It rests on stone pillars and foundations, and has large draw-off cocks in the cone, for running off waste lyes while the soap is pumped away through a pipe (D) passing through the side of the kettle.

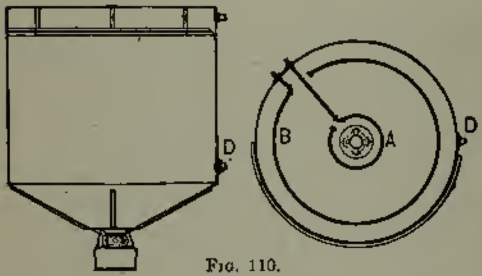

Fig. 110.

Soaps are made by various processes, but the most common are the following: —

(1) The fat is treated with the exact amount of caustic alkali needed to saponify it, *leaving the glycerine in the soap*. The so-called "cold-process" soap is the most common example of this method.

(2) The fat is boiled with solutions of caustic alkali until saponification is complete, or until the soap attains certain desired properties. The glycerine remains mixed with the product, as in the case

of **soft** and " **marine** " **soaps**; or it is excluded, as in the case of **yellow, laundry, mottled,** and **curd soaps.**

(3) A free fatty acid is neutralized by treatment with an alkaline hydroxide or carbonate, as in the case of oleic acid.

The **cold process** is the simplest of soap-making methods, but requires carefully calculated quantities of caustic and fat, and the latter must be well refined. Since it is difficult to calculate the exact amount of alkali, such soaps usually contain free fat or free alkali, or both. Cocoanut oil and tallow are chiefly used, and are melted and run into a mixing tank heated by steam, or into a crutcher (p. 376). Then a definite quantity of strong caustic soda lye, 32° to 36° Bé., is added, and the mixture well stirred for a few minutes. The heat of the reaction is sufficient to carry it on when once started. After saponification is well under way, the stirring is stopped and the mixture is run into " frames " (p. 376), where it stands several days, to complete the reaction and to cool. This leaves all the glycerine and any excess lye in the soap. The product looks well when fresh, but is very apt to turn yellow and become rancid.

Most soaps are **boiled.** The process is usually divided into several stages. The melted fat and lye of about 15° Bé. (1.115 sp. gr.) are run into the soap kettle together, while free steam is blown in to mix them, and to form an emulsion of the oil and lye, which is essential to the beginning of saponification or, as the soap-boiler terms it, " to kill the stock." When the emulsion forms, the lye has " caught the stock." If the lye is too strong at first, it does not " catch," and water is added and the heating continued until the emulsion forms. Strong lye is then carefully added in small portions at a time, and boiling is continued to complete the saponification. If a wooden stirring paddle be pushed into the mass at this time, the soap adheres to it when drawn out, and long strings of soap hang down from it. There is no separation of the lye. When the process is finished, as is shown by the soap having a dry, firm feel between the fingers, the soap is " **grained** " or " **salted out,**" by adding common salt. This causes a separation of the soap from the lye and glycerine, which is shown by the soap sticking to the paddle while the lye runs off. When properly salted, the soap boils in broad, smooth patches, and is hard, and not sticky, when cold. The steam is then cut off and the soap allowed to stand for several hours, when it rises to the top. The salt lye, which contains most of the glycerine, is drawn off, leaving the soap in the kettle. Strong lye, 25° Bé. (1.205 sp. gr.) is now added, and for **yellow laundry soaps,** rosin is introduced; for white soap, tallow or cocoanut oil is used instead of the rosin. The boiling is continued for two or three days, until the soap becomes clear and semi-transparent. This second boiling is called the "**rosin change**" or the "**strong change**"; during this time, the soap rises fully one-third the depth of the kettle, and often stands higher than its sides. For this reason, the kettle is not filled more than two-thirds full at first. When the rosin or cocoanut oil is saponified, the kettle is allowed to stand quietly for a number of hours, when the lye is drawn off. The next step is called "finishing," "settling," "pitching," or "fitting." Water is added to the boiling soap until it loses its granular appearance, after which it is allowed to settle for several days. This removes excess caustic and any insoluble impurities. The contents of the kettle separate into three layers, the soap on top, and the lye at the bottom, and between them a dark-colored layer, called "**nigre,**" containing caustic lye, soap, water, and various organic impurities.

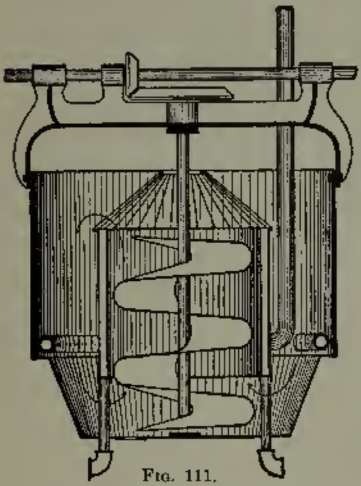
FIG. 111.

The lye and nigre are drawn off into separate tanks, and the soap is pumped into the **crutcher**, which is a very efficient mixing machine. One form (Fig. 111) consists of a broad, vertical screw, working within a cylinder, which is placed in a larger tank. The action of the screw draws the liquid soap in at the bottom and discharges it over the top of the cylinder, to again pass through the apparatus. A thorough mixing is thus secured. The perfume, and any filling material, such as silicate of sodium, sodium carbonate, borax, talc, etc., are added in the crutcher. These ingredients are well mixed with the soap, which becomes lighter colored, and then stiff and thick. After crutching for from 3 to 15 minutes the soap is run into "**frames**" (Fig. 112), which are large sheet-iron boxes, mounted on wheels, and

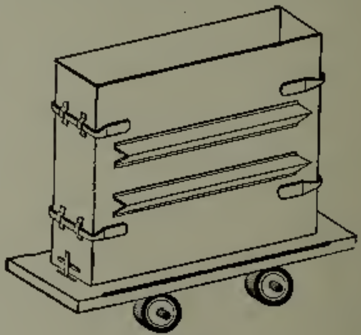
FIG. 112.

having removable sides. Each frame holds from 1000 to 1700 pounds, or one crutcher full. When it has solidified, after 24 to 36 hours, the sides are removed, and the block of soap stands several days in the air to cool thoroughly. Then it goes to the "**slabber**" (Fig. 113), a machine containing a number of tightly stretched steel wires, which are pushed against the block of soap, cutting it into slabs of the desired thickness. These then pass through a "**cutter,**" a similar machine, which forms them into rough bars, which are put into the dry room, kept at a temperature of about 90° F., for 12 to 15 hours. They are then run through the press, which forms the commercial bar and stamps on it the trade mark, name, or other design. They finally pass on an endless belt to the wrappers, who enclose them in separate papers and pack them in boxes, which are immediately nailed up for market.

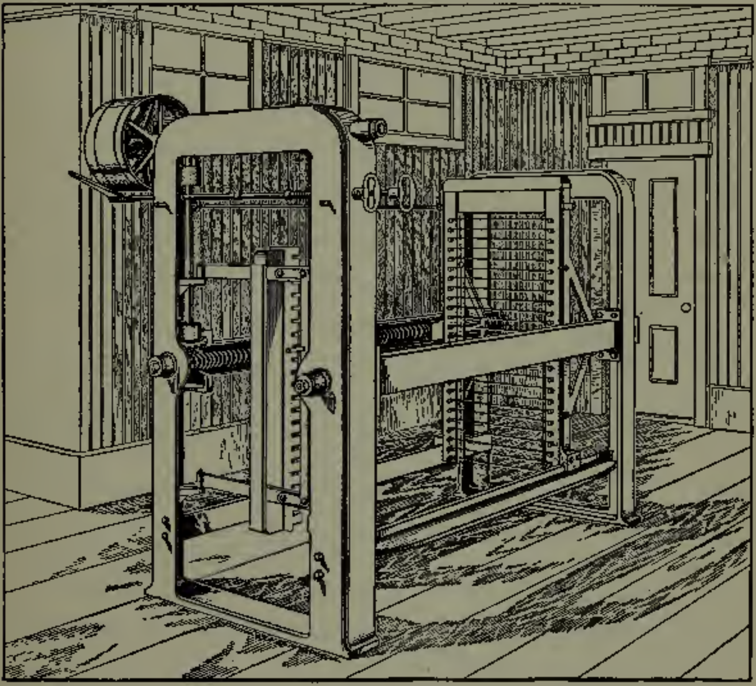

FIG. 113.

"**Boiled-down soap**" is made by treating the soap, after the lye has been drawn off, with strong brine, and then boiling it down. Sometimes the soap is settled and the nigre and lye separated before boiling down. This reduces the percentage of water in the soap, leaving it dry and hard. If soaps in which no rosin is used are boiled down on the lye until the latter becomes concentrated enough to precipitate the soap, and then run into frames and cooled very slowly, the small quantity of lye and other impurities mechanically enclosed segregate during the cooling into those parts of the mass which are the last to solidify, and cause the appearance called "**mottling.**" By adding a small amount of copperas, ultramarine, lampblack, or other pigment, the mottling becomes more prominent. Castile or Marseilles soaps have a green mottle, changing to red on exposure to the air. This is due to the presence of copperas, which precipitates the ferrous hydroxide with the lye in the soap; on contact with the air, the green hydroxide is changed to the red ferric salt. Rosin produces a more uniform soap, without mottle.

Toilet soaps are made in the same general way as the yellow soap, but from finer stock and with greater care to secure the complete removal of free alkali. Any excess of alkali is usually carbonated during the shaving and milling process.

Three classes of toilet soaps are made, — milled, remelted, and transparent. **Milled soaps** are made by shaving thoroughly dried bars of good soap to fine chips, and drying again until only about 10 per cent water remains. The dried soap is then ground in an edge-runner mill, and the perfume or other ingredients desired are added at the same time. After thorough incorporation, the soap is forced through a die plate by heavy pressure, forming a long bar, which is cut into cakes; these are stamped and pressed into the desired shape. This process allows the use of very delicate perfumes and other ingredients which would be destroyed by heat. It also furnishes a hard cake which does not wear away so rapidly when in use.

Remelted soaps, chiefly made in England, are prepared by remelting one or more kinds of soap, together with the perfumes and other ingredients, in a steam-jacketed kettle. By rapid agitation of the melted mass with paddles, air bubbles can be disseminated through the soap, which gives the cake sufficient buoyancy to float on water after stamping.

Transparent soaps may be made in two ways: (*a*) A common soap is dissolved in alcohol, the solution decanted from insoluble impurities, and the alcohol distilled off, leaving the soap as a transparent jelly, which is carefully dried in moulds to form the cake. (*b*) A cold-process soap is made as above and coloring matter, perfumes, etc., are added. The glycerine formed, remaining in the soap, causes the latter to have a translucent appearance. By adding more glycerine, with a little alcohol, or a solution of cane sugar, the transparency is increased.

Special **scouring soaps** for cleaning metal and unpainted woodwork are made by adding powdered sand, glass, or pumice-stone to a yellow soap. Strongly alkaline soaps often contain ground soda-ash, borax, and sodium silicate as "fillers," or frequently as intentional adulterants. Sodium silicate is generally added to yellow soaps, as it hardens them somewhat and possesses detergent properties itself.

Soap powders are made by mixing soda-ash with a soap solution containing just enough water to furnish the crystal water for *sal soda.* Since sal soda does not form above 34° C., the mixture can be made hot, and on cooling sets to a dry, solid mass. This is ground, packed, and sold as soap powder. Abrasive materials, as powdered quartz (*silex*), or ground feldspar, are frequently added with the soda-ash. These soap powders are also made from red oil (p. 382) by neutralizing with dry soda-ash.

A few insoluble soaps of the heavy metals are prepared for use in pharmacy, the most important being lead soap or "**lead plaster,**" which is made by decomposing a neutral soap with a soluble lead salt, or by heating olive oil with a paste of lead oxide in water.

CANDLES

The materials used for candles are: free fatty acids, especially palmitic and stearic; hydrocarbons, such as paraffine and ozokerite; and certain esters of the fatty acids, especially tallow and waxes. The requisites for candle stock are: that it shall burn freely without smoke or smell; that it shall not soften at so low a temperature that it loses its form from the heat of its own flame; and that when melted it shall be a fluid capable of being drawn into the wick by capillarity. Some glycerides, such as tallow, burn with a foul-smelling, smoky flame, and hence are only used in the cheapest candles. Also, they soften at too low a temperature, and the candle readily bends and gutters. Both these objections also apply to paraffine and to some of the solid fatty acids.

Candles are made by dipping, pouring, and moulding. For **dipped candles**, the wick is repeatedly introduced into the melted stock, each layer of fat being allowed to solidify before the next dip. Tallow dips, the poorest candle made, are prepared in this way.

Poured candles are made by pouring the melted stock in a slow stream over the wick, which is stretched in a frame. This method is used for wax candles, since the wax contracts too much on cooling to allow casting. While still plastic, they are rolled on a flat table under a board, to give them a uniform diameter.

Most candles are now **moulded** in a cylindrical metal form through which the wick is drawn in the line of its axis. The mould can be surrounded with hot or cold water to facilitate the casting and removal of the candles. Wicks are of plaited or twisted cotton yarn, usually flat, except for tallow dips, when they are round. They are so prepared that the end curls over and burns off as the candle is consumed, thus making snuffing unnecessary;* also, they are often treated with ammonium phosphate or borate to prevent their smouldering and emitting bad odors when the candle is extinguished.

Paraffine, ozokerite, and sperm candles (from spermaceti) are moulded. In order to prevent softening at too low a temperature, and to render them less brittle when handled, a little stearic acid is usually added.

The most important candle stocks are palmitic and stearic acids and paraffine wax.

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* This is accomplished in several ways; one side of the wick may be dipped in size, or one thread be drawn a little tighter than the rest.

Palmitic and **stearic acids** are usually made from tallow or palm oil by saponifying with lime, or water, the hydrolysis with the latter being often assisted by the addition of a little acid. **Saponification with lime** is carried on in two ways: (*a*) by boiling in open vessels with about 16 per cent of lime. The resulting insoluble lime soap consists of calcium oleate, palmitate, and stearate. It is separated from the lye and free glycerine which is also formed, and is decomposed by treatment with sulphuric acid and steam, setting free the fatty acid. (*b*) Or the fat may be saponified by **Milly's process**; *i.e.*, boiled in closed vessels called *autoclaves*, under pressure of from 8 to 10 atmospheres, with from 2 to 4 per cent of lime. The latter probably merely starts the hydrolysis, which is finished by the steam and water present. The products of the reaction are lime soap, free fatty acid, and glycerine. The turbid mixture is treated hot with just sufficient sulphuric acid to decompose the lime soap. The calcium precipitates as sulphate, while on top of the water (which contains the glycerine) is a layer of fatty acid. This is skimmed off and treated with water acidulated with sulphuric acid to insure complete decomposition of the lime soap.

Twitchell's process * is one of the more recent improvements in saponification methods. In this a compound of sulphuric acid with a fat acid (particularly sulpho-oleic acid), and an aromatic body with excess of sulphuric acid, is boiled with the oil or fat and water in a tank, until the glycerides are decomposed. The sulpho-fat acid is called the "saponifier," and about 1 to 1¼ per cent is added. The mixture is thoroughly stirred and steam blown in to effect the boiling, the time of which depends upon the amount of saponifier added; with 1 per cent from 12 to 24 hours are required. When saponification is complete, the emulsion is broken by adding sulphuric acid, or a mixture of sodium carbonate and sodium sulphate; on settling, the fatty acids come to the top and the glycerine lye may be drawn off from below. With a neutral fat the addition of some free fatty acid is advisable, in order to increase the solubility of the saponifier in the fat. The process works at low temperature, the fatty acids are of good color, and the yield is good. The fatty acids are much used for soap making, as well as for candles; the glycerine is refined in the usual way (p. 385).

The melted fatty acids obtained by any of these processes are run into shallow pans and allowed to stand a few days at a temperature of about 30° C., when the palmitic and stearic acids crystallize. The magma is first pressed cold, and then at 40° C., in bags in a hy-

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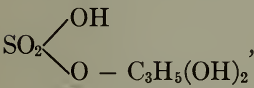
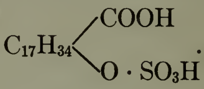
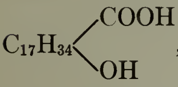
* Wagner's Jahresbericht, **1900**, 548.

draulic press; the liquid oleic acid separated forms the commercial "**red oil**" or "**olein**" employed for soap stock; the solid fatty acids compose the candle stock, which is called "**stearin.**"* It melts at 52° to 55° C. The yield from tallow or palm oil is 44 to 48 per cent stearin.

Saponification by water alone is accomplished by heating the fat in an autoclave with water to about 200° C. under pressure of about 15 atmospheres. A current of superheated steam is introduced, thus thoroughly mixing the contents of the vessel. The free fatty acid and the glycerine both distil over with the steam, the former condensing in the first receiver, while the latter passes on to another. This process needs much care in the regulation of the heat and to secure the complete decomposition of the glycerides, but, when properly worked, yields very pure products. The fatty acids are chilled and pressed as above described, to separate the olein. The yield of stearin is about 50 per cent from tallow or palm oil. Slightly rancid stock is more easily decomposed than neutral fat.

By adding from 4 to 5 per cent of strong sulphuric acid to the water in the autoclave, the hydrolysis is accomplished at 120° to 150° C. A part of the glycerine is converted into glyceryl-sulphuric acid,  $SO_2\begin{cases}OH\\O - C_3H_5(OH)_2\end{cases}$, while some of the oleic acid, which is an unsaturated body, forms sulpho-stearic acid,  $C_{17}H_{34}\begin{cases}COOH\\O \cdot SO_3H\end{cases}$. By the action of the water, this is converted into hydroxystearic acid,  $C_{17}H_{34}\begin{cases}COOH\\OH\end{cases}$, while sulphuric acid is regenerated. The hydroxystearic acid separates as a solid with the free stearic and palmitic acids, and in the subsequent purification of these by distillation with superheated steam, it is decomposed, separating more water and the residue polymerizing to form iso-oleic acid ($C_{18}H_{34}O_2$), a solid, melting at 45° C. Thus the yield of solid fat acids is slightly increased, being about 55 per cent from tallow.

Another method of acid saponification consists in heating the fat with concentrated sulphuric acid for a few minutes only, until the cell walls of the fat are destroyed and the hydrolysis is begun. The saponification is completed by boiling with water.

The mixed palmitic, stearic, and oleic acids are chilled and pressed

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* Not to be confounded with the glyceride of stearic acid, p. 350.

as already described. Saponification with acid gives a discolored product, which is usually purified by redistilling with superheated steam.

The liquid " **olein** " separated from the fatty acids by any saponification method is of less value than the solid acids. A process for producing palmitic acid from this oleic acid is based on the following reaction: —

$$C_{18}H_{34}O_2 + 2\,NaOH = C_{16}H_{31}O_2 \cdot Na + C_2H_3O_2 \cdot Na + H_2.$$

Caustic soda solution and oleic acid are heated together in an iron vessel provided with an agitator, until all the water is evaporated. The heat is then raised to a little over 300° C., when the evolution of hydrogen becomes active. When the hydrogen ceases to escape, the product is treated with water, which dissolves the sodium acetate and any undecomposed caustic, leaving sodium palmitate undissolved. This is decomposed with sulphuric acid to obtain the free fatty acid. But the product is too soft and is an unsatisfactory candle stock, hence the method is not now in use.*

After purification, the free fatty acids, obtained by any of the processes above described, are employed for candle stock. The aqueous solutions of glycerine (" **sweet waters** "), resulting from the saponification, are used in the manufacture of pure glycerine.

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* J. Soc. Chem. Ind., **1897**, 391.

GLYCERINE

There are two kind of refined glycerine, $C_3H_5(OH)_3$, on the market, **dynamite glycerine** and **chemically pure** glycerine. These differ only in color and in the content of pure glycerine. It is largely recovered from the spent lyes from soap making and from the " sweet waters " from the digesters where fats have been saponified with lime or with water under pressure.* Much crude candle glycerine is imported into this country from Europe, that from France, Italy, and Spain being derived from olive oil.

Spent soap lyes are very dilute solutions of glycerine and contain much impurity. The successful recovery of glycerine from them is one of the recent triumphs of chemical industry. The **Van Ruymbeke process** is most generally used. In this the lye is settled and drawn off from the sludge. It is then treated with a special chemical called " persulphate of iron," the exact composition of which is not disclosed, but which contains about 50 per cent of sulphuric acid. It is possibly a mixture of ferrous and ferric sulphates. This forms a copious precipitate, consisting of ferric hydroxide and iron soaps, which drags down all other insoluble impurities. This precipitate is removed by filter-pressing and the clear liquid tested for any excess of iron sulphate. If any is present, it is exactly neutralized with caustic soda and the precipitate filtered off. This leaves the lye almost water white and ready for the evaporation, which is done under high vacuum (27 to 28 inches), in a still, across the middle of which is a steam chest having small vertical tubes. Fresh lye is introduced, as the evaporation progresses, to maintain the level of the liquid. A salt-catch is placed below the steam chest in the evaporator, and in this the salt and sodium sulphate which separate, collect, and at the end of the operation are removed through a door in the front. The salt thus recovered is sent to the soap maker, to be used again in salting out soap.

The vapors from the evaporator pass through a series of " catch-alls " to retain any lye, and then go to a wet vacuum pump, which is provided with a jet condenser. The evaporation is usually carried on in two or more stages; sometimes it is continued to a point at which sodium sulphate will crystallize, which is thus removed; by further evaporation in vacuum, the common salt is crystallized.

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* Saponification with acid destroys much of the glycerine.

When the lye attains a density of 32° Bé. (1.295 sp. gr.), it contains about 80 per cent of glycerine, and is called **crude glycerine.** This is then distilled under a very high vacuum (28 to 29 inches) in a still consisting of a cylindrical iron shell containing a closed steam coil and a perforated pipe, through which superheated steam is introduced. The glycerine in the crude liquid passes over with the steam into coolers, which are simply cast-iron drums, cooled by the outside air. Most of the glycerine condenses here, while the uncondensed steam and some glycerine passes on to a surface condenser. The vacuum is maintained by a dry vacuum pump. The glycerine collected in the cooling drums is concentrated in vacuum pans until its specific gravity reaches 1.262. It is then passed through a filter press, which removes any suspended dirt, and gives a clear, bright product. As a rule, the glycerine recovered from soap lye is not bleached, and is generally sold as **dynamite glycerine.**

Chemically pure glycerine is made from candle crude glycerine by a modification of the Van Ruymbeke process. The crude liquid, having a density of 28° Bé., is diluted, and treated with milk of lime to neutralize any acid. It is then treated with a bleaching material known as "black," the composition of which is kept secret. After filter-pressing, the glycerine is concentrated to a density of about 31° Bé., in an apparatus similar to that used for dynamite glycerine. It is then distilled, as in the case of the latter, and the product condensing in the coolers is thoroughly bleached by treatment with more "black," and is then filter-pressed. The density of chemically pure glycerine is not required to be so high as that of dynamite glycerine, hence no final concentration is necessary. A very fine grade of chemically pure glycerine is sometimes prepared from dynamite glycerine by subjecting it to the same process employed for candle crude glycerine.

Of the other methods for recovering glycerine, only the **Glatz process** needs consideration here. In this the lye is treated with a small amount of milk of lime, and then all alkali neutralized with hydrochloric acid, and the liquid filter-pressed to remove the precipitated matter. By evaporating the filtrate under a vacuum, crude glycerine is obtained, which is distilled under low vacuum with superheated steam, the still being heated by direct fire. The product is then concentrated in a Yaryan or similar evaporator, until heavy enough for market.

The yield of glycerine is always calculated on the amount of fat saponified. By careful work, 6.75 per cent of marketable glycerine can be obtained by the Van Ruymbeke process.

Glycerine is a thick, viscid liquid, having a sweet taste and unctuous properties. It is soluble in water and in alcohol. High-grade dynamite glycerine is of a very pale, yellow color, odorless, and free from acids. It contains no iron, lead, or calcium salts, and only a trace (0.006 per cent, at most) of chlorides. The ash is not over 0.01 per cent. The specific gravity should not be less than 1.262 at 15° C. It is chiefly used in making nitroglycerine; also to some extent as a solvent; in the preparation of printers' ink-rolls, and for increasing the body or viscosity of other liquids. Chemically pure glycerine is colorless, containing less than 0.009 per cent carbonaceous residue, no chlorides, and leaves no ash. Its density is about 1.260 sp. gr. It is largely used as a preservative for tobacco; for confectionery; in pharmacy; in the preparation of cosmetics; as a sweetening agent in fermented drinks, and in preserves; and owing to its non-volatile and non-drying character, as an addition to inks intended for rubber stamps.

REFERENCES

Technology of Soap and Candles. R. S. Christiani, Philadelphia, 1881.
Das Glycerine. S. W. Koppe, Wien, 1883. (Hartleben.)
The Art of Soap Making. A. Watt, London, 1887.
Handbuch der Seifenfabrikation. C. Diete, Berlin, 1887.
Guide pratique du Fabricant de Savons. G. Calmels and E. Saulnier, Paris, 1887.
Traité pratique de Savonnerie. E. Morride, Paris, 1888.
Manufacture of Soaps and Candles. W. T. Brannt, Philadelphia, 1888.
Seifenfabrikation. (2 Bänder.) A. Englehardt, Wien, 1888.
Der praktische Seifensieder. H. Fischer, Weimar, 1889. (Voigt.)
Die Seifen-Fabrikation. F. Wiltner, Wien, 1891. (Hartleben.)
A Handbook of Modern Explosives. (Glycerine.) M. Eissler, New York, 1890.
Savons et Bougies. J. Lefevre, Paris, 1894.
Soaps, Candles, Lubricators, and Glycerine. W. L. Carpenter, 2d ed., London, 1895.
Soaps and Candles. J. Cameron, 2d ed., London, 1896. (Churchill.)
Manufacture of Explosives. (Glycerine.) O. Guttmann, London, 1896.
Manufacture of Soaps. G. H. Hurst, 1898.
Soap Manufacture. W. L. Gadd, London, 1899. (Bell & Sons.)
American Soaps. H. Gathman, 2d ed., 1899.
Manufacture of Hard and Soft Soaps. A. Watts, 1901.
Textile Soaps and Oils. G. H. Hurst, 1904.
American Soaps, Candles, and Glycerine. L. L. Lamborn, New York, 1904.
Die Gewinnung und Verarbeitung des Glyzerins. B. Lach, Halle, a. S., 1907.
Die Stearinfabrikation. Bela Lach, Halle, a. S., 1908.
Journal of the Society of Chemical Industry, **1889**, 4. O. Hehner.
American Chemical Journal: **17**, 59. Evans and Beach.
Journal of Analytical and Applied Chemistry: —
IV, 147. J. F. Schnaible. V, 379. E. Twitchell. VI, 423. W. H. Low.
Railroad and Engineering Journal: —
65, 495 and 551. C. B. Dudley. **67**, 199 and 215. C. B. Dudley.

ESSENTIAL OILS

The **essential** or **volatile oils** are liquids which give the peculiar odors to plants. They occur already formed in the plants, or are produced by the combination of substances in the plant, which react in the presence of water. They have strong and characteristic odors and pungent taste, and are generally volatile without decomposition. They are liquid at ordinary temperatures and are usually nearly colorless when fresh, but become darker and thick on exposure. Many are optically active. They are nearly insoluble in water, but impart their peculiar odor or taste to it. They dissolve in alcohol, carbon disulphide, petroleum ether, and fatty oils. Excepting those containing organic ethers, they are not saponifiable.

An essential oil is usually composed of several chemical substances, all of which are volatile with steam, and may possess either open- or closed-chain molecules. A few oils consist almost wholly of one constituent. The more important classes of bodies found in essential oils are: *terpenes* of the general formula $C_{10}H_{16}$; *camphors,* oxygenated substances of alcoholic or ketone structure; *geraniol,* $C_{10}H_{17}OH$, and *citronellol,* $C_{10}H_{19}OH$, and derivatives of these, for the most part of open-chain structure; *benzene derivatives,* or ring-form hydrocarbons, phenols, alcohols, aldehydes, ketones, and acids; *aliphatic bodies,* consisting of open-chain alcohols, aldehydes, and acids, or of esters of these; *sulphides, thiocyanates,* and *nitrogenous bodies* in a few oils. The oils sometimes contain resins, in solution, and are then called oleo-resins, or balsams.

Some of the essential oils can be prepared synthetically; some are extracted from the plant with solvents, by maceration in fat, or by *enfleurage,* or absorption in fat. But most commercially important essential oils are obtained by distillation with water or steam or by pressing.

In the distillation process, the oil-bearing material is put into a still with a considerable quantity of water, which is then brought to boiling. The steam carries the oil into the condenser mechanically, where a mixture of oil and water is obtained, which is usually milky at first. On standing, it separates into two distinct layers, the oil usually, but not always, on top. The water is drawn off, and returned to the still with the new charge; or the receiver is so arranged that the water returns continuously to the still through a siphon.

When extraction is employed, alcohol, carbon disulphide, ether, or petroleum naphtha may be used. The solvent is evaporated from the oil, and recovered.

Some oils, especially those of lemon and orange, are obtained by the use of hydraulic or screw presses. The product is fragrant, but rather deeply colored.

Maceration in fat is employed for some essences which are injured by high temperatures. The fat used is a perfectly pure and sweet lard, tallow, or heavy paraffine oil which is melted in a water bath. The flowers or leaves are stirred in and digested until exhausted. The fat takes up the essential oil and is treated with alcohol, which extracts part of the essence. These alcoholic solutions are much used in perfumery; the fat, still containing some of the essential oil, is used for pomades and similar purposes.

Enfleurage is employed for those very delicate oils whose odors are destroyed by even moderate heat. The flowers to be extracted are laid in a wooden frame on the glass bottom of which a thin layer of perfectly neutral fat is spread. A number of frames are placed in a pile and allowed to stand for some hours, when the flowers are replaced by fresh ones. This is repeated until the fat has become strongly charged with the perfume.

Oil of turpentine or **spirits of turpentine** is derived from coniferous trees, especially from the pine, *Pinus palustris,* Mill., and *P. tæda,* L., and from the Scotch fir, *P. sylvestris,* L. The trees are "boxed," *i.e.* a cavity is cut near the root, and the bark channelled with shallow cuts which lead down to the box. The crude turpentine (an oleo-resin) flows from the cuts and collects in the box, from which it is dipped out at intervals. It forms an exceedingly sticky, viscid liquid balsam which is distilled with steam. The volatile oil of turpentine (about 17 per cent) passes over with the steam, while a residue of resin (rosin or colophony) remains in the still.

The oils obtained from different varieties of *coniferæ* differ somewhat in their properties. Three commercial grades are important: (*a*) **French turpentine** consisting chiefly of a terpene, $C_{10}H_{16}$, and called *terebenthene* or *lævopinene,* which has a lævo-rotary action on polarized light rays; (*b*) **American** or **English turpentine** consisting of a terpene, $C_{10}H_{16}$, called *australene,* which has the same specific gravity, boiling point, and chemical properties as terebenthene, but is dextro-rotary; (*c*) **Russian turpentine** which contains the terpene, *sylvestrine,* and some of a pinene resembling australene. The oil first distilled is usually washed with caustic soda solution to saponify rosin acids, and is then redistilled for "rectified spirits of turpentine." Commercial oil of turpentine or "turps" is a water-white, mobile, refractive liquid of 0.640 to 0.872 sp. gr., distilling between 156° and 170° C. It is insoluble in water and in glycerol, but soluble in ether, absolute alcohol, carbon disulphide, chloroform, benzene, fatty and essential oils. It dissolves sulphur, phosphorus, wax, caoutchouc, and resins, and is used as a solvent in varnishes and paints. It burns with a smoky flame. It absorbs oxygen from the air, becoming resinous. According to Kingzett, oxidation of turpentine forms camphoric peroxide, $C_{10}H_{14}O_4$, which with water yields camphoric acid and hydrogen peroxide. By passing air into Russian turpentine in the presence of warm water, the disinfectant "**sanitas**" is made.

Turpentine is now largely produced by the destructive distillation of resinous pine wood, often with the aid of steam injected into the retort; acetic acid and wood alcohol are by-products.

Camphor,[*] $C_{10}H_{16}O$, is an oxygenated essential body (probably a ketone) occurring in some crude volatile oils. Commercially it is obtained from the wood of the camphor laurel, *Cinnamomum Camphora*, Nees & Eberm., native in Japan and Borneo. The trunk and branches of the tree are roughly distilled with water, and the crude camphor purified by sublimation.

Artificial camphor may be made in several ways,[†] by oxidizing borneol or isoborneol with permanganate, ozone, oxygen, air, chlorine, or nitrous gases. Catalytic reagents may be used to accelerate the reaction, as when the vapors of isoborneol and air or oxygen are passed over platinized asbestos, metallic copper, or bits of earthenware at 175° to 180° C., thus producing a mixture of camphor, camphene, and isoborneol, from which the camphor is separated. Or isoborneol dissolved in benzene is treated with chlorine; camphor is produced and remains dissolved in the benzene from which it is crystallized. The reaction is $\underset{\text{Isoborneol}}{C_{10}H_{18}O} + 2\ Cl = 2\ HCl + \underset{\text{Camphor}}{C_{10}H_{16}O}$.

Camphor is a white, translucent body having a penetrating odor and pungent taste; it melts at 175° C., boils at 204° C., is volatile at ordinary temperatures, and burns with a luminous smoky flame. Its specific gravity is 0.986 to 0.996. It is slightly soluble in water, easily so in alcohol, ether, chloroform, carbon disulphide, acetone, and essential oils. It is largely used in the manufacture of celluloid

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[*] J. Soc. Chem. Ind., **1884** (3), 353.

[†] *Ibid.*, **1904**, 75, 881; **1905**, 249, 857, 902, 1188. U. S. Pats., 770940, 790601, 801483, 801485, 802792, 802793.

(p. 584), in explosives, in medicine, and pharmacy, and as a protective against the ravages of insects.

Thymol, $C_{10}H_{13} \cdot OH$, is a phenol occurring in the oil of thyme and in some other volatile oils. It is similar to carbolic acid in its character, and it is obtained by washing the crude oil with caustic soda, the alkaline solution of thymol being separated and decomposed with mineral acid; or the oil is chilled and the thymol crystallizes and may be filtered out.

It is a colorless crystalline body, having a specific gravity of 1.028, and melting at 44° C. It is very slightly soluble in water, but readily so in alcohol, glacial acetic acid, ether, etc. It is a powerful antiseptic, and is much used in medicine and in pharmacy.

Menthol, $C_{10}H_{19} \cdot OH$, is an alcohol occurring in oil of peppermint, and which crystallizes when the oil is chilled. It is a white solid, very sparingly soluble in water, but readily so in ether, alcohol, and fixed and volatile oils. It does not combine with caustic alkalies. It melts at 41° to 43° C. It is much used as a remedy for neuralgic pains and headache.

The **essential oil of almonds** is produced by the action of *emulsin,* a nitrogenous ferment upon *amygdalin,* a glucoside. To obtain it, the marc of almond kernels left after pressing for the fixed oil is distilled with water. It contains benzaldehyde, with some hydrocyanic acid and other nitrils. It is purified by redistillation over a mixture of lime and ferrous sulphate. It is readily oxidized on exposure to the air, forming benzoic acid. Artificial almond essence is made by boiling benzal chloride with lead nitrate or calcium carbonate and water. This oil is used in making dyes and as a flavoring extract.

Nitrobenzene is used under the name "mirbane" as a substitute for almond essence for scenting soaps.

Oil of bergamot is prepared from the fruit of a species of orange, *Citrus Bergamia,* Risso, by hand pressing or distillation with water. It is a light green, pleasant-smelling oil, containing a large amount of a terpene, *citrene,* $C_{10}H_{16}$, boiling at 175° to 177° C. It is chiefly used in perfumery.

Oil of Cajaput, prepared from the leaves of *Melaleuca Leucadendron,* L., is a green liquid of peculiar odor, distilling at 170° to 180° C.

Cedar oil is obtained by distilling the wood of red cedar, *Juniperus Virginiana,* L., with water. It contains a mixture of *cedrene,* $C_{15}H_{24}$, and a camphor-like body, $C_{15}H_{26}O$.

Chamomile oil, distilled from *Anthemis nobilis,* L., consists of isobutyl and amyl esters of angelica and tiglic acids.

Cinnamon oil or oil of cassia is distilled from the inner bark of *Cinnamomum Zeylanicum*, Nees. It is a yellow oil, consisting mainly of cinnamic aldehyde, with a little cinnamic acid. It is slightly heavier than water.

Oil of cloves is obtained by distilling cloves (the flower buds of *Eugenia caryophyllata*, Thunb.) with water. It is a mixture of a terpene, $C_{15}H_{24}$ (boiling at 251° C.), and eugenol, $C_{10}H_{12}O_2$. It is yellow, of a penetrating odor, and heavier than water.

Eucalyptus oil, distilled from the leaves of several Australian trees, *Eucalyptus Globulus*, Labill., and others, is used in perfumery, in medicine, and in scenting soaps. It contains terpenes (especially pinene, $C_{10}H_{16}$), cymene, and eucalyptol or cineol, $C_{10}H_{18}O$.

Geranium oil is distilled from the leaves of *Pelargonium Radula*, L'Herit. Its odor resembles that of rose oil, which it is chiefly used to adulterate.

Lavender oil is distilled from the flowers of *Lavandula vera*, D. C. It has little odor when first prepared, the perfume being developed by exposure to the air. **Oil of spike** is obtained from *L. Spica*, Cav. It is similar to lavender oil and is used in porcelain painting.

Oil of lemon is expressed from the rind of the fruit of *Citrus Limonum*, Risso. Poor grades are made by distilling the rind. The oil contains a terpene (limonene), $C_{10}H_{16}$, boiling at 176° C. It is chiefly used in perfumery, and as a flavoring essence in confectionery.

Mustard oil is distilled from the seeds of *Brassica nigra*, Koch., after the fixed oil has been removed by pressing. It contains nitrogen and sulphur, and its essential principle is allyl thiocarbamide, $C_3H_5N:CS$. It is a pale yellow oil of 1.015 to 1.025 sp. gr., boiling at 148° C., and having a pungent, disagreeable odor. It is a powerful irritant and produces blisters on the skin. It is not present in dry seeds, but is formed by the action of a ferment, *myrosin*, upon a glucoside, *potassium myronate*, in the presence of water. Artificial mustard oil is prepared by distilling allyl iodide with potassium thiocyanate: —

$$C_3H_5I + KSNC = KI + C_3H_5 \cdot N:CS.$$

Oil of peppermint, obtained by distilling the herb *Mentha piperita*, L., is a colorless or greenish yellow liquid, of strong pungent taste and odor, having a specific gravity of 0.900 to 0.920. It is a mixture of menthol, $C_{10}H_{19} \cdot OH$, with several terpenes. It is much used in medicine and as a flavoring essence.

Attar of roses is obtained by distilling the flowers of various species of rose. It is a pale yellowish liquid, somewhat lighter than water, having a very delicate, rich odor. It crystallizes at ordinary temperatures and deposits an inodorous body resembling paraffine. The constitution of the oil is not known. Owing to its high price, it is frequently adulterated with geranium oil, which resembles it somewhat in odor.

Oil of rue is distilled from the herb *Ruta graveolens,* L. It consists mainly of methyl nonylketone, $C_9H_{19} \cdot CO \cdot CH_3$.

Oil of sassafras is distilled from the root of *Sassafras officinale,* Nees & Ebern. It contains safrol, $C_{10}H_{10}O_2$, and some pinene, $C_{10}H_{16}$. Safrol melts at 8° C. and boils at 228° to 235° C. Sassafras oil is much used for flavoring.

Oil of thyme or **origanum** is derived from the leaves and flowers of *Thymus vulgaris,* L. It is yellowish red, has a pungent taste, and a specific gravity of 0.900 to 0.930. It contains a lævo-pinene, $C_{10}H_{16}$, boiling at 160° C.; thymol, $C_{10}H_{14}O$, and cymene, $C_{10}H_{15}$, boiling at 175° C.

Oil of wormwood is distilled from the herb *Artemisia Absinthium,* L.

Oil of wintergreen is distilled from the leaves of *Gaultheria procumbens,* L. It contains methyl salicylate, $C_6H_4 \cdot (OH) \cdot COO \cdot CH_3$, with a little terpene. It is a liquid of pleasant smell and taste, boiling at 218° C., and of 1.175 to 1.185 sp. gr. at 15° C. It rotates the plane of polarization to the left. It is used as a flavoring essence.

An artificial oil is made by heating salicylic acid with oil of vitriol and methyl alcohol.

REFERENCES

Treatise on the Manufacture of Perfumes. J. H. Snively, New York, 1890.
Die flüchtigen Oele des Pflanzenreiches. G. Bornemann, Weimar, 1891.
Handbuch der Parfumerie- und Toilettenseifen-fabrikation. C. Deite, Berlin, 1891. (J. Springer.)
The Art of Perfumery. C. H. Piesse, London, 1891. 5th ed.
Treatise on the Manufacture of Perfumery. W. T. Brannt, Phila., 1902.
Odorographia; a Natural History of Raw Materials and Drugs used in the Perfume Industry. J. C. Sawer, London, 1892, Part I. 1894, Part II.
Perfumes and their Preparation. Askinson-Furst, London, 1892.
Fabrication des Essences et des Parfums. P. Durvelle, Paris, 1893.
Descriptive Catalogue of Essential Oils and Organic Chemical Preparations. F. B. Power, New York, 1894. (Fritsche Bros.)
Die Riechstoffe u. Ihre Verwendung. St. Mierzinski, Weimar, 1894.
Aether und Grundessenzen. Theodor Horatius, Leipzig, 1895.
Semi-Annual Reports. 1892+. Schimmel and Co. (Fritsche Bros.), Leipzig and New York.
Huiles essentielles et leurs principaux constituants. Charabot, Dupont et Pillet, Paris, 1899.
Chemistry of Essential Oils and Artificial Perfumes. E. J. Parry, New York, 1900.
Die Aetherischen Oele. F. W. Semmler, Leipzig, 1906.
Die Aetherischen Oele. Gildemeister und Hoffmann, Berlin, 1910.
The Volatile Oils. E. Gildemeister and F. Hoffmann. Translated by Edward Kremers. New York, 1914.

RESINS AND GUMS

Resins are oxygenated bodies, generally produced by the oxidation of terpenes or related hydrocarbons in plants or in essential oils. They are found as natural or induced exudations from plants, often mixed with the essential oil, forming oleo-resin or balsam, or with mucilaginous matter, forming gum-resin. True resins are compact masses, insoluble in water, devoid of marked taste or odor, and usually composed of substances of an anhydric or acid nature. They are nearly all soluble in alcohol, ether, benzene, and in most volatile oils, and may usually be saponified with caustic alkali. When heated, they soften below their melting points, but cannot be distilled undecomposed. The chief uses of resins are: in making varnish; for soap; as a constituent of sealing wax; in medicine, and in sizing paper and cloth.

Common rosin, or **colophony**, is a resin obtained by the distillation of turpentine oil from crude turpentine (p. 388). Three grades of rosin are in the market, — "virgin," yellow dip, and hard. Virgin rosin is made from the first turpentine that exudes after the tree is "boxed." It is of a very light yellow or amber color. The greater part of the crude turpentine furnishes yellow dip. The hard is made from the scrapings from the tree after the turpentine has become too thick to run into the box; it is very dark, being nearly black.

Rosin is brittle, melts at 100° to 140° C., and has a specific gravity of about 1.08. It contains a large amount of abietic anhydride, $C_{44}H_{62}O_4$, which is readily converted into abietic acid, $C_{44}H_{64}O_5$. Rosin is converted by alkalies into "rosin soap" (p. 373), which is deliquescent and very soluble in water. Rosin is used as a constituent of laundry soaps; as an addition to cheap varnishes; as a flux in soldering and brazing metals; in pharmacy; in ship calking; and as an adulterant of fats, waxes, and mineral oils.

Rosin must not be confounded with wood-tar, or pitch, obtained by the destructive distillation of wood.

Rosin may be distilled *in vacuo*, or by the aid of superheated steam, with very little decomposition; but when heated in a retort, it yields decomposition products consisting of gases, liquids, and pitch. The liquid distillate is composed mainly of "**rosin spirit**,"[*] a very complex body, boiling below 360° C. (resembling oil of turpen-

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[*] Renard. J. Chem. Soc., **46**, 843.

tine, for which it is sometimes substituted), and "**rosin oil**,"* a heavier liquid, boiling above 360° C.

The rosin oil is purified by treatment with a little sulphuric acid, followed by lime water, and then redistilled, sometimes with caustic soda in the still. It has a specific gravity of 0.980 to 1.110; is water white to brown in color, and is only slightly soluble in alcohol, but easily dissolved in fatty oils, ether, chloroform, etc. It is nearly odorless, and has a strong, peculiar taste. It is not subject to true saponification, although when treated with milk of lime, a combination between the terpenes of the oil and the calcium hydroxide takes place, forming a solid mass. This is stirred up with more rosin oil, to form a soft mixture of about the proportions, $13\ C_{10}H_{16} \cdot Ca(OH)_2$, which is the commercial "**rosin grease**," used as a lubricant on iron bearings. Rosin oil is largely used in making such lubricants, and as an adulterant for olive and boiled linseed oils.

Burgundy pitch is a resin resembling common rosin, but obtained from the Norway spruce, *Picea excelsa*, Link. The trees are scarified, and the resin allowed to harden, when it is collected and treated with boiling water, to remove the volatile oils. Its chief constituent is abietic anhydride. When stirred up with fats and water, melted rosin forms a mass resembling Burgundy pitch in its opacity and other properties.

Mastic and **Sandarac** are somewhat similar resins, obtained from evergreen shrubs which grow along the shores of the Mediterranean Sea, especially on the island of Chios, and in northern Africa. The former, derived from *Pistacia Lentiscus*, L., occurs in commerce as small translucent grains, or "tears," which soften when masticated, and have a slightly bitter, aromatic taste. It is soluble in acetone, alcohol, and turpentine oil, and is used in varnish making and in pharmacy.

Sandarac, also called "gum juniper," is obtained from *Callitris quadrivalvis*, Vent., an evergreen growing in northern Africa. It is used in varnishes.

Amber is a fossil resin found along the coast of the Baltic Sea, in Germany. It is the hardest and heaviest of all resins, is capable of taking a high polish, and is insoluble in most of the ordinary solvents. Its color varies from very light yellow to deep brownish red. It often contains perfect specimens of fossil insects. When heated above its melting point, it is partly decomposed, and then becomes soluble in alcohol and in oil of turpentine.

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* Renard. J. Chem. Soc., **24**, 304, 1175.

Transparent pieces of amber are much prized for jewelry, fancy articles, mouth-pieces for pipes and cigar holders, and for other ornamental purposes. It is also used in preparing a fine transparent varnish for use on negatives in photography.

When subjected to destructive distillation, amber yields a gas, an organic acid (succinic acid), and an oil called "oil of amber." This oil and the acid are used somewhat in pharmacy. By treating oil of amber with fuming nitric acid, a substance resembling musk in odor and other properties is obtained.*

Copal is a valuable resin. Soft copal, soluble in ether, is obtained from living trees in Java, Sumatra, the Philippine Islands, Australia, and New Zealand. The better quality, hard copal, is a fossil gum, found in irregular lumps, buried in the earth, in the East Indies, Madagascar, West Africa, and South America, the last variety being called **gum animi**. Hard copal varies in color from pale yellow to brown. Its specific gravity is usually 1.059 to 1.072. It has a higher melting point than soft copal, and is insoluble in ether or volatile oils. But by heating above its melting point, a partial decomposition takes place, and the resin is rendered more soluble in these solvents.

Hard copal is the hardest of all resins, except amber, and is most valuable for varnish making. For this it must first be melted, or "run," and while in the liquid state, hot oil of turpentine is slowly added and mixed with it.

Dammar is obtained from a coniferous tree, *Agathis loranthifolia,* Salisb., in the Moluccas. The resin exudes from the tree in drops, and is collected after it dries. It is soluble in essential and in fixed oils, in crude benzene, and partially so in alcohol and ether. It is very light colored, and makes a transparent varnish.

Kauri, or **Australian dammar**, is obtained from a New Zealand tree, *Agathis australis,* Stend. Much of the kauri of trade is a fossil resin, and is somewhat darker colored than the true dammar and copal. It is extensively used for varnish making, being cheaper than copal.

Dragon's blood is a deep crimson red resin, which exudes from the fruit of a palm tree, *Dæmonorops Draco*, Blume., indigenous in the East Indies. It is collected by the natives and made into irregular lumps, or cast into long sticks in moulds made by rolling palm leaves into cylinders and closing one end. It is freely soluble in

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* The artificial musk of commerce is now made from butyl toluene, by the action of nitric and sulphuric acids. Bauer. Berichte der deutschen chemischen Gesellschaft, **24**, 2832.

nearly all of the ordinary solvents, except petroleum ether, oil of turpentine, and ether. It is slightly soluble in the two latter. It is used in pharmacy, and in certain colored varnishes.

Guaiacum is a resin derived from certain West Indian trees, especially *Guaiacum sanctum*, L., and *G. officinale*, L. It exudes from the trees through incisions, and forms "tears" or lumps which are sent to market. It is soluble in ether, alcohol, chloroform, acetone, and caustic soda. Its alcoholic solution is employed as a reagent for oxidizing substances, with which it shows a blue color, which is destroyed by reducing agents, but reappears when again oxidized. Hydrogen peroxide, however, does not change the color to blue unless in the presence of blood. Hence guaiacum in alcohol, with hydrogen peroxide, is used as a reagent for detecting blood stains. Guaiacum is also used in medicine in treating rheumatism and gout.

Lac is a resin produced by the bite or sting of certain insects, *Coccus lacca*, Kerr, on the small twigs of several species of East Indian trees, of which *Ficus Indica*, L., and *F. religiosa*, L., are the chief. The resin appears to be formed from the plant sap by the female insect, from whose body it exudes, ultimately burying the insect and her eggs, and forming a thick excrescence on the twigs. It is collected, together with the twigs which it envelops, and is brought into commerce as "**stick lac.**" The insect also secretes a brilliant red dye which is extracted by macerating the crude lac in warm water. The aqueous solution is evaporated to dryness, and the residue sold as **lac-dye.** After the dye is extracted, the resin is known as "**seed lac.**" This is refined by carefully melting and straining through muslin bags to remove foreign matter. The melted lac is then poured in thin films over cold porcelain, copper, or wood cylinders, or plates, and allowed to cool, when it hardens and scales off in thin flakes, and is called "**shellac.**" Or it is poured into moulds to form "**button,**" or "**garnet lac.**" The shellac is the better quality, and is of a pale orange, or red color, and is nearly transparent. It is used for spirit varnish.

Lac is partially soluble in strong alcohol, forming a turbid, gummy liquid much used as a varnish and wood filler. It is partly soluble in ether, chloroform, and turpentine, but is completely dissolved by caustic alkalies and borax solutions. Such solutions are used as water varnishes. Lac is also used as the basis of the better grades of sealing wax.

Bleached shellac is made by the action of sodium hypochlorite on an alkaline solution of lac; the lac, precipitated with acid, is melted under water and "pulled" to make it white and fibrous. It is used for white varnishes, but becomes insoluble in alcohol after some time.

Elemi is a resin obtained from certain trees, *Canarium commune*, L., in the Philippine Islands, *Canarium Mauritianum*, Blume., in Mauritius, *Amyris elemifera* in Mexico, and from several varieties of *Icica* in Brazil. The resin varies from white to gray in color, and is soft and tough. It softens at 75° C., and melts completely at 120° C. It is soluble in alcohol and other solvents, and is used chiefly to give toughness to varnishes made from harder resins.

VARNISHES

The resins are chiefly important as furnishing the material for varnish making. A varnish is a solution of a resin, or of a drying oil, which, when exposed to the air, becomes hard and impervious to air and moisture, through evaporation of the solvent or oxidation of the oil. Three classes of varnishes are important: (1) **Spirit varnishes**, consisting of resin dissolved in alcohol, petroleum spirit, acetone, or in any other volatile solvent; (2) **turpentine varnishes**, in which the resin is dissolved in oil of turpentine; and (3) **linseed oil varnishes**, which may consist of linseed oil alone, or with the addition of resin and turpentine oil.

Spirit varnish dries rapidly, leaving the resin as a thin and brilliant film on the surface to which it is applied. This film is brittle, and liable to crack and scale off. The addition of turpentine overcomes this difficulty to some extent. Spirit varnishes are often colored with dyes soluble in alcohol, or with dragon's blood, gamboge, or cochineal. The most important spirit varnishes are made with shellac, though mastic, sandarac, and dammar are used.

Turpentine varnish is tough and flexible, but much slower in drying than the spirit varnishes. The resin is simply dissolved in the hot oil, and after cooling is ready for use.

Linseed oil varnishes are the most important. If well-boiled oil (p. 357) is applied to a surface, it dries to a hard film, but without much brilliancy of surface. By dissolving a resin in the boiled oil and thinning to the proper consistency with turpentine, a varnish is obtained which dries with a hard, glossy surface, impervious to air and moisture. The resins used are mainly amber, copal, anime, kauri, and dammar, for transparent varnish. The hard resins are not directly soluble in the oil, but must first be partly decomposed or "run," by heating above their melting points. There is considerable evolution of irritating gases during this fusion, and an oily distillate is often collected. The residue in the pot is then soluble in the hot boiled oil, which is run direct from the boiling kettle into the resin melting kettle. After thorough stirring the mixture is usually heated some time longer to secure homogeneous solution. It is then cooled to about 130° or 140° C., and thinned to the desired consistency with oil of turpentine. The varnish is allowed to stand in storage tanks for several months, or even for a year or two, until thoroughly clarified.

The boiling of the oil and of the varnish involves considerable risk from fire. The oil froths very much, and the vapors given off are inflammable, hence it is usually the custom to build the furnace with the fire-door opening through a partition into another room. The vapors should be led into a flue having a good draught.

OLEO-RESINS

Oleo-resins are mixtures of the resin and the essential oil of the plant from which they exude. Among them is a group of substances which have peculiar odor and pungent taste, and which are called **balsams.** They are the exudations from tropical trees belonging to the genera *Myroxylon* and *Styrax*. The most important are **Benzoin, Peru, Tolu,** and **Storax balsams.** They contain free benzoic or cinnamic acids, or compounds of them, to which their peculiar properties are due. The balsams are chiefly used in medicine and pharmacy, and for incense and perfumes.

The so-called Canada balsam is an oleo-resin containing turpentine, and is not a true balsam.

GUM RESINS

Gum resins are exudations from plants; they are the inspissated juice, and contain both gum and resin. They form emulsions with water, a portion of the gum dissolving.

Ammoniacum is derived from a Persian plant, *Dorema Ammoniacum*, Don. It forms drops, yellow on the surface and milky within. It is partly soluble in water, and has a peculiar odor and bitter taste. It is employed in medicine.

Asafœtida is obtained from the roots of two plants, *Ferula Narthex*, Boiss., and *F. fœtida*, Regel, native in Thibet and Turkistan. It forms tears and nodules, frequently contaminated with earthy impurities. It has a powerful garlic odor and bitter taste. It is mainly used in medicine as a stimulant.

Euphorbium is derived from a species of cactus, *Euphorbia resinifera,* Berg., native in Morocco. It has a very pungent taste, an aromatic odor, and the powdered gum irritates the throat and nose. It is a violent emetic and purgative, and is chiefly used in veterinary medicine.

Galbanum is obtained from Persian plants, probably *Ferula galbaniflua,* Boiss. & Buhse. It forms tears, or irregular lumps, of brownish yellow color, aromatic odor, and bitter taste. The several varieties found in commerce are used in medicine, and as constituents of incense.

Gamboge (p. 241) is an orange-red substance, derived from a tree, *Garcinia Hanburyi,* Hook., or *G. Morella,* Desr., native in Cochin China and Siam. It is soluble in alcohol, has an acrid taste, and is a powerful purgative. Its chief uses are in medicine, and as a pigment.

Myrrh is obtained from a shrub, *Commiphora Myrrha,* Engl., growing on the coast of Arabia. It comes in commerce as red-brown, dusty lumps, breaking with an oily-appearing fracture. It has a fragrant odor and bitter taste, and emulsifies with water. It is used as a tonic in medicine, and in preparing incense.

Olibanum or **frankincense** is derived from several species of *Boswellia,* the trees being native in Africa and Arabia. It forms tears of a yellow-brown color and milky appearance. It has a slight turpentine-like taste, and an aromatic odor. It forms an emulsion with water, and was formerly much used in medicine. It is now chiefly employed in preparing incense.

GUMS

Gums are amorphous bodies of complex constitution, nearly all of vegetable origin, and soluble in, or, at least, gelatinizing with water, but insoluble in alcohol. When boiled with dilute acid, they yield sugars, and when oxidized are converted into oxalic or mucic acids.

Acacia, Gum Arabic, or **Gum Senegal,** is derived from numerous plants of the *Acacia* family, mostly native in Africa. It forms lumps of various sizes, ranging in color from transparent white to red-brown. Its chief constituent is arabic acid, or *arabin,* $C_{12}H_{22}O_{11}$, as calcium salt. It dissolves in cold or hot water with equal readiness, and is much used in pharmacy in preparing emulsions. Low grades are used for mucilage, in calico printing, in thickening ink and water colors, and as stiffening in cloth.

Tragacanth is an exudation from *Astragalus gummifer*, Labill., growing in the Levant. It forms dull white, translucent plates, which swell in water and partly dissolve, forming a thick mucilage. Its uses are similar to those of gum arabic.

Agar-agar or **Bengal isinglass** is a dried seaweed, *Gracilaria lichenoides* and *Eucheuma spinosum*, collected in China. It forms a jelly with water.

Iceland moss, *Cetraria islandica*, yields a jelly containing two gums, *lichenine*, $C_6H_{10}O_5$, and *isolichenine*. The former is not colored blue by iodine, while the latter is.

Irish moss, *Chondrus crispus*, yields a soluble gum, which is not colored blue by iodine.

REFERENCES

Report on the Gums, Resins, Oleo-resins, and Resinous Products of India. M. C. Cooke, London, 1874.

Varnishes, Lacquers, Siccatives, and Sealing Waxes. E. Andres. Translated by Wm. T. Brannt, Philadelphia, 1882. (H. C. Baird & Son.)

Oils and Varnishes. James Cameron, Philadelphia, 1886. (Blakiston, Son & Co.)

Der Fabrikation der Lacke und Firnisse. Paul Lohmann, Berlin, 1890.

Fossil Resins. C. Lawn and H. Booth, New York, 1891.

Die Fabrikation der Lacke Firnisse, u. s. w. E. Andres. 4te Auf. Wien, 1891.

Notes on Varnish and Fossil Resins. R. I. Clark, London, 1892 (?).

Painters' Colours, Oils, and Varnishes. G. H. Hurst, London, 1892.

The Chemistry of Paints and Painting. A. H. Church. 2d ed. London, 1892.

Pigments, Paints, and Painting. G. Terry, London, 1893. (Spon & Co.)

Fabrication des Vernis. L. Naudin, Paris, 1893.

Die Fabrikation der Copal-, Turpentinöl- und Spiritus-Lacke. L. E. Andes. 2te Auf. Wien, 1895. (Hartleben.)

Couleurs et Vernis. G. Halphen, Paris, 1895.

Die Harze und ihre Producte. G. Thenius, Wien, 1895. (Hartleben.)

Gummi arabicum u. dessen Surrogate in festem u. flüssigem Zustande. L. E. Andes, Wien, 1896. (Hartleben.)

Die Aetherischen Oele. Gildemeister und Hoffmann, Berlin, 1899.

The Chemistry of Essential Oils and Artificial Perfumes. E. J. Parry, New York, 1900.

STARCH, DEXTRIN, AND GLUCOSE

Starch is widely and abundantly distributed in the vegetable kingdom, occurring in nearly all plants in a greater or less quantity. It forms rounded grains of characteristic appearance in the several varieties, and is most abundant in the fruit, tubers, seeds, and stems of the plants from which it is industrially obtained. It is a typical carbohydrate, and on analysis corresponds to the formula $C_6H_{10}O_5$; but it is probable that the true symbol is some multiple of this, and that the formula should be written $(C_6H_{10}O_5)_n$, where n is 4 or more. Starch has not yet been prepared synthetically, and even its formation in plants is not fully understood; but it appears that the chlorophyl (the green coloring matter in plants) enters into the reaction in some way, perhaps as a "contact" substance. The carbon dioxide of the air is reduced by the joint action of the chlorophyl and sunlight, the carbon being assimilated, and part of the oxygen, at least, being set free. The formation of starch might be represented thus: —

$$6\ CO_2 + 5\ H_2O = C_6H_{10}O_5 + 6\ O_2.$$

It is, however, probably not formed directly, but may be an alteration product of the sugar which is so formed. As hypothetical reactions, the following will serve to show the outline of the process, but it is by no means certain that these truly represent the exact changes which occur: —

$$6\ CO_2 + 6\ H_2O = C_6H_{12}O_6 + 6\ O_2.$$
$$C_6H_{12}O_6 = C_6H_{10}O_5 + H_2O.$$

It appears somewhat improbable that substances of such high molecular weight as glucose, $C_6H_{12}O_6$, or starch, should be formed directly from the reduction of carbon dioxide. According to Baeyer,* it is more probable that formaldehyde, CH_2O, is first produced, and then by a polymerization process, the glucose is formed, from which starch is derived: —

$$6\ CO_2 + 6\ H_2O = 6\ CH_2O + 6\ O_2.$$
$$6\ CH_2O = C_6H_{12}O_6.$$

The starch is formed in the leaves and green parts of the plant, being then transported in soluble form to the other parts, where it is

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* Berichte der deutschen chemischen Gesellschaft, **3**, 67.

at once applied to the building up of the tissues, or is deposited as reserve material for the future nourishment of the plant, or of a new individual; the greatest deposits are generally found in the roots, tubers, or seeds.

As seen under the microscope, a starch granule is made up of different layers, arranged around a nucleus, a dark interior portion, generally at one side of the granule. Each granule consists of an interior substance called "granulose," and an exterior transparent covering, inert and insoluble, and resembling cellulose in structure. But recent investigations tend to prove that the "starch cellulose" is not present as such in the granule, but is formed from the starch substance by the action of acids or by fermentation.

Starch is entirely insoluble in cold water, but when heated to 70° or 80° C., the granules swell and finally burst, and the starch substance, "granulose," combines with the water to form *paste*. When this is boiled in an excess of water, it goes into solution and may be filtered. The solution yields an intense blue color with iodine, hence its use as an "indicator"; it is optically active and rotates the plane of polarization to the left.

By exposing starch to the action of cold dilute mineral acid for several days, it is converted into a soluble modification called **amylodextrin**, which dissolves in warm water without forming a paste. When heated dry to 200° C., starch is converted into dextrine or British gum.

The chief industrial sources of starch are potatoes, wheat, corn, rice, arrowroot, and certain varieties of palm trees (sago). In Europe, potatoes, rice, and wheat are used, while in this country corn and wheat are mainly employed. The separation of the starch, which is mixed with various nitrogenous and fatty matters and some mineral impurities, is essentially a mechanical process; but much care is needed to prevent changes which would spoil the product.

Corn starch * is usually made by the alkaline or "sweet" process; sometimes by an acid or fermentation method similar to that employed for wheat starch. In the **alkaline process** the grain is run through a fanning mill to blow away dust, husks, etc., and is then steeped in water at from 70° to 140° F. for from three to ten days, when the softened grains are crushed between rolls. This steeping removes much of the oil and swells the gluten and albuminous matter so that it is readily attacked by the alkali. After a time putrefactive fermentation sets in and hydrogen sulphide is evolved. Since this

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* J. Soc. Chem. Ind., **1887**, 80. **1902**, 4. Geo. Archbold.

causes a nuisance, the method has been replaced in some factories by the **Durgen system**, in which a continuous stream of water at 130° to 140° F. flows slowly through the steeping tanks. After three days the grain is soft, while a large quantity of extractive matter has been washed away. The grain is then ground in buhrstone and roller mills through which water is flowing; the starchy magma goes to revolving sieves of brass wire for the coarser straining, and then to cylindrical reels covered with bolting cloth. The mass which passes over the sieves is reground and again sifted. The waste glutinous matter is pressed and dried for cattle feeding, or is sold wet as "swill" for hogs.

The milky liquor from the sieves is settled and drawn off from the crude starch, which is washed twice with fresh water and then pumped into vats having good stirring apparatus, and provided with holes in the sides, closed by plugs and used for decanting the liquor. A dilute caustic soda solution of 7° or 8° Bé. is stirred into the starch until the liquid becomes greenish yellow; then the whole is stirred for several hours. When a test shows that the suspended matter settles in two layers, the starch on top, sedimentation is allowed to take place and the supernatant liquor, containing much oil and nitrogenous matter in solution, is drawn off. The sediment is stirred up with water, allowed to stand until the gluten has deposited, and then, by pulling the plugs in succession, the starch in suspension is "siphoned off" into tanks. By several repetitions of this process the starch is nearly all removed from the gluten and at the same time is separated into several grades. The residue then flows on to a long, slightly inclined table, or "run," from 60 to 120 feet long and having a fall of 3 or 4 inches. A stream of water flows slowly over it and washes away the gluten and fibrous matter, while the starch deposits on the table.

The starch collected in the several tanks is washed with water and sometimes again siphoned, and is then run through bolting cloth to the settling tanks, where it deposits in a dense compact layer from which the water can be drawn off. The wet starch is then shovelled into frames lined with cloth and having perforated bottoms, through which the water drains. The cake of damp starch is cut into smaller blocks and placed on porous floors of plaster of Paris or brick, which absorb the adhering water.* The starch is removed to the dry room and kept at a temperature of 125° F. for several

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* These floors may be subsequently dried by passing hot air through flues arranged in them.

days. While it is drying, the impurities still remaining in it find their way to the surface, where they form a yellowish deposit which is cut away when the starch is nearly dry. The block is then wrapped in paper and further dried at 150° to 170° F. for several days. During this time the mass contracts and cracks into a number of irregularly shaped prismatic rods, called " crystals," though they are not true crystals. The entire drying process requires several weeks, and the product as sent to market contains about 10 to 12 per cent of water.

An improved process is now used as follows: The shelled corn is screened to remove dirt, husks, etc.; it then passes magnets to remove nails or bits of iron, and then goes into wooden " steep-tanks " of 1000 to 1500 bushels capacity. Each tank has a false bottom, and a circulation pipe on the outside, passing from the false bottom to near the top of the tank. Steam can be injected into the pipe to maintain the circulation and keep the steep water at about 60° C. Steeping continues 24 hours or more, and the steep liquor contains about 0.3 per cent sulphurous acid to prevent fermentation. The liquor is drawn off and the softened grain crushed in " cracker " mills to loosen the germs. These mills are large disks, set face to face, having projecting teeth and rotating in opposite directions.

The coarse meal passes to " separators," long, narrow tanks, containing a starch milk of 10° to 12° Bé., calcium chloride being sometimes dissolved in the liquor to increase its density. The germs, being light, float over the dam at the end of the tank, while the hulls and starchy portions sink, and pass out by an opening at the bottom of the tank. The germs pass over copper screens or " shakers," where they are sprinkled with water to free them from adhering starch; the starch milk thus obtained is returned to the separator.

The germs are pressed to remove water, dried, and ground fine; the meal is heated and heavily pressed in a hydraulic press (p. 353) to obtain the corn oil; the oil cake is sold for cattle food.

The hulls and starchy matter from the separators are ground fine in buhrstone mills and passed over copper "shakers," some of the starch milk going back to the separators, and the rest passing to shakers covered with silk bolting cloth; the chaff and husks are reground and passed through a slop machine to remove the last portion of starch.

The starch liquors, containing gluten and other substances, are agitated in a mixing tank with dilute caustic soda solution; this dissolves some of the gluten, swells the remainder, neutralizes the acid, and coagulates the fine suspended impurities. The magma then goes to the " runs," or " table," where the starch deposits, the lighter gluten being washed into a settling tank, from which it is pumped into a filter-press to remove the water. The gluten is then dried and sold as such, or is pulverized and mixed with the bran and husks from the slop machine. The steep water from the softening of the grain carries considerable soluble matter and is evaporated to about 30° Bé., and mixed with the bran and husks before drying.

The "green starch" from the tables is usually mixed with water and again passed over the tables, when dry starch is to be made.

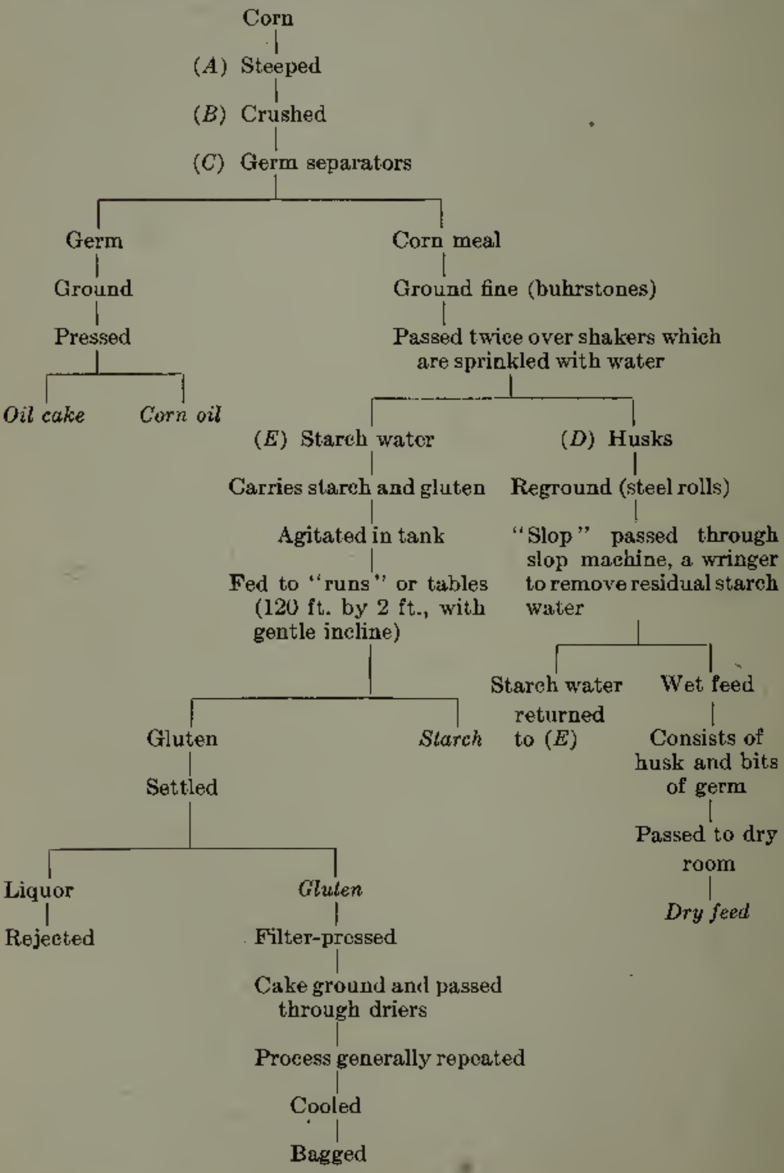
Centrifugal machines are sometimes used for separating the starch from the wash water. These machines are of two kinds, those having a perforated basket, and those in which the basket is of unperforated sheet metal. In the latter, the starch is thrown against the cylinder wall and packed so firmly that it remains as a thick layer, while the water collects in the middle of the drum and can be drawn off very completely, carrying with it much of the glutinous and fibrous matter. In a perforated drum the water passes through, leaving the solid matter behind. The starch, being heavier than the cellulose, forms a layer directly on the basket walls, while inside of this is a layer of gray starch containing the impurities; this latter is scraped off and washed again. The starchy liquid running into the basket must not be too thick, otherwise the load does not distribute itself evenly in the basket.

Corn contains about 54 per cent of starch, and the actual yield obtained in technical work is about 50 per cent, or 28 pounds of starch from a bushel (56 pounds) of corn. About 13 pounds of gluten suitable for cattle food is also recovered per bushel of corn.

The best grade of corn starch is largely consumed for food, but its principal use is in laundry work. Lower grades are chiefly employed in manufacturing and in textile industries. In some technical operations the so-called "**green starch**" is used. This is the product obtained directly from the inclined table, settling tanks, or centrifugal machine after a partial drying. It contains some impurities and is generally damp, often containing 40 per cent of water. It is mainly employed for glucose making, for stiffening and size, in color mixing for calico printing, and in the manufacture of paper boxes.

The old fermentation processes of starch extraction destroy the gluten and cause incipient hydrolysis of the product; the paste made from such starch is more limpid than that of starch made by newer methods in which these changes do not occur. In modern work, to obtain this quality of "thin boiling" paste, the starch, after separation from the gluten, is given a mild treatment with mineral acid at temperatures of 26° to 40° C. Thin boiling starch is preferred for textile work because of the greater fluidity and better penetration of the paste into the fabric.

OUTLINE OF THE PROCESS FOR CORN STARCH



Wheat starch is made by the fermentation or "sour" process, or by Martin's process without fermentation.

By the **sour process**, all the gluten, of which wheat contains a large amount, is destroyed, consequently there is considerable loss. The grain is soaked in water until soft, and then crushed between rolls or pressed in bags. The starch is washed out of the crushed pulp with water, and the milky liquid is run into tanks and allowed to ferment. In order to hasten this, some of the sour liquor from a previous fermentation is added. The temperature is kept at about 20° C., and the contents of the cistern well stirred frequently. The fermentation lasts from 10 to 14 days; the sugar, albumin, and gummy matters of the wheat undergo an alcoholic fermentation, followed by the development of acetic, lactic, and butyric acids. These acids then attack the gluten, dissolving it in part, and destroy its tough and sticky properties, so that it is easily washed free from the starch. The washing is done in revolving sieves, in which the swollen gluten, cellulose, etc., remain. The starch is repeatedly washed and sieved, or levigated, until sufficiently pure and white, when it is dried as already described under corn starch; but more care is necessary, because of the tendency of the mass to cake together, owing to the presence of a trace of gluten. The process must be carefully watched lest the fermentation go too far and putrefaction set in, thus causing a loss of starch. The acid waste liquors are difficult to dispose of, and cause considerable nuisance in the neighborhood. Usually about 59 pounds of starch and 11 pounds of bran are obtained from 100 pounds of wheat. But only a small quantity of sour gluten is recovered.

By **Martin's process** part of the nitrogenous matter (gluten) is recovered. Ordinary wheat flour from which the bran has been removed is used instead of the whole grain. The flour is kneaded with 40 per cent of water to form a stiff dough, which is then washed in small portions at a time in a fine sieve, while small jets of water continually play upon the mass, carrying away the starch. By treating the partly washed starch with a solution of caustic soda (sp. gr. 1.013) and allowing it to stand a few hours, the remaining gluten is swollen and may be removed by sieving on bolting cloth. The pasty mass of gluten left in the sieves is utilized in the manufacture of macaroni, noodles, and gluten bread, but more especially for paste and for cement for leather, and as a thickening material instead of casein or albumin in textile working.

Fesca's modification of Martin's process consists in stirring wheat flour into water to form a thin " milk," which is then run into centrifugal machines. The starch, being heavier than the gluten, collects next the revolving sieve. The interior layer, consisting of a mixture of starch and gluten, is removed, washed with water, and again " centriffed." But much starch remains in the gluten.

The yield by Martin's method is about 55 pounds of starch and 12 pounds of gluten from 100 pounds of wheat. By Fesca's process, only 40 to 45 pounds of starch are obtained from 100 pounds of wheat.

Potato starch is most important in Europe. The tubers contain an average of about 20 per cent of starch and 75 per cent water. The skin contains some fats and coloring matter, but no starch. The adhering dirt and sand are carefully removed by washing in a revolving drum made of wood or iron slats with narrow openings between them for the escape of the dirt, etc. Inside the drum are revolving arms which rub the potatoes together, or revolving wire or bristle brushes which scrub them as the drum turns. The washing must be thorough or the quality of the starch suffers. The tubers are next rasped or ground in a machine consisting of a revolving cylinder or roll, around whose outer surface are set a large number of narrow knife-edges or saw-blades, which project about one-fifth of an inch. These knife-edges rotate very close to fixed wooden bars which catch and hold the potato while it is scraped into soft pulp.

The starch in the potato is enclosed in little cells or bags of cellulose, a number of granules being in each cell. Since the starch can only be washed away from the ruptured cells, the finer the pulp the larger the yield of starch. But even with the best raspers many cells escape unbroken, and usually about 15 per cent of the starch is lost. Sometimes the pulp is reground after it has been washed, which increases the yield of starch slightly.

The pulp, consisting of starch and cellulose fibre and tissue, passes into a series of shaking sieves, where the starch is washed away with a limited amount of water. A better apparatus consists of a series of revolving wire gauze cylinders (30 to 35 meshes to the inch), containing brushes which revolve in a direction opposite to the motion of the cylinder. Fine jets of water play upon the pulp and wash out the starch. The milky liquor passes to a revolving sieve with 50 meshes per inch, which retains any fibre that passes through the coarser screens. Long semicylindrical sieves containing brushes set in the form of an Archimedian screw around a revolving shaft are sometimes used. The brushes push the pulp along from one end to the other, at the same time thoroughly working it over, while the starch is washed out by jets of water. The waste pulp passing over the sieves is treated by **Büttner and Meyer's process**; it is pressed and dried rapidly until the moisture is about 12 per cent. It is sold as a low-grade cattle food.

The starch suspended in the wash water is run over inclined tables similar to those already described. The crude product is stirred up with water in a tank, and after the sand and heavy dirt have settled, the starch in suspension is rapidly "siphoned" off through holes in the side of the tank. By levigation, the starch is obtained in several grades of purity. Centrifugal machines are also employed to separate the starch and wash water, but with less success than in the case of corn, wheat, or rice starch.

The crude starch obtained by any of these methods is purified by repeated washings and levigation, with an occasional passing through sieves or bolting cloth to remove fibre. The purified starch is dried in much the same way as is corn starch.

Potato starch is also made by the "**rotting**" **process**, in which the moist, sliced material is heaped in a warm room. Fermentation and ultimate decomposition of the cell walls takes place, so that the starch can be washed out of the pulp. Much care is necessary that the fermentation does not attack the starch itself. The mass must be turned over frequently during decomposition.

The wash waters from potato starch contain much potash, phosphoric acid, albumin, and nitrogenous matter, which soon ferment and become very offensive. If possible, they should be used at once to irrigate land. Much ingenuity has been expended to devise means of making them less offensive, but without much success.

The yield from 100 pounds of potatoes is about 15 or 16 pounds of dry starch. The product is chiefly used in the textile industries, for laundry purposes, and in glucose and dextrine making; for the two last mentioned it is customary to use the "green starch," containing from 30 to 40 per cent water.

Rice starch* is chiefly produced in Europe, only the broken grains separated with the husks in the cleansing mills being used. Rice contains nearly 80 per cent of starch, but its separation is difficult, since the cells of the grain are composed of dense glutinous material and the starch granules are cemented together solidly by albuminous and gummy matter. In order to soften the gluten, the rice is macerated in dilute caustic soda (sp. gr. 1.007) containing

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* J. Berger, Chem. Zeitung, **14**, 1440 and 1571; **15**, 843.

about 0.5 per cent caustic. After soaking about 18 hours with frequent stirring, the liquor is drawn off and a fresh caustic solution is added. When the grain is soft, it is crushed in mills while a stream of dilute caustic plays over the mass, dissolving a part of the glutinous matter, and swelling the remainder so that it, together with the fibrous matter, may be removed by sieving. The starch is then separated from the liquor by centrifugal machines, and further purified by washing it with water, running it through centrifugal machines or settling tanks, and finally filter-pressing and drying in much the same way as for corn starch. The yield is about 85 per cent of the total starch in the rice. The fibrous matter and gluten passing over the sieves are used as cattle food, or if carefully dried and pulverized, are sometimes sold as "rice meal." The caustic solutions contain gluten which is precipitated by acidifying them. Much care is necessary to prevent any fermentation of the liquors or of the wet starch, if the drying be too slow. In order to correct the slight yellow tinge, due to traces of impurity in the starch, a little ultramarine is generally added in the settling tanks or centrifugals. Prussian blue or alkali blues which are not fast against alkali should not be used.

Sago is a starch prepared from the pith of several varieties of palm trees (genera *Metroxylon, Arenga,* and *Borassus*), indigenous in the East Indies. The trees are cut down and the pith, sometimes amounting to 700 pounds from one tree, is removed from the trunks. It is a mixture of starch and woody fibre and is pounded fine in wooden mortars; the starch is washed out with water and purified by sieving and washing as in other cases. This furnishes the **sago flour** of commerce. **Pearl sago** is made by kneading the sago flour to a dough with water, and then working the dough through a sieve into a hot pan, greased with oil, and kept shaking constantly; a portion of the starch is converted into paste by the heat, and coats the outside of the granules, which then stick together and form little translucent globules. Imitation sago is now made from potato or other starch. Sago is chiefly used as food and swells in hot water without destroying the globular form.

Arrowroot * starch is obtained from the roots of several varieties of plants belonging to the genus *Maranta.* The long, slender roots are soaked in water until the coarse outer skin softens, when it is stripped off. After washing, the roots are rasped to a pulp, from which the starch is washed with water, sieved, and settled to remove fibrous matter and soluble impurities. Owing to the large amount

* J. Soc. Chem. Ind., **1887**, 334.

of fibre present, fine grinding is difficult, and considerable starch is lost in the waste pulp. Also, there is much trouble in sieving; hand sieves are used, since mechanical ones soon become choked by the fibres. The starch is dried in the open air on wire screens until no more than 14 to 17 per cent of water remains. The drying house is a light shed, open on all sides for the free circulation of air. In damp weather much care is necessary to keep the wet starch from souring, especially if any impurity is present. Arrowroot starch is much used for food, but is also desirable for laundry and sizing purposes. It forms a stiffer jelly than do most other starches.

Cassava starch is similar to arrowroot and is obtained from the roots of several species of *Manihot,* which are indigenous in Brazil, but which are now cultivated in other tropical countries. The starch is also called Brazilian arrowroot and is prepared similarly to the true arrowroot. By heating the damp starch in shallow pans while stirring actively, the granules burst and adhere together, forming the mass into small, irregularly shaped translucent kernels, known as **tapioca**. This is somewhat soluble in cold water, and is very easily swelled by boiling water to form a transparent jelly.

There are several other starches similar to sago and cassava which are used as food, the most important of these being **curcuma, tous-les-mois,** and **arum.** Some starch is prepared from the nuts of the horse-chestnut tree, *Æsculus Hippocastanum,* L., which contains about 25 per cent of starch. But since it is nearly impossible to remove the bitter principles, the starch is only used for stiffening and sizing purposes.

The chief uses of starch are: for stiffening purposes in laundry work and finishing cotton cloth — rice starch is best for this and the addition of a little paraffine or stearin increases the gloss; for thickening material in calico printing; as paste for adhesive purposes — for which wheat starch is best; in sizing paper; for glucose making, in which corn or potato starch is generally used; as a food; and as a toilet powder, for which rice starch is generally preferred.

Starch is readily detected by the microscope or by use of a solution of iodine. There are several methods for determining the amount of starch in a given substance, but nearly all of them depend upon the direct isolation of the starch, or its conversion into sugar, which is then determined by means of Fehling's solution.

DEXTRIN

Dextrin corresponds to the formula $(C_{12}H_{20}O_{10})_n \cdot H_2O$ and is sometimes considered an intermediate product between starch and dextrose. The commercial product, called **dextrine**, or **British gum**, is made by heating dry starch to a temperature of 200° to 250° C. in a revolving iron cylinder over free flame, or in an oil bath, or by a steam jacket; or the starch may be moistened with nitric or hydrochloric acid, dried at 50° C. and then heated to 140° to 170° C.; this gives a lighter colored product, but since it contains some sugar, its adhesive power is less than if made without acid. After roasting, the dextrine is cooled quickly to stop the conversion, and is powdered in a mill and sieved on bolting cloth. The product is an indefinite mixture of several dextrins with unchanged starch. The dextrins are soluble in cold water and form a thick, viscous syrup which has strong adhesive properties and is therefore much used as a substitute for gum arabic in preparing mucilage and for thickening colors in calico printing.

By acting upon starch paste with diastase, a syrupy liquid containing dextrin and sugar (maltose) is obtained; starch is mixed with water at 50° C., and then heated to 65° C., when the necessary amount of malt (carrying the diastase) is added, and the temperature raised to 73° C., until iodine gives a reddish violet, instead of a blue color. The solution is then boiled to destroy any remaining diastase, cooled, filtered, and concentrated *in vacuo* to the desired density. It is established that there are several dextrins produced simultaneously with the formation of the sugar by this action. Dextrin syrups are used in brewing, for thickening tanning extracts, and in confectionery.

The products obtained by these various methods vary somewhat in their properties, and have been assigned distinguishing names, — erythrodextrin, achrodextrin, and maltodextrin. They are all soluble in water, insoluble in alcohol, strongly dextro-rotary, and yield dextrose by hydrolysis. Erythrodextrin yields a red color with iodine, while the others yield no color.

GLUCOSE

Under the name " glucose " are grouped not only substances derived from starch by hydrolysis, such as dextrose, maltose, dextrins, etc., but also those resulting from the inversion of sugar, such as levulose.

Dextrose, $C_6H_{12}O_6$, and the isomeric **levulose** occur in the juice of many fruits, such as grapes, cherries, bananas, pears, etc., but in quantities varying in the same fruit, according to the season and the degree of ripeness. But these sugars are seldom made from fruit juice; dextrose being more easily obtained from starch. Dextrose is sometimes sold as "fruit sugar," "grape sugar," or starch sugar. Levulose is prepared by artificial inversion of cane sugar with mineral acids or invertase.

Common **honey** is a mixture of dextrose, levulose, sucrose, water, and small quantities of non-saccharine matter; the levulose is probably formed within the body of the bee, by the action of some enzyme, which inverts the sucrose in the nectar gathered from flowers by the insect.

Dextrose is less soluble in water than is cane sugar, but does not crystallize readily from solution. When crystallized at moderate temperatures, it contains one molecule of crystal water; but from hot water or from alcohol it separates in the anhydrous state. It is a little more than half as sweet as sugar, and yields an anhydride, $C_6H_{10}O_5$ (glycosan), which is tasteless. Dextrose rotates the plane of polarization to the right 52.5°. It is readily fermentable, and reduces alkaline copper solutions (Fehling's solution). It occurs in nature in combination with other organic substances, forming the "glucosides."

Levulose is very soluble in water, but crystallizes from alcohol without crystal water. It rotates the plane of polarization of the light ray very strongly to the left (about $-92°$), but the rotation is variable with the concentration and temperature. It also reduces alkaline copper solution. It has a very sweet taste, and is easily fermented by yeast.

Maltose, see p. 449.

Commercial glucose is always prepared from starch as the cheapest and most convenient raw material. By boiling starch paste with mineral acids, it is converted into dextrin, maltose, and dextrose, the amount of the last depending upon the time of the boiling. The acid does not appear to enter into the reaction, but merely assists the combination between the starch and water, by which the glucose is formed. This is a process of "hydrolysis." It might be represented by an equation: —

$$(C_6H_{10}O_5)_n + nH_2O = n(C_6H_{12}O_6),$$

but this does not represent the changes which actually occur, for a number of intermediate products are formed; of these, the dextrin is never entirely converted into sugar, some remaining unchanged in the commercial glucose. The yield of dextrose is seldom more than 85 or 90 per cent of the theoretical, as calculated from the above equation. The best conversion is obtained with hydrochloric acid, which is generally used in this country, but in Germany sulphuric acid is used, as it is more readily separated from the product. In Europe potato, rice, and sago starch are chiefly used for glucose making, but in this country corn starch is exclusively employed. It is used "green," and is prepared on the premises. The corn is steeped from 3 to 5 days in water at 150° F., with the addition of 250 gallons of sodium bisulphité liquor of 8° Bé. to each 2000 bushels of corn; the starch is then prepared as described on p. 404.

The process of making glucose varies slightly, according as syrup or solid grape sugar is to be the final product. For syrup, less acid is used, and the boiling is stopped as soon as a test with iodine gives a port-wine color. This may leave a large amount of dextrin in the product. For solid dextrose, the boiling is continued for a short time after alcohol * causes no precipitate to form in a test portion of the liquid.

For the conversion, the starch is stirred with water in a tub, to form a "milk" of about 20° Bé. Sometimes a part of the acid is added to this milk, and the mixture warmed to about 38° C. It is then pumped in a small stream into the boiling dilute acid (1 to 3 per cent acid) contained in the converter, the rate of inflow being so regulated that the boiling of the acid liquid is not interrupted.

The converter may be an open vat of wood, lined with lead, and provided with stirring apparatus and steam coils. But open converters are now abandoned nearly everywhere in favor of closed converters (Fig. 114). These are usually made of copper or gun metal, strong enough to withstand a pressure of 5 or 6 atmospheres. Steam at 25 to 30 pounds pressure is admitted through the perforated copper pipe (A). The starch milk is pumped in through the copper pipe (B) [the di-

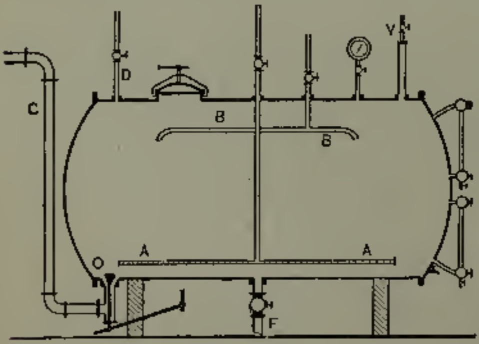

Fig. 114.

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* Starch and dextrin are precipitated by alcohol, but dextrose is not.

lute acid having been previously introduced through (D)], the air vent (V) being opened at this time, while the pressure is kept at 25 pounds. As soon as the converter is full, the air vent is closed, and the pressure is raised to 30 pounds for about 50 minutes, or until the iodine test shows that the conversion is complete. For syrup, the average time elapsing from the beginning of the starch introduction to the discharge of the converter is about 1 hour and 10 minutes, and the density of the liquid about 16° Bé.; for grape sugar, about an hour and a half is necessary, with the above pressure and amount of acid. Conversion is also carried on at pressures up to 50 pounds per square inch, with corresponding shortening of the time of heating to 10 to 15 minutes.

The liquid is now cloudy, and cannot be clarified by filtration. The valve (O) is opened, and the liquid is blown through the pipe (C) into the neutralizer. The converter is provided with a waste pipe (F) for cleaning purposes. The **neutralizer** is a tank (Fig. 115) provided with an effective stirring apparatus (A, A). Immediately after the converter liquid has been received into the neutralizer it is treated with sodium carbonate solution,* introduced through the sprinkler (B), to remove the excess of acid. It is left very slightly acid to litmus, a pinkish lilac color being about right. If made alkaline, the syrup becomes colored in the char filtration, and if too acid, it has a turbid appearance. Much of the dissolved gluten is precipitated during the neutralizing, and forms a greenish drab scum.

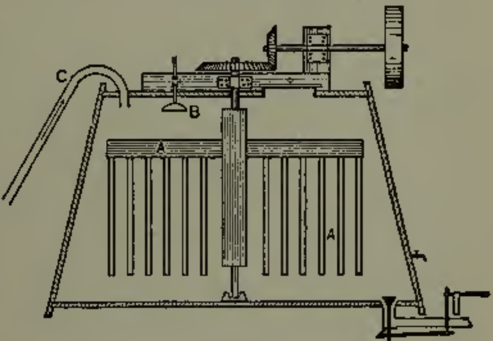

FIG. 115.

The liquid, called "**light liquor**" is run through bag filters to remove suspended impurities, and the clear, amber-colored liquid is then run through bone-char filters, displacing the "heavy liquor" for which the filters have previously been used. About 8000 gallons of "light liquor" are run through 16 tons of bone-char, which has been used to clarify about 3500 gallons of "heavy liquor." The filtrate is colorless, or faintly amber-colored, and has a slightly acid

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* In Europe powdered chalk is often used to neutralize the sulphuric acid, the precipitate of calcium sulphate being separated from the liquor by filter-pressing.

reaction. It is now concentrated in a triple-effect evaporator to a density of 27° to 28° Bé., when it forms the "**heavy liquor**" above mentioned. The bone-char in the filter is freshly calcined, dusted and "tempered" with acid, and washed with water. The wash water is removed by compressed air, and the filter is filled with the heavy liquor. After standing about an hour, the outlet pipe is opened, and the filtrate runs out in a slow stream, while more unfiltered liquid enters. The flow is secured by the hydrostatic pressure of the liquid entering the filter from a tank elevated above it. The filtrate is practically colorless, and has a very faint odor. It is concentrated in a vacuum pan to a gravity of 40° to 44° Bé. (1.375 to 1.43 sp. gr.). During this evaporation a small amount of a solution of sodium bisulphite (8° Bé.) is added to the syrup to bleach it, and to prevent any tendency to fermentation, or to become brown when heated. The syrup, composed of maltose, dextrose, and dextrin, is known in commerce as "glucose"; the name "grape sugar" is applied to the solid product obtained by carrying the conversion further. Grape sugar forms a compact mass of waxy texture, but containing no separate crystals of dextrose.

A method for the production of crystallized glucose (dextrose) has been devised by Behr, in which a concentrated glucose solution is allowed to stand at about 35° C. in contact with some crystals of pure anhydrous dextrose, until a large part of the dextrose separates as a mass of crystals. By running through a centrifugal machine, the uncrystallized syrup is thrown off, leaving the pure crystals. If glucose is dissolved in hot concentrated methyl alcohol, on standing the solution deposits crystals of pure anhydrous dextrose.

The **bone-char filters** * used for glucose are cast-iron cylinders, built up in segments. As commonly constructed (Fig. 116) one holds about 16 tons of bone-black. In the bottom is a perforated grating (A), covered with burlap, on which the char rests. Beneath this grating is the outlet pipe (B), which is carried up outside the filter to the level of the top of the char when the filter is full. By this arrangement no liquor flows from the filter until the char is entirely covered, the liquor filters slowly and with less tendency to form channels, and the char does not pack nor become clogged. On one side, near the bottom, is a manhole through which the exhausted char is removed. In the top is another manhole for introducing the char, and also an inlet pipe (C) for the liquid to be filtered, another

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* Similar filters are used for filtering sugar, oils, etc. In large sugar refineries they hold from 30 to 40 tons of bone-black.

(D) for steam, and an air vent (E). A pipe (G) serves for the introduction of compressed air, to assist in forcing the liquor or wash waters through the char when emptying the filter, and for running off the overflow of wash waters when boiling out the char. A branch (F), placed in the outlet pipe directly below the filter, permits connection with steam through (H), or with a hot-water pipe (J), to be used in washing the char; it also connects with a waste pipe (L), through which the waste liquors can be run off. The inlet pipe (C) is so arranged that it may be connected by means of a rubber hose with the pipes supplying the "light liquors" (N), "heavy liquors" (P), wash waters (S), or tempering acid (T). The outlet pipe (V) is also connected in the same way with pipes leading to the storage tanks for the filtered syrups and "sweet water." Below the lower manhole runs an endless belt which receives the spent char and conveys it to the revivifying kilns.

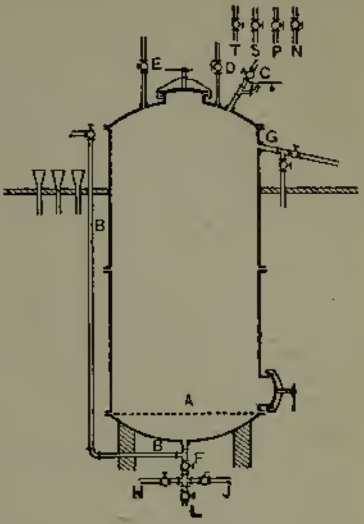

Fig. 116.

The **bone-black** is made by charring bones in retorts, and then crushing to grains about 2 or 3 mm. in diameter. When new, it has a velvety black or brownish color, and often contains traces of tar and other impurities. After it has been used a few times, the grains become rounded, and many of the impurities are washed away. The syrup first run through the filter is completely decolorized by the action of the char; but after a time its decolorizing power is impaired, and the filtrate begins to show a faint yellow color. Finally it runs so deeply colored that no advantage is gained by filtration. Then the light liquor remaining in the filter is displaced by water (usually condensed water); when the gravity of this wash water falls below 10° Bé., it is collected in a special tank as "sweet water,"* until the gravity falls to 1° or 2° Bé. Then boiling water is introduced through (F) at the bottom of the filter, and run out through (G) at the top, and then to the sewer, as long as any matter can be washed out of the char.

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* The "sweet water" is used to wash the bag filters, or it is added to the "light liquors."

The washed char is drained, and then "steamed down" by steam from (D) to displace the wash waters. It is then shovelled out through the lower manhole on to the conveyer, and carried to the kilns where it is **revivified**, *i.e.* its decolorizing power is restored by destroying the adsorbed coloring matter and organic impurities by ignition to carbon. It is dried by passing over tubes heated by waste gases from the furnace. The dry char passes automatically into narrow vertical retorts of cast-iron kept at a full red heat. The lower ends of these retorts project below the furnace, and end in sheet-iron tubes into which the hot char passes, and is cooled before it is exposed to the air. At the bottom of each tube is a valve which automatically discharges a certain quantity of the char at regular intervals on to a belt conveyer running below the kiln, and which carries the revivified char to revolving reels, where it is sieved to remove the fine particles before returning it to the filter. The fine char ("spent black") falling through the sieve is of no further use, and is sold to the fertilizer maker. In order to replace this constant waste as fine dust, about 200 pounds of new char are run into the filter with each charge. Much new char at a time is undesirable, since the tarry matters in it tend to color the syrup. After revivifying, the char is boiled one-half an hour in the filter with hydrochloric acid; then it is drained through (F), and the acid washed away with condensed water. The char is now ready for use. The life of the char in glucose making is about 3 months of continuous service, and during that time it is revivified about once in every 3 or 4 days.

Glucose is not so freely soluble in cold water as is cane sugar, nor is it so sweet. When the glucose is to be used for syrup, some manufacturers have tried to increase its sweetening power by adding a small quantity of **saccharine**, an intensely sweet organic substance. But this is probably not practised to any great extent.

Considerable discussion relative to the healthfulness of glucose as a food has been aroused at times; but when properly made, it is improbable that it is in any way injurious to health.

Dextrose belongs to that class of sugars which are capable of fermentation, with the formation of alcohol, water, and carbon dioxide. Because of this, glucose is often added to wine and beer wort before fermenting, in order to increase the percentage of alcohol in the beverage. In alkaline solution, glucose has a very strong reducing action, and finds some use in the arts for this purpose; *i.e.* for the reduction of indigo to the soluble form known as "indigo white," in the dye vat. It is also extensively used in the manufacture of confectionery, jellies, preserves, medicines, and table syrups. Being a thick, heavy liquid, glucose syrup is much used as a thickening agent in many industries and to give body to many extracts and decoctions in pharmacy. Since it is a neutral substance, odorless and colorless, it is a favorite adulterant for thick liquids, such as extracts of logwood, tannins, and natural dyewoods.

Sugars can be made from cellulose $(C_6H_{10}O_5)_n$, the conversion being effected in about the same way as when starch is used; but it is more difficult and less complete with dilute acid (see Classen's process p. 461).

REFERENCES

Die Chemie der Kohlenhydrate. R. Sachsse, Leipzig, 1877.
Die Stärkefabrikation. F. Stohmann, Berlin, 1879.
Starch, Glucose, and Dextrin. Frankel and Hutter, Philadelphia, 1881.
Report on Glucose by the National Academy of Sciences to Commissioner of Internal Revenue. Washington, 1884. (Government Printing Office.)
Die Stärkefabrikation, Dextrin- und Traubenzucker-fabrikation. L. von Wagner. 2te Auf. Braunschweig, 1886. (Vieweg.)
Die Fabrikation der Stärke, des Dextrins. K. Birnbaum, Braunschweig, 1887.
Handbuch der Kohlenhydrate. B. Tollens, Breslau, 1888.
Manual of Sugar Chemistry. J. H. Tucker. 3d ed. New York, 1890.
Fabrication de la Fecule et de L'Amidon. J. Fritsch, Paris, 1892 (?).
Die Stärke-Fabrikation. B. von Posanner, Wien, 1894. (Hartleben.)
Die Stärke-Fabrikation u. die Fabrikation des Traubenzuckers. F. Rehwald. 3te Auf. Wien, 1895. (Hartleben.)
Zucker- und Stärke-fabrikation. Otto.
Essai des Farines. Cauvert.
Die Fabrikation der Kartoffelstärke. O. Saare, Berlin, 1897. (Springer.)
J. Soc. Chem. Ind., **1909** (28), 343. T. B. Wagner.

CANE SUGAR

Sucrose or **cane sugar**, $C_{12}H_{22}O_{11}$, is found in many plants, but usually in association with other substances which render its extraction difficult and unprofitable. The presence of dextrin, glucose, " invert sugars " (dextrose and levulose), and dissolved mineral salts in any considerable quantity prevents the crystallization of much of the sucrose. The commercially important sources of sugar are sugar cane, *Saccharum officinarum*, L., sugar beet, *Beta vulgaris*, L., sugar maple, *Acer saccharium*, Wang., and the date palm, *Phœnix dactylifera.* The sorghum plant, *Sorghum vulgare*, Pers., contains considerable sugar, and although much experimenting has been done, owing to its varying content of sugar and its large percentage of gums and dextrin, it does not afford a satisfactorily crystallized product. **Maple sugar** is only of special value for its peculiar flavor as a crude sugar. If refined, it loses this characteristic taste and is not distinguishable from ordinary cane sugar. **Date palm sugar** is produced in India as a low-grade crude sugar; it is known as " jaggary " and is shipped for refining.

The popular term " sugar " was originally used to include all substances having a sweet taste; hence the names, cane sugar, fruit sugar, sugar of lead, etc. But now the name is restricted to sucrose as obtained from cane or beets. The chemical term " sugar " includes a large class of bodies belonging to the carbohydrates. Sucrose is a crystallized body, soluble in one-half its weight of cold water, and in much less hot water. Its specific gravity is 1.593. It forms salts called sucrates, with certain metallic bases, such as potassium, calcium, barium, and strontium, and on this fact depends the use of lime, baryta, and strontia for recovering sugar from molasses. The sucrose derived from the various sources is identical in all cases, though the raw sugars differ somewhat in flavor and color, owing to the nature of the impurities they contain.

The sugar cane and sugar beet supply nearly all the sucrose of commerce. The former grows only in those climates which are warm and moist, with intervals of hot, dry weather; the most of the supply comes from the West Indies, the Philippines, Java, the Sandwich Islands, Brazil, and Louisiana. Sugar beets thrive best in a temperate climate and are extensively raised in Germany and France. Extensive experiments in raising them have been made in this country, and there seems to be no obstacle in the way of climate or soil to their cultivation; in Colorado, California, Michigan, and other states sugar beets are raised, but the growth of the industry is slow.

In the growing plant, the only sugar present is glucose, the sucrose not being secreted until the plant reaches maturity. Analysis of the ripe cane gives the following average: —

Sugar	18.%
Fibre	9.5
Water	71.

Analysis of the ripe cane juice shows: —

Water	80.%
Sucrose	18.
Glucose	0.30
Gums (Albuminoids)	1.40
Mineral Salts	0.30

But, owing to the imperfect extraction of the juice, and to losses during its evaporation and clarification, the actual yield of sugar is much less than the analysis would indicate. Usually from 16 to 20 per cent of the juice is left in the "*bagasse*," *i.e.* the waste cane pulp.

The preparation of **raw sugar** from sugar cane may be considered under four heads: (*a*) extraction of the juice; (*b*) clarification; (*c*) evaporation; and (*d*) separation of the crystals.

(*a*) **Extraction.** — The cane is stripped of its leaves in the field and taken to the mill, where it is crushed and as much as possible of the juice is expressed. This must be done soon after cutting, or fermentation begins and much sugar is lost. The mills (Fig. 117) consist of two or three horizontal rolls from 30 to 60 inches in diameter, so set that their axes are parallel, and either at the vertices of an isosceles triangle (as in the figure), or in the same perpendicular. The rolls are set in adjustable bearings. When there are three rolls, the cane passes between the top roll (T) and first bottom roll (B), and then between the top and the second bottom roll (D), which are set closer together, so that it is crushed twice. It is usually passed through two or three mills, and about 60 or 70

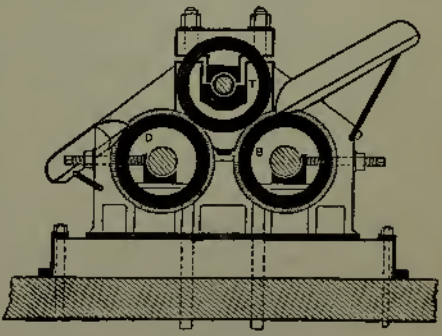


Fig. 117.

per cent of the juice extracted. It is customary in Louisiana to use shredder machines. These consist of toothed wheels, revolving at different speeds, which cut and break the cane into a soft, pulpy mass before it goes to the mills. This increases the yield of juice to a little over 75 per cent of the total content of the canes. The crushed cane, coming from the extraction mills, is generally macerated in about 10 or 12 per cent of cold or hot water, to which a little milk of lime has been added, and is then again passed through the mill. This gives an additional increase of 2 or 3 per cent in the yield of juice. The expressed juice is caught in a trough under the mill and is run off; the *bagasse* or " trash " is burned under the boilers. The furnace must be large and a forced draught is used to keep them white hot.

Diffusion methods for extracting cane juice, similar to those used for sugar beets (p. 425), but at a temperature of 90° C., have been tried, but, excepting on a few plantations in Louisiana, with no great success, since the refuse needs much handling and drying before it can be burned, and an abundant supply of water is necessary.

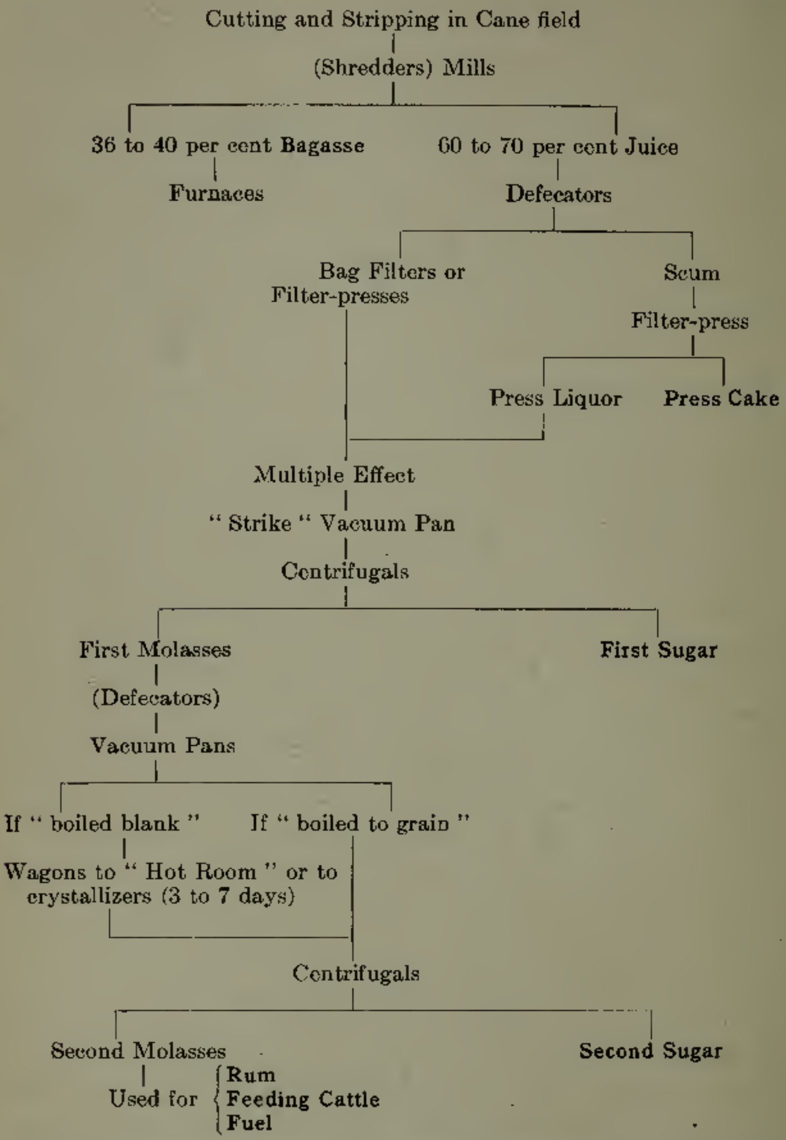
(*b*) The bits of cane floating in the juice when it comes from the mills are removed by straining through wire screens. The juice also contains organic acids, nitrogenous bodies, and invert sugar in solution, which are very susceptible to fermentation. To remove these, the juice is **defecated**. It is passed through a heater, placed in the vapor pipe of the vacuum pan, and then into the defecator tanks, which are heated by a steam coil. Here milk of lime is added in such proportions that the acids are almost neutralized and the juice left very slightly acid to litmus. The lime, aided by the heat, coagulates the albumin and precipitates lime salts of organic acids, which serve to adsorb the gums, but very little of the color. The liquid is rapidly heated to boiling, which causes the coagulum to rise as a scum, usually about 2 inches thick and holding all the suspended impurities mechanically entangled in it. After standing one-half an hour or an hour, the scum begins to crack and is skimmed off; or the juice is drawn off from beneath it. The scum is run into scum tanks, where it is mixed with more lime and with sawdust to assist in the subsequent filter-pressing by making the cake more porous. The filtrate is mixed with the juice from which the scum is decanted, and the whole is then ready for evaporation.

Calcium acid phosphate is sometimes used instead of lime for defecation, but not generally. The juice contains gummy matter and other impurities, which interfere with the crystallization of the sugar somewhat, but they cannot be removed entirely, since no cheap, non-poisonous material is known that will coagulate all the gums. Defecation is probably the most important step in sugar making, since on its successful working depends in a great measure the amount and quality of the sugar produced.

(*c*) The process of **evaporation** of the juice has been greatly improved in recent years in the larger sugar houses. By the old method it is boiled down in open pans until the mass begins to "grain," *i.e.* to crystallize, and then it is emptied into shallow tanks where it is stirred while cooling. The mixture of crystallized sugar and molasses is then filled into hogsheads; holes are bored through the ends of the casks, which are then placed on end, in a rack, for several weeks, and the molasses allowed to drain out into a receptacle underneath. The holes are then plugged and the hogshead of sugar is sent to market. The best grades of sugar made in this way are called *muscovado;* they are light brown in color and contain from 87 to 91 per cent of sucrose. This process is now but little used, and only in the less progressive countries. Probably no planter can derive any profit from muscovado sugars in the present state of the industry; there is too much invert sugar produced, together with coloring matter formed during the boiling. Low-grade sugars are produced in this way, especially the jaggary sugars. The molasses from muscovado sugar was formerly used as table syrup, and some is still so used. *Concrete sugars* are made by evaporating the juice directly to a hard mass in a special pan called a "concretor," no attempt being made to separate the crystals from the molasses. In all the more modern sugar houses, the juice is evaporated in vacuum pans. It is generally concentrated in a triple-effect apparatus, until the solution contains about 50 per cent solids, and the separation of crystals is about to begin. It is then transferred to a simple vacuum pan, called the "**strike pan**," where the evaporation is continued slowly under high vacuum; the object is to build up the crystals on the crystal points.

(*d*) When the grain has reached the desired size, the mixture of crystals and syrup, which is called "*masse-cuite*," is emptied into storage tanks, where it cools somewhat. It is then run into centrifugal machines which separate the molasses from the sugar. The latter is called the "**first sugar**" and is at once packed for market. When of good quality, these centrifugal sugars are light colored and contain 95 to 97 per cent pure sugar. Sometimes the juice is treated with sulphur dioxide in the defecators, and the sugar, which is then nearly white, is called "plantation granulated."

SYNOPSIS OF RAW SUGAR MAKING FROM SUGAR CANE



The molasses separated from the first sugar is called **first molasses** and contains 45 to 50 per cent of sucrose. It is diluted and defecated with lime or, with calcium acid phosphate, and the clarified syrup is reboiled in the vacuum pans to obtain a " second

sugar." This is slow to crystallize, and the concentrated syrup is allowed to stand from 3 to 7 days in a room kept at a temperature of 60° C., until the crystallization is complete. The mass is then "centriffed," yielding a "second" or "molasses" sugar, and "second" molasses. This sugar is of variable quality, and may be sent to market for what it will bring, or it may be dissolved in water and the syrup added to the juice going to the vacuum pan.

The second molasses contains about 40 per cent sugar, which it does not pay to recover. It is sometimes fermented for making rum or alcohol; or, since it contains a high percentage of carbonaceous matter, it is often injected into the furnace in a fine stream, where it has a certain fuel value. A small amount is used for feeding cattle. It is not suitable for use as a table syrup or for culinary purposes; but a small amount of the first molasses is used in this way.

The preparation of **raw sugar from beets** is an extensive industry in Europe. It consists in the following operation: (*a*) washing and slicing the beets; (*b*) extracting the juice; (*c*) clarifying it; (*d*) evaporating it; (*e*) separating the crystals; (*f*) treating the molasses.

(*a*) The beets are **washed** in long troughs, each containing a revolving shaft which carries pins set in the form of a screw. These push the beets along against a stream of water flowing through the trough, and by rubbing them against each other, loosens the sand and loam, which are carried away by the water. The beets are then cut into slices, from 0.5 to 1 mm. thick, by a machine containing revolving knives.

(*b*) The juice is now usually extracted from the sliced beets by the **diffusion process.** The chips are put into vertical iron cylinders, and systematically digested with water at a temperature of 80° C. The digesters are arranged in batteries of ten, and between each two is a "**juice warmer**" or "**calorisator,**" to maintain the temperature of the apparatus. These are similar in construction to the economizer of a Feldmann's apparatus (p. 152), and consist of narrow brass pipes surrounded by a steam jacket. When the chips are exhausted, they are removed, the digester refilled and made the last of the series. Fresh water is admitted to the tank containing the most nearly exhausted chips, and passes into the others in succession, finally leaving that most recently filled, as a sugar solution containing nearly as much sucrose as does the original beet sap; all but 0.5 per cent of the sugar is extracted. About 150 parts sugar solution are obtained for every

100 parts, by weight, of beets. The spent chips are rich in nitrogenous matter and are often pressed and dried for cattle food; or they are returned to the field for fertilizing.

The process of diffusion depends upon osmosis. When the vegetable cell is surrounded by water, or by a sugar solution of less density than is the sap, the sugar and other *crystallizable* substances are displaced by the water and pass through the cell walls, while the colloid bodies (gums, albuminoids, etc.) are, for the most part, retained by the membrane. Thus the juice obtained by diffusion is much purer than that obtained by other means.

Sometimes the beets are rasped to a soft pulp in machines similar to those used in making starch from potatoes. The juice is then expressed in hydraulic presses or between rolls.

In the **maceration process** the rasped pulp is systematically lixiviated with water, while in other methods centrifugal machines are used to extract the juice.

(*c*) The juice is clarified in the same way as that from sugar cane. After passing through a sieve to remove floating dirt, the juice is **defecated** with lime. As it is nearly free from invert sugar and glucose, an excess of lime may be used without injury to the sugar. If heated with glucose present, lime colors the product more or less brown or yellow. In defecating, the lime neutralizes the organic acids and in conjunction with heat coagulates albumin and mucus. Excess of lime is removed by the "**carbonation process,**" or **saturation**, in which carbon dioxide in excess is forced into the neutralized liquor; this decomposes any insoluble calcium sucrate, thus preventing loss of sugar. The carbonation is carried on in two or three stages, to avoid re-solution of the lime (as bicarbonate); the first treatment, at about 90° C., continues until the alkalinity (as calcium oxide), shown by titration, is about 0.1 per cent. After filter-pressing the liquor is again saturated at about 100° C., with the carbon dioxide, until the alkalinity is reduced to from 0.01 to 0.02 per cent.

Sulphur dioxide gas is often introduced along with the carbon dioxide, or a third saturation with sulphur dioxide alone may be used. This is always used when making white sugars. Sulphur dioxide has some decolorizing action on the juice, and seems to precipitate certain lime salts not removed by the carbon dioxide. The saturated juice is filtered again to remove precipitated matter carried down with the calcium carbonate.

After the final saturation, the clarified juice should retain very slight alkalinity, to avoid tendency to inversion of the sucrose by the heat; but too much lime causes slow formation of crystals during the evaporation in the vacuum pan.

(*d*) The **evaporation** of the clarified juice is carried on in two stages, by the use of triple effects and a strike pan, much in the same way as is that from sugar cane. The syrup may be "boiled to grain," in which case sugar crystals are formed in the strike pan; or it is "boiled blank," by which a clear, thick liquid is obtained, which deposits sugar crystals on cooling. The first method is generally employed and gives the largest yield of sugar; but a very pure syrup is required.

(*e*) The mixture of molasses and sugar is separated in centrifugal machines as described on p. 423. The raw sugar so obtained is similar to the first sugar from cane. The molasses is boiled down for a second sugar and second molasses; the latter contains 40 to 50 per cent of sucrose and large amounts of colloidal organic substances and potassium salts, which prevent crystallization of the sugar. The organic matter consists in part of nitrogenous bodies (amines?), which impart an unpleasant odor and taste, rendering the molasses unfit for table use.

(*f*) The **molasses** is nearly free from dextrose and levulose and the recovery of much of its sucrose by chemical treatment thus becomes feasible. Three methods of treatment are in use: —

The **Steffens' process**, using lime, depends on the formation of an insoluble calcium sucrate, possibly $C_{12}H_{22}O_{11} \cdot 3\ CaO$, which precipitates while the non-sugar substances remain in solution. Powdered quicklime is slowly stirred into the cold (below 15° C.), diluted molasses, until a test shows an excess has been added over the amount needed to precipitate all the sugar. The magma is filter-pressed, the press-cake washed with cold water, and then used instead of lime for defecating the fresh juice. When treated with carbon dioxide, calcium carbonate is precipitated and the sugar is left in solution.

Scheibler's strontium process, much used in Europe, depends on the formation of insoluble di-strontium sucrate ($C_{12}H_{22}O_{11} \cdot 2\ SrO$), which precipitates. A hot (70° C.) concentrated solution of strontium hydroxide, amounting to about $2\frac{1}{2}$ times the weight of the sugar in the molasses, is mixed with the hot molasses and stirred vigorously, while raising the temperature to boiling; the di-sucrate separates from the hot liquor and is rapidly filtered in bag-filters, and washed with hot strontium hydroxide solution. The crystals are dissolved in cold strontium hydroxide liquor and the solution cooled below 10° C.; after several days a large part of the strontium sucrate decomposes, separating strontium hydroxide as crystals and leaving the sugar with some strontium hydroxide in solution. The liquor, decanted from the crystals, is saturated with carbon dioxide, precipitating all the strontium as carbonate, and leaving a pure sugar solution. The strontium carbonate is calcined to the oxide and returned to the process. Similar processes employing barium hydroxide and sulphide have also been used abroad.

The **osmosis process** depends on dialysis, the mineral salts passing through parchment paper membranes more rapidly than the sugar. The apparatus resembles a filter-press, the compartments separated by parchment paper; the alternate compartments are filled with molasses and water, heated to about 90° to 100° C. The salts pass into the water and some water passes into the molasses; the two liquids, being kept in circulation through the several cells, finally flow from the apparatus as diluted and purified molasses and a solution of salts. The molasses is reboiled to crystallize part of its sugar. The water may be evaporated to recover potash salts, but often goes to waste.

SUGAR REFINING

Raw sugar derived from any source is more or less deeply colored and impure, and must be refined to yield the pure white sugar for consumption. It would seem that, on economical grounds, the refining should be done at or near the place where the sugar is produced. But at present the refineries are not in the same countries that produce the raw sugar; indeed, they exist solely to remedy the errors and careless work of the raw-sugar maker, or to circumvent unfavorable import duties levied on the refined sugar.

Sugar refining is, in theory, a simpler process than the preparation of the raw sugar, but it requires great care and attention to detail, as well as much expensive machinery. It consists in dissolving the crude material, separating the impurities, and recrystallizing the sugar. A refinery needs a frontage on navigable water and ample dock and storage sheds. An abundant water supply for condensers, or washing purposes, for melting the sugar, and for boiler use is absolutely necessary. A large refinery, capable of treating 900 tons of sugar per day, will use about 1,700,000 gallons of water daily; of this, about 1,000,000 gallons are used in the condensers of the vacuum pans. The next largest consumption is in washing the char filters.

On the ground floor of the refinery are the melting tanks, in each of which usually 16,000 pounds of sugar can be dissolved, to form a syrup of 1.25 sp. gr. and containing 55 per cent solids. If a centrifugal * or superficially colored raw sugar is to be used, it is first dumped into elevators which carry it to the washing plant. There it is mixed with a syrup and some cold water, and the thick magma passed into centrifugal machines, where the syrup, carrying most of the superficial coloring matter and some of the glucose, gums, and dirt, is thrown off. This leaves the raw sugar about 99 or 99½ per cent pure; it is then sent to the melter. The syrup goes to the melter later, and is mixed with a lower grade of sugar.

The **melter** is heated by closed steam coils, contains an efficient stirring apparatus, or mixer, and has a false bottom, to retain coarse impurities, such as straw, bits of cane, leaves, sticks, and stones. In starting the day's work, it is customary to begin with the purest sugar, *e.g.* the centrifugal, and after a certain amount of this has been dissolved and pumped away, to melt a less pure sugar, *e.g.* the muscovado; then the temperature is raised, and molasses and poor concrete sugars are put into the melter; next come the syrups from washing the raw sugar, together with various syrups from the refining process; these are followed by the various scums and "sweet waters" (wash waters) of the refining.

The melter is filled about one-third full of water at 170° F., the stirrer put in motion, and the first charge of sugar dumped in; after 15 minutes it is dissolved, and the liquor, varying in color from a light straw color to dark brown, is pumped directly to the "blow-ups."

The **blow-ups** are defecators, capable of holding one melt (16,000 pounds of sugar). They are heated by closed steam coils, and each has a perforated coil, through which air is forced to agitate the liquor. The temperature is kept at 160° F., for centrifugal sugars, but lower grades must have more heat. This defecation is intended to remove the gums, organic acids and impurities (amines, etc.), and any fine suspended dirt. The materials used are lime, alum, clay, blood, or other form of albumin, soluble phosphates, and often fine bone-char. Sugars which contain but little glucose will bear a large quantity of lime, without risk of darkening the color. Liquid blood is often used, about 4 gallons being necessary for each blow-up. The coagulated blood rises to the top as a scum, entangling the impurities, which are thus separated from the liquor. Soluble calcium phosphate (acid phosphate) is now much used instead of blood, the amount being about one-half of one per cent of the weight of the

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* Centrifugal sugars, as distinguished from concrete or muscovado sugars, are those from which the molasses has been separated by the use of centrifugal machines.

sugar. The mixture is agitated for about 20 minutes, and then exactly neutralized with lime, when a flocculent precipitate separates, carrying with it the gums and suspended matter by adsorption.

After the defecating material has been added, the temperature is raised to 212° F., and the air blast turned on for about 20 to 30 minutes. When a number of deep cracks appear in the scum, the reaction is ended, and the liquor is drawn off.

From the blow-ups the defecated liquor passes into **bag filters**, from which the filtrate must run perfectly clear, or the sugar will not be white. The bags are similar to those described on page 15. They are suspended in a closed room, about 12 by 6 by 8 feet, fitted with an open steam coil, by which the bags are heated to 180° F. before the liquor is allowed to run into them. The first runnings are muddy, and are refiltered. When it runs clear, the liquor is collected in tanks placed above the char filters. The bags finally become clogged with mud, which is very slimy, and the filtration is very slow, but is usually allowed to continue for about twenty hours. Then the bags are flushed with "sweet water," which is drawn out by a suction pipe, and returned to the defecators. The bags are then flushed with hot water, until the liquor draining from them contains only 2 per cent of solids. They are then turned inside out, in a tank of hot water, to wash off the soft mud, and are finally thoroughly washed with clean water and dried.

The mud washed from the bags contains about 20 per cent sugar and is sent to special tanks, where, after further dilution with water, lime is added until the liquor is strongly alkaline, when it is filter-pressed. The clear liquor from the filter-press is used to flush the bag filters and to mix with the melting water for raw sugar. The mud in the filter-press is washed with hot water, the wash waters, constituting the "sweet waters," being used for diluting and flushing. The mud, still containing about 2 per cent of sugar, which it does not pay to recover, is thrown away.

The clear, straw-colored liquor from the bag filter is now run into the char filter. These are similar to those used for glucose (Fig. 116, p. 417), but are larger, averaging 24 feet deep and 8 feet in diameter. The bone-char is in grains, which pass a No. 16 sieve, but remain on a No. 30 sieve. Finer grains clog the filter, and coarser ones have less action on the coloring matter in the syrup. The char is washed with hot water before the liquor is run in, but it is not "tempered" with acid, as is the case in glucose filtering. About 1 pound of char is used for each pound of sugar melted, and it takes 6 hours to fill the filter before the filtrate begins to run. After revivifying, the char enters the filter at about 150° F., and the liquor is filtered at the same temperature. After some time the filter becomes clogged, and it is often necessary to use compressed air to force the liquor through the char. At first the liquor is water white, but later it becomes colored, and finally the char is "spent," and must be revivified. The char is washed with hot water, and the wash waters are saved until they contain only 2 per cent of solids; below this they are thrown away. This cleansing of the char requires about 20 hours. It is then revivified, as described on page 418.

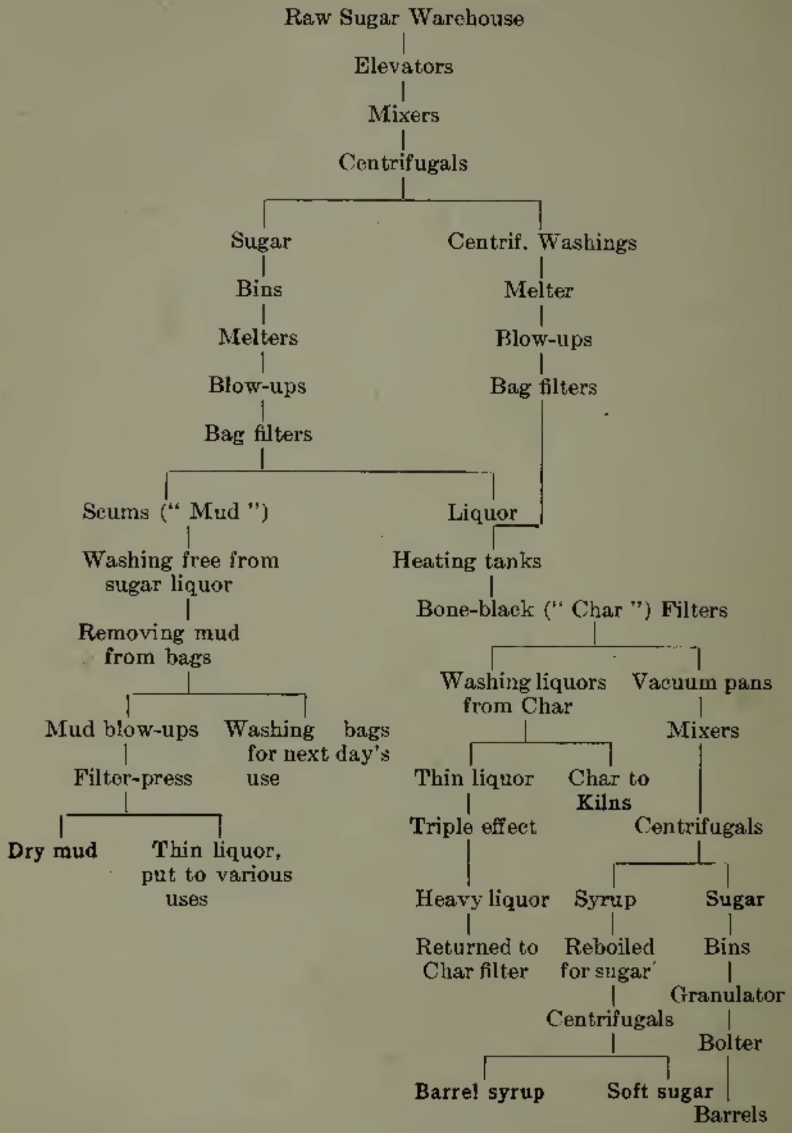
The revivifying process causes the pores of the char to become slowly clogged with vegetable carbon, which seems to have no decolorizing action. By passing the spent char through a rotary kiln to which a limited amount of air is admitted, the vegetable carbon can be more or less destroyed before the animal carbon is attacked; thus the usefulness of the char can be considerably prolonged. The average life of the char is about three years in sugar refining.

In Germany, bone-char is but little used, since pure beet sugar is produced directly from the juice after defecation.

The **filtered liquor** then goes to the vacuum pans, which are of copper, about 12 feet high and 10 feet in diameter, a "goose-neck" connecting each pan with the condenser. A pan full of syrup is called a "skipping." For granulated sugar, the syrup is run in until the steam coil is covered, and the boiling is carried on at 160° F., until grains appear; then more syrup is added, slowly, and the grains grow until the desired size is reached. Tests are taken from time to time, by means of the "proof stick," a solid brass rod passing through a stuffing box and projecting into the interior of the pan. In one side of the rod, near the inner end is a small cavity, about one-half inch deep. When the rod is pulled out until this cavity is outside the stuffing box, 2 or 3 cubic centimeters of syrup mixed with crystals are obtained. Thus small samples are readily obtained at any time, without interrupting the vacuum; and from the appearance of these samples, the sugar-boiler judges of the progress of the evaporation. The time required to complete the process is from 2 to 3 hours.

When the grain is large enough, the vacuum pumps are stopped and air is slowly admitted to the pan. The bottom valve is then opened, and the magma of sugar and syrup drops into **coolers**, or **mixers**, directly beneath, and is stirred while cooling, to prevent the grains agglomerating. The sugar and syrup are separated in cen-

SUGAR REFINING



trifugal machines. The former is washed in the centrifugal, to remove adhering syrup, and is then dropped into a storage bin, from which it is carried by a belt conveyer to the **granulator**. This is a long, rotating cylinder of iron, set at a slight incline, and heated by steam. By passing through this hot tube, the sugar is thoroughly dried, while the rotation prevents the grains sticking together. It then passes through a series of sieve reels, which usually separate the grains into three or four sizes, the commercial sizes being packed in barrels for market.

The syrup from the centrifugals is reboiled with more fresh syrup, or, if its color is too deep for this, it is sent back to the char filter, after which it is boiled to grain for **soft sugars**, the temperature in the vacuum pan being 110° to 125° F. These soft sugars are "centriffed," but not put through the granulator, and are boiled to a finer grain than is the granulated. In many cases they are redissolved and converted into granulated sugars. The syrup from them is amber colored or brown, and is barrelled for table syrup or for manufacturing purposes.

AVERAGE ANALYSIS OF SUGARS

Raw Sugar	Cane Sugar	Glucose*	Water	Organic Matter	Ash
Good centrifugal	96.0	1.25	1.00	1.25	0.50
Poor centrifugal	92.0	2.50	3.00	1.75	0.75
Good muscovado	91.0	2.25	5.00	1.10	0.65
Poor muscovado	82.0	7.00	6.00	3.50	1.50
Molasses sugar	88.0	2.80	3.00	3.50	2.70
Jaggary sugar	75.0	11.00	8.00	4.00	2.00
Manila sugar	87.0	5.50	4.00	2.25	1.25
Beet sugar, 1st	95.0	0.00	2.00	1.75	1.25
Beet sugar, 2d	91.0	0.25	3.00	3.25	2.50
Refined Sugar					
Granulated sugar	99.8	0.20	0.00	0.00	0.00
White coffee sugar	91.0	2.40	5.50	0.80	0.30
Yellow X C sugar	87.0	4.50	6.00	1.50	1.00
Yellow sugar	82.0	7.50	6.00	2.50	2.00
Barrel syrup	40.0	25.00	20.00	10.00	5.00

The **loaf sugar** of commerce is made by running the magma of syrup and fine crystals from the vacuum pan into conical moulds where it is allowed to stand for some time. A further crystallization of sugar takes place which cements the grains together, while the uncrystallized syrup drains off through a small hole opened in the point of the cone. A little water is poured on the surface of the sugar, and, percolating down through the mass, displaces any

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* The term "glucose" includes sugars which reduce Fehling's solution, but are not necessarily optically active.

syrup remaining. This draining is slow, and it is now customary to place several of the cones in a centrifugal machine, with their points towards the outside of the drum. The syrup and wash waters are forced through the mass, which is left as a dry, hard conical lump, the " sugar loaf " of trade.

REFERENCES

A Treatise on the Manufacture of Sugar from the Sugar Cane. Peter Soames, London, 1872. (Spon & Co.)

Guide pratique du Fabricant de Sucre. N. Basset, 3 vols., Paris, 1875.

Manuel pratique de Diffusion. Elie Fleury et Ernst Lemaire, Paris, 1880.

The Sugar Beet. L. S. Ware, Philadelphia, 1880. (Baird & Co.)

Manual of Sugar Chemistry. J. H. Tucker, New York, 1881.

Die Zuckerarten und ihre Derivate. E. von Lippmann, Braunschweig, 1882.

Traité theorique et pratique de la Fabrication du Sucre. Paul Horsin-Déon, Paris, 1882. (Bernard et Cie.)

Report on Sorghum Sugar by a Committee of the National Academy of Science, Washington, 1883.

Lehrbuch der Zuckerfabrikation. K. Stammer. 2te Auf. Braunschweig, 1887.

Handbuch der Kohlenhydrate. B. Tollens, Breslau, 1888.

Sugar. A Handbook for Planters and Refiners. C. G. W. Lock and B. E. R. Newlands and J. A. R. Newlands, London, 1888. (Spon.)

Die Zuckerrübe. H. Briem, Wien, 1889.

Manuel Pratique du Fabricant de Sucre. P. Boulin, Paris, 1889.

A Guide to the Literature of Sugar. H. L. Roth, London, 1890.

Handbuch der Zuckerfabrikation. 4te Auf. F. Stohmann, Berlin, 1899.

Introductory Manual for Sugar Growers. F. Watts, London, 1893.

Die Zuckerfabrikation. B. von Posanner, Wien, 1894.

Le Sucre et l'Industrie sucrière. Paul Horsin-Déon, Paris, 1894.

Handbook for Sugar Manufacturers and their Chemists. G. L. Spencer. 3d ed. New York, 1897. (Wiley & Sons.)

Handbook for Chemists of Beet-sugar Houses and Seed-culture Farms. G. L. Spencer, New York, 1897. (Wiley & Sons.)

The Technology of Sugar. J. G. McIntosh, 1903.

Cane Sugar and the Process of its Manufacture. Geerligs, 2d ed., 1909.

Calculations used in Cane-sugar Factories. I. H. Morse, 1904.

Die Zucker-Fabrikation. H. Classen, Magdeburg, 1904. (Schallehn u. Wollbrück.)

Manuel-Guide de la Fabrication du Sucre. R. Teyssier, Paris, 1904.

Beet Sugar Manufacture. H. Claassen. Trans. by W. T. Hall and G. W. Rolfe, New York, 1906. (Wiley.)

Beet Sugar Manufacture and Refining. 2 vols. L. S. Ware, New York, 1907.

Cane Sugar. Noel Deerr, Manchester, 1911. (Rodger.)

FERMENTATION INDUSTRIES

Fermentation is a general term applied to various chemical changes caused by the action of bodies called ferments. These are: (*a*) Unorganized chemical substances, called enzymes, secreted by living cells; and (*b*) certain micro-organisms. **Enzymes** include such bodies as diastase, invertase, pepsin, ptyalin, emulsin, etc. They usually assist in the nutritive functions of the animal or plant in which they occur, the changes which they cause being sometimes of the nature of hydrolysis. Buchner has isolated from the expressed liquid of comminuted yeast cells, an enzyme called *Zymase*, which changes sugar into alcohol, without the presence of the yeast plant itself. This indicates that the change of the sugar is not directly connected with the life functions of the plant, and the enzyme acts as a catalyzer. Micro-organisms cause complex changes in the substance on which they act, due in part to the enzymes which they secrete. The product formed varies with the kind of organism predominating in the liquid, and the fermentation is designated as alcoholic, acetic, lactic, butyric, etc.

Organized vegetable ferments are (1) Mould growths; (2) Yeast plants (*Saccharomycetes*); (3) Bacteria (*Schizomycetes*).

These are all capable of growth and reproduction, and associated with the former are the chemical changes called fermentation and putrefaction. It is generally true that alcoholic fermentation is caused by the yeasts, while putrefactive fermentation is due to bacteria; but there are some exceptions.

Organized ferments may be reproduced by microscopic spores, which propagate when introduced even in *small quantities* into a fermentable liquid, and cause the chemical change of a large part of it. Consequently these spores, floating in the dust in the air, find their way into fermenting liquids which, when freely exposed to the air, may, therefore, contain many kinds of ferments.

The **moulds** are threadlike plants, devoid of chlorophyl, and forming a somewhat felted mass called the *mycelium*. They grow readily upon fruit, damp wood, wet grain, or on the walls of damp cellars and similar places, forming greenish, bluish, or gray vegetations, which emit a characteristic musty odor. They exert an oxidizing action upon organic matter and hydrolyze starch. Since they develop musty or sour odors and taste in the nutrient medium, destroy sugars, and often form coloring matter, they are injurious in fermenting processes. But their presence is mainly due to negligence and lack of cleanliness and proper ventilation.

The **bacteria, splitting ferments, Schizomycetes,** are microscopic plants of the lowest order, forming rods, or spiral, threadlike, or rounded cells. These propagate by fission with astounding rapidity, if the conditions are favorable; if not, some forms develop spores, which may be exposed to extreme cold or to moderately high temperature without losing their power of germinating when brought into a proper medium. These spores are scattered everywhere, in the soil, the air, and water; being very minute, they are transported by every puff of wind, and thus readily find access to liquids and moist substances exposed to the air. For their nutriment and progagation they need about the same substances and condition of temperature as the yeasts (see below). They cause oxidation and decomposition, and often putrefaction, in many bodies containing albuminous and nitrogenous material, and the products of these reactions are sometimes extremely poisonous. Some of them cause acute diseases in man and in animals. Many of the "diseases" of wine and beer, as well as acetic, lactic, butyric, and other fermentations, are caused by them. Also the production of nitrates and nitric acid in the soil (p. 146) is attributed to the action of bacteria.

Bacteria are much more susceptible to the action of antiseptic substances than are the yeasts, but heat and cold affect them less. Thus the process of Pasteurization (p. 442) is not a sure protection against their action.

The **yeasts,** *Saccharomycetes,* have great technical importance, owing to the part they take in alcoholic fermentations. Several species are recognized, each playing some particular rôle in the fermentation. Thus *Saccharomyces cerevisiæ* is the particular ferment for beer; *S. ellipsoideus* is the chief organism present in fermenting wine, and in any spontaneous fermentation of fruit juices.

Yeast consists of an aggregation of plant cells, forming a slimy, yellow mass of peculiar odor, and having an acid reaction. Under proper conditions, the cells propagate with great rapidity. The temperature must be constant at from 6° to 26° C.,* and substances necessary for the growing plant must be present; these are a fermentable sugar, nitrogenous matter, and certain mineral salts, such as phosphates and sulphates of calcium, potassium, or magnesium. Air (oxygen) is desirable, especially at first; later it is often excluded to prevent secondary fermentations, by which the alcohol

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* A higher temperature is conducive to the formation of fusel oil.

formed is converted into acetic acid or other products. Through alcoholic fermentation the fermentable substance in the liquor is converted into alcohol and carbon dioxide: —

$$C_6H_{12}O_6 = 2\ C_2H_5OH + 2\ CO_2.$$

But this does not express the true decomposition, for a large number of other substances are formed at the same time, the more important being glycerine, succinic acid, butyl, isobutyl, and amyl alcohols (fusel oil), and various organic ethers. Owing to these secondary reactions, the yield of alcohol is somewhat reduced.

When the amount of alcohol formed in the liquid equals 14 to 15 per cent, the yeast can no longer propagate itself, and the fermentation ceases. The presence of certain mineral salts, such as borax, mercuric chloride, sulphurous acid, and free caustic alkalies, often retards or prevents fermentation.

The fermentable substance in the liquid to be fermented with yeast is generally a sugar, dextrose being the most readily converted; and it is quite possible that other sugars are first changed to glucose before the real fermentation begins. For example, cane sugar is not in itself readily fermented, but by the action of the invertase secreted by the yeast, it is converted (hydrolyzed) into dextrose and levulose, which are readily fermented. The invertase is not destroyed in this hydrolysis, and hence there is scarcely any limit to the amount of cane sugar which may be hydrolyzed by a small quantity of invertase. Maltose, $C_{12}H_{22}O_{11}$, is also readily converted, by yeast, into fermentable dextrose, and thence into alcohol and carbon dioxide; or, perhaps the maltose is fermented directly, without the intermediate formation of dextrose. Starch is not capable of direct alcoholic fermentation, but must first be converted into fermentable sugar. This conversion is easily accomplished by the action of diastase, which changes the starch into maltose.

Yeasts are also grouped in two general classes, viz.: **top yeasts** and **bottom yeasts.** The former require rather high temperature (15° to 30° C.) for the fermentation, which is very active, the rapid evolution of carbon dioxide causing the liquid to bubble violently, and carrying the yeast to the surface. This yeast is used for heavy ales and beer, for alcohol and high wines, and for some wine. Bottom yeast acts at a lower temperature (4° to 10° C.), and the fermentation is slow; the evolution of carbon dioxide is gradual, and the yeast remains on the bottom of the vat.

The researches of Pasteur, Reess, Hansen, and others have thrown much light on the nature and properties of the yeasts. Hansen divides the Saccharomyces into six typical species, as follows: —

Saccharomyces cerevisiæ, — the beer ferment most commonly employed in breweries and distilleries. It may be a top yeast, *i.e.* floating on the surface of the fermenting liquid, or a bottom yeast, according to the conditions existing during the fermentation.

Saccharomyces Pastorianus I., — a beer ferment which causes an unpleasant bitter taste in beer. It is a bottom yeast, remaining on the bottom of the vat during the fermentation.

Saccharomyces Pastorianus II., — a top yeast found in beer, but which appears to have no action upon it.

Saccharomyces Pastorianus III., — a beer ferment causing cloudiness and disease in the beer. It is a top yeast, resembling the last two.

Saccharomyces ellipsoideus I., — a bottom yeast, the true wine ferment. It occurs on the grapes.

Saccharomyces ellipsoideus II., — a yeast causing the cloudiness in turbid beer. It is a bottom yeast, and resembles the last mentioned above.

In addition to the above, Hansen also isolated from a brewer's yeast two varieties, known as *Carlsberg Nos. 1* and *2,* and closely resembling *S. cerevisiæ.* No. 1 yields a beer with less carbon dioxide than No. 2, and is mainly employed for bottle beers; No. 2 is used for export beers.

All these yeasts ferment glucose, sucrose after inversion, and maltose, but not lactose. Other yeasts are known which ferment sucrose, but not maltose, and still others which contain no invertase, and will not ferment sucrose.

For technical purposes, it has long been the custom to use cultivated yeasts for alcoholic fermentation; but Pasteur showed that these contain many "**wild yeasts,**" *i.e.* plants whose nature and actions were either unknown, or are detrimental to the product. Hansen reasoned from his observations on the effect produced by the eight above-described yeasts, that for a uniform quality of product there must be exactly the same kind, or kinds, of yeast employed in each brew. Hence he devised his system of pure yeast cultures, obtained in sterilized nutrient material by propagation from a single plant. Thus a single variety of yeast is obtained, by the use of which the fermentation is more easily controlled.

In fermentations at a high temperature, where the amount of alcohol formed is near the maximum, the yeast plant generally dies; but by low temperature fermentation the propagation of the plant may be controlled and the variety kept unchanged through a considerable period of time; a sufficient amount of carefully selected yeast is preserved for the next liquor to be fermented. But in some cases, a fresh lot of yeast is especially prepared each time.

There are three purposes for which the alcoholic fermentation is carried on technically: (*a*) for the manufacture of the yeast; (*b*) for the carbon dioxide formed; (*c*) for the alcohol.

The first of these is usually associated with the third, and consists in growing a pure yeast free from wild yeast and other ferments. The process of growth is carefully watched by the aid of the microscope, and the appearance of any injurious variety condemns the whole lot.

Those most generally cultivated are the *S. cerevisiæ* and *S. ellipsoideus.* The cells are filtered out of the liquid in which they are grown, by fine sieves, usually of bolting cloth, and are washed with cold water, filter-pressed, and the cake heavily pressed. It is then mixed with from 25 to 50 per cent of starch or flour and brought into market as "**compressed yeast.**" By drying at a low temperature the plant retains its vitality for the most part, and will grow when put into a fermentable solution.

The liquid from which the yeast cells have been filtered is sometimes allowed to ferment further until the action ceases; it is then distilled for alcohol. The yeasts are grown in a filtered extract of malt, and since they require free access of oxygen for their greatest development, it is now customary to force a blast of sterilized air through the fermenting liquid. This hastens the process and increases the yield of yeast, but decreases the formation of alcohol so that its recovery is unprofitable.

At a low temperature, compressed yeast will keep for a long time; but in warm, moist air it rapidly decomposes or develops mould growths. Dried yeast is less active than the compressed, but will bear exposure to the air and can be kept for a longer period. The chief use of commercial yeast is for bread making.

Fermentation for the carbon dioxide is practically confined to the manufacture of bread. In this a mixture of flour and water is allowed to ferment. The nitrogenous matter in the flour furnishes nutriment, and the starch is partly converted into fermentable sugar by the ferments always present in the flour and yeast. A vigorous alcoholic fermentation begins, liberating a considerable volume of carbon dioxide, which, being retained by the pasty dough, causes the whole mass to swell and become porous. When bread dough is baked, the heat kills the yeast, stopping all fermentation, and at the same time evaporates off the alcohol, and finally it hardens the gluten, dextrin, and starch paste, retaining the porous structure in the mass.

Fermentation for the alcohol may take place without the addition of prepared yeast, as in the case of most wines; but the germs of the ferment are then derived from the air or are present upon the skins of the fruit, and so when the latter is crushed they are mixed with the juice. In all cases, however, where starch is to be converted into alcohol, malt and yeast are employed.

WINE

Wine is fruit juice which has undergone an alcoholic fermentation; it is most commonly made from grapes. The fermentation is spontaneous and progresses without special attention until the sugar has been converted to alcohol. The fermentable sugars in grape juice are dextrose, levulose, and some inosite; when fully ripe, it contains on an average 18 per cent of fruit sugar, in addition to tartaric acid (as potassium bitartrate), malic acid, a little butyric acid, albuminoids, non-nitrogenous matter, and ash. All these vary in quantity according to the kind of grape and the nature of the soil and climate. The grape skins contain tannin ($C_{14}H_{10}O_9$), oils, and (except in white grapes) coloring matter (œnocyanin). These all pass into the juice when the grape is pressed.

The character of the soil in which the vine grows influences the fruit materially. It must be light and porous, and contain salts of potassium, lime, magnesium, iron, and sodium, especially sulphates, phosphates, chlorides, and silicates. Decomposed volcanic rock, such as granite and lava, appear to furnish the best soil. A warm summer with only a moderate amount of rain is essential for a high percentage of sugar in the juice, and the highest percentage is usually obtained in October in latitude near 40°. If the grapes are allowed to hang until overripe, the amount of sugar decreases somewhat, but the wine sometimes has a peculiar bouquet which is much prized.

When ripe, the grapes are carefully picked and sometimes sorted into several grades. For the finest wines they are removed from the stems, since these contain an excess of tannin and tartaric acid. They are crushed between wooden rolls or by pounding in mortars, or by treading with the bare feet. The juice is extracted by pressing, or better in centrifugal machines. It is called "**must**" and contains the soluble matter of the grape. The quality of the wine depends in a great measure on the ratio of the sugar to the free acids (tartaric and malic). The most favorable ratio is 1 part of acid to 29 parts of sugar, but the average is about 1 to 16.

For red wines it is customary to allow a partial fermentation of the mash before pressing out the juice. The alcohol thus formed extracts the coloring matter from the skins more thoroughly than it can be directly expressed. White wine is made from white grapes, or from juice which has been separated from the marc before fermentation.

Through the action of the wine ferment, *Saccharomyces ellipsoideus*, present on the grape and in the air of grape-producing regions, fermentation begins in the must at once. It takes place in two stages: the active fermentation, which lasts from one to three weeks; and the still fermentation, continuing for several months. The former takes place in open vats or tubs at a moderate temperature (10° to 30° C.). It may be a "**bottom fermentation,**" where the temperature is from 10° to 15° C., or a "**top fermentation**" at 20° C. or above. The former is generally practised in northern Europe and produces wines low in alcohol but having a fine aroma or "**bouquet.**" Top fermentation, which is more rapid, seldom lasting more than a week, is carried on in southern Europe, and yields wine high in alcohol but lacking bouquet.

In a few hours after being put into the fermenting vats the clear must becomes turbid and acquires a sour taste and smell; soon a rapid evolution of carbon dioxide begins and a froth forms on the surface. Some manufacturers expose the must freely to the air and stir it frequently to aerate it, but others exclude the air as much as possible. A moderate amount of aeration, especially at first, is doubtless beneficial; but towards the end of the active fermentation too much air admission may introduce the acetic ferment, *Bacterium aceti*. During this fermentation the albuminoids are largely consumed by the growing yeast. Finally the active fermentation becomes slow and the must is now known as "**new wine.**" It is drawn into closed tubs or casks which are filled quite full and the opening loosely closed to prevent the access of the acetic ferment. Here the still fermentation takes place, the time depending largely upon the temperature of the fermenting cellar; the lower the temperature, the less rapid the fermentation. The yeast settles, and as the alcohol content increases, a crystallization of acid potassium tartrate, together with some calcium salts and coloring matter, takes place, forming as a deposit called **argol**; this is the source of the "**cream of tartar**" of commerce.

When it has become clear, and nearly the whole of its sugar content has been converted into alcohol, the wine is drawn off into large casks. The bungs are closed and the wine allowed to "ripen" for perhaps two or three years. During this process, which is essentially an oxidation, the albuminoids and tannins are largely precipitated, together with some of the coloring matters and other impurities. At the same time the higher alcohols or fusel oil formed during the fermentation combine with the free acids present to form organic ethers which impart the peculiar flavors to wines. In order to hasten the ripening process, the wine is frequently drawn off from the casks and a little gelatine, isinglass, milk, blood, or albumin added each time. This forms a precipitate which drags down the fine suspended matter. Gelatinous silicic acid, kaolin, gypsum, or plaster of Paris are also used for this clarifying. The last two, however, react with the tartrate of potassium always present in the wine, forming potassium sulphate and precipitating calcium tartrate. The former remains in the wine, and since it has an injurious action on the human system, the use of plaster and gypsum is prohibited in some countries. When the ripening process is complete, the wine is bottled and is ready for consumption.

The use of pure cultures of yeast for the fermentation of wine has recently been introduced with good results, yielding products which ripen more readily and have good keeping qualities.

Wine is subject to various "diseases" due to bacteria and other ferments. Sourness is caused by an acetic fermentation due to too much exposure to the air. Ropiness is the result of mucus fermentation. Stale or flat taste and bitterness are produced by a peculiar fungus or plant growth. These troubles may be prevented by care in handling the wine, attention to cleanliness, and by always keeping the casks full to prevent the entrance of air. Any shrinkage through evaporation or leakage should be replaced with more wine at once. Those diseases which are caused by ferments can usually be remedied in the early stages by heating the wine to about 70° C., which kills most of the injurious germs and renders the wine capable of long keeping and transportation. This process, called **Pasteurizing**, does not injure the aroma and other qualities. It is carried out by immersing the bottled wine in hot water, or by running the wine from the cask through long pipes placed in tanks of hot water.

Other methods of improving the keeping qualities of wine are the addition of salicylic or boric acid, but these are considered injurious to health and are prohibited in some countries. A general practice is to fume the casks with sulphur dioxide and to wash them with sodium bisulphite solution before filling with wine. Sometimes sulphurous acid is added to the wine to act as a preservative.

Wine made from grape juice as it is expressed from the fruit is rarely found in market. The juice varies from year to year according to the amount of rain, sunshine, average temperature, fertilization, and other causes; thus the proportion of sugar, tannin, acid, etc., changes, and the wines vary somewhat on fermentation. For this reason, must or new wine is "improved." A common method is to mix in the juice of other kinds of grapes or to add new wine of different character. If the must is too high in sugar and low in acid, a sour wine is added until the desired ratio is obtained. If already too sour, it is "**Gallized**" by adding water and sugar, or "**Chaptalized**" by neutralizing the excess of acid with marble dust or precipitated calcium carbonate. To make a sweet wine, a considerable amount of cane sugar is added.

These modifications are restricted by legal enactment in most countries, and the addition of large quantities of alcohol, glucose, and glycerine (**Scheeleizing**) is generally prohibited. But in the case of certain heavy Spanish and Portuguese wines, such as Port and Madeira, the addition of rectified alcohol is recognized as legitimate. But such substances as logwood, cochineal, kermes, or other natural or coal-tar coloring matters, are considered adulterants.

Much inferior wine is made by leaching the pulp ("marc") from the wine-press with water, adding sugar, and fermenting the extract. This gives a cheap wine, much used by the poorer people of European countries. But it must not be sold as a natural wine.

Considerable **artificial wine** is made by mixing water, alcohol, sugar, glycerine, tartaric acid, tannin, fruit essences, etc., to produce a liquor resembling the natural product. Within a few years an industry has been established in France for the manufacture of wine from raisins and prunes. These are macerated in a mixture of water, brandy, sugar, tartaric and tannic acids, and the whole fermented with yeast. The product is colored if desired.

Champagne is made from certain sweet white wines. The must is pressed from the grape as soon as possible after picking, and then fermented. The new wine is clarified with isinglass and "improved" very carefully by mixing with other wines. A certain amount of cane sugar mixed with Cognac is then added and the wine bottled (the best corks, which have been soaked in wine, are used) and placed in a room warmed to 24° C. A fermentation takes place in the bottle and the wine becomes highly charged with carbon dioxide. The amount of sugar added is calculated to liberate enough of this gas to cause a pressure of about five atmospheres in the bottle.* The bottles are placed on the side and left for some months; then they are turned with the cork down, until the sediment collects just above it. The cork is then carefully removed for an instant, until the sediment has blown out. The loss is replaced with *liqueur* (a solution of cane sugar and aromatic essences in the best Cognac), the cork is replaced and wired in, and the liquor is ready for market.

An imitation champagne is largely made by forcing carbon dioxide into a sweet, white wine, to which some *liqueur* has been added.

Beside grape wines, other fermented fruit juices are used as beverages. Of these, the commonest in this country are **hard cider** and **currant wine**. These do not keep well unless sugar has been added before fermenting.

Palm wine is made in tropical countries from the sap of the palm.

Pulké is a drink prepared in Mexico from the juice of certain cactus plants.

Kumiss is a winelike drink made from the fermented milk of cows, mares, or goats. The milk sugar is converted into lactic acid, alcohol, and carbon dioxide. It is chiefly made by the inhabitants of the Russian steppes.

BREWING

Brewing involves alcoholic fermentation, but it differs from wine making in that it is always started by the addition of yeast to the liquid to be fermented. Spontaneous fermentation is not desired, and precautions are taken to prevent it.

Beer is a fermented alcoholic drink intended for consumption during the after-fermentation, while still charged with carbon dioxide. It is made from sprouted grain (malt), starchy materials, and hops. The malt is generally barley, as this yields the largest percentage of diastase and affords the richest, best flavored beer.† The starchy material is derived from unmalted corn, rice, or other grain.

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* From 5 to 8 per cent of the bottles burst.

† Wheat, corn, and other grains are occasionally malted for certain kinds of beer.

The quality of the water used for brewing is important as affecting the product. In general, the water should be moderately hard and the salts desired in it are calcium and magnesium sulphates and sodium chloride. If much iron is present, the water should be purified; very soft water is improved by the addition of gypsum. Water containing much organic matter in solution, or an unduly large number of bacteria, should not be used.

The process of brewing may be divided into malting, mashing (including the boiling and cooling of the wort), fermentation, and bottling or barrelling.

Malting is now generally done by separate concerns, except in only the largest breweries. The process consists in cleaning softening, sprouting, and drying the grain. During the sprouting, two ferments, **diastase** and **peptase**, are formed, while the cell walls enclosing the starch are softened and disintegrated so that the interior of the kernel becomes "mealy," thus facilitating the transformation of the starch into sugar. The production of diastase is the chief aim of the maltster. The secretion of this ferment increases as the germination proceeds, until it reaches a maximum, after which it decreases if the germination is not stopped. The amount of diastase is estimated by the length of the sprout or acrospire, and is greatest when this has extended about three-fourths of the length of the grain. The appearance and length of the rootlets also serve as a guide to the experienced maltster.

The mode of the formation of the diastase is not yet known. It is a nitrogenous body, easily soluble in cold water and possessing the power to convert large quantities of starch into maltose ($C_{12}H_{22}O_{11}$), and dextrin. Since good malt contains a great excess of diastase over the amount needed to convert its own starch into sugar, mixtures of raw grain and malt are allowed to react until the starch of the former is converted into sugar, and then the whole is fermented.

The dust, dirt, dead and broken kernels, and foreign seeds are first removed by careful sieving in revolving sieves, the dust and chaff being blown away by a strong blast of air.

The grain is then "**steeped**" by soaking it for two or three days in water at 12° C., in wood-lined tanks or cemented cisterns. It is stirred frequently, and the dead kernels float and are removed. The water extracts much soluble matter, oil, etc., from the grain, and is changed as it becomes colored.

The grain increases about 20 or 25 per cent in volume and about

50 per cent in weight, and when a test of a few kernels shows that they are so soft that the skin may be readily removed, the grain is **couched** by piling in a nicely levelled heap about 20 to 24 inches deep, on the malting floor, which is made of cement and is kept very clean. The room is usually only moderately lighted, and the air is kept moist by frequently sprinkling the grain and floor with water; a good circulation of air in the room to supply plenty of oxygen to the grain is a prime essential. Great care is taken to keep the temperature even, at about 15° to 16° C. Higher temperature tends to cause mould growth and excessive root development. After a few hours the temperature begins to rise within the couch, and, as the grain heats, it becomes moist on the surface (" sweats ") and evolves an agreeable odor. The germination has begun, and soon the rootlets appear. The time of couching is from 20 to 30 hours, according to the temperature and time of steeping.

The grain is then **floored** by spreading it with wooden shovels on the floor, in an even layer about 10 inches deep. To prevent its heating too rapidly, it is turned over every 5 or 6 hours, thus bringing new grain to the top; each succeeding day the layer is spread thinner, until it is finally only 4 inches deep; the grain is sprinkled from time to time to keep it moist. The germination is rapid and must be carefully watched; after from 6 to 12 days, when the acrospire has reached the desired length, the growth is stopped by spreading it in thinner layers; the moisture evaporates and the germ withers. The "**green malt**" is then transferred to the drying room, which usually has two floors, made of wire gauze or perforated iron plates. The malt is spread on the upper floor and dried at a temperature of 38° to 50° C. To produce kiln-dried malt, it is transferred to the lower floor, where it is much hotter, and is dried at 100° C.; sometimes it is even partially charred. The air in the drying room may be heated by fire gases passing through pipes under the gratings, or by an open fire in the lower part of the room; in this latter case the products of combustion pass through the malt, imparting a darker color and a peculiar taste to it and to the beer made from it. The character and color of the beer are much influenced by the mode of drying the malt. The higher the temperature, the more diastase is destroyed and the less soluble the protein is rendered. After drying, the rootlets are brittle and are easily removed by passing the malt through cylindrical sieves containing rotary brushes.

The production of a malt uniform in its properties throughout by the above method is difficult, while different lots are sure to vary a good deal, according to the temperature and humidity of the air. Consequently, at certain seasons of the year, it was customary to suspend operations. **Pneumatic malting**, as it remedies the above difficulties, prevents mould and acidity, is easily controlled, and requires less labor and less floor space, has replaced the old system in all large malt houses. Two forms of pneumatic malting have been devised.

The **Galland process** consists in placing the softened grain in a rotating drum (Fig. 118), containing along its inner circumference several channels (A, A), covered with wire gauze and opening into the chamber (C) at the end of the drum. A tube (B) of wire gauze extends along the centre of the drum and connects with an outlet pipe (E). Into the chamber (C) a pipe (D) opens, which contains a valve that makes connection with the flue (F), or with the pipe (G), as desired. Air is drawn through coke towers, kept at a constant temperature of about 14° C., and through which water trickles. The air then passes down the flue (H), where it is in contact with a fine spray of water escaping under pressure from the supply pipe (J). It is thus cooled, or warmed, as necessary to the constant temperature of 14° C., and, laden with moisture, passes through (F) and (D) into the chamber (C), and thence into the drum, through the channels (A, A). The drum is filled about two-thirds full with the swollen grain; and as it rotates about once in 40 to 50 minutes, there is a

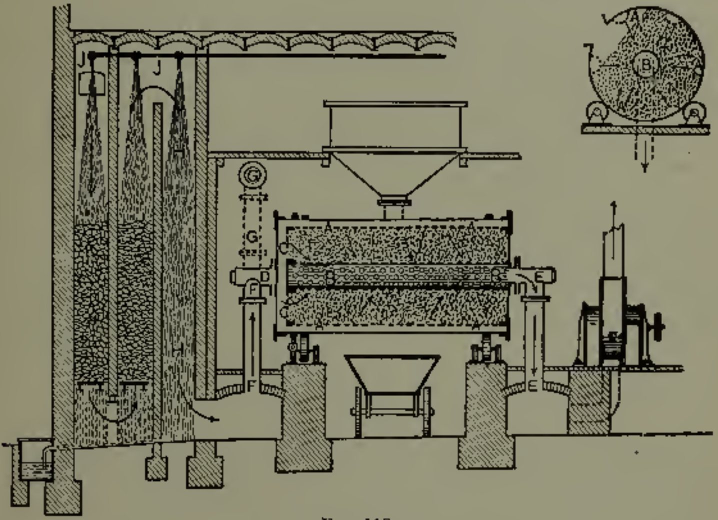

Fig. 118.

slow turning over of the whole mass of the grain. The air, entering through (A, A), passes through the mass, and enters the inner tube (B), from which it passes to (E), and thence to the exhauster, which drives it out of the building. Thus the grain is kept at a constant temperature in a moist atmosphere, with effective circulation of air, and a constant change of surface of the kernels, which prevents undue heating. The grain sprouts as on the malting floor, but there is no handling and consequent breaking and crushing of the kernel, and no opportunity for the development of mould; since the air is filtered, very few germs are introduced. When the germination has gone as far as is desired, the valve in (D) is changed to cut off the moist air, and connection is made with (G), from which warm, dry air is drawn into the drum, rapidly drying the acrospire and rootlets. The drums hold from 1½ to 5 tons of barley at a charge, and the time necessary for the process is about 8 days.

By the **Saladin system**, the softened barley is placed in a long tank, having a false bottom of gauze, and provided with a mechanical stirring apparatus, travelling from one end of the tank to the other on a movable carriage. This stirrer hangs down into the grain, and mixes it effectively without crushing any kernels. Moist air enters under the false bottom, and passing through the wet grain, escapes into the room, and is drawn away by an exhauster. When the sprouting is ended, warm, dry air is drawn through the malt, as above described.

Mashing consists in converting the starch in the mixture of grain and malt into maltose and dextrin, through the action of the diastase in the malt, and at the same time extracting the soluble carbohydrates and nitrogenous bodies. The peptase, going into solution, is supposed to convert part of the albuminoids into peptones and amides, which are readily soluble in water, and constitute a part of the "extract" present in the finished beer. Some of these bodies, however, if present in a large amount, may cause cloudiness in the product, as they are precipitated from cold solution by alcohol. It is generally supposed that by drying the malt at a high temperature these protein substances are rendered less soluble in the mash liquor, and being thus filtered out, the beer is clear and bright. The use of unmalted grain, especially corn or rice, in mashing, is also advocated,* on the ground that it contains no protein matter to cloud the

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* Robert Wahl, Indian Corn in the Manufacture of Beer, U. S. Dep't Agriculture, Washington, 1893.

beer. But the real nature and value of peptones in the mash liquor is not yet definitely settled.

The most favorable temperature for the action of the diastase is from 60° to 65° C., at which point it rapidly hydrolyzes the starch, and converts it into maltose and numerous dextrins, — amylodextrin, erythrodextrin, and archodextrin probably being intermediate products. About one-fourth of the starch is usually left in the form of dextrin.

According to Ost, the large starch molecule decomposes into several smaller dextrin molecules: —

$$mn(C_{12}H_{20}O_{10}) = n(mC_{12}H_{20}O_{10}).$$

Of these dextrins, some combine with water to form maltodextrin, an intermediate product between dextrin and maltose, which ferments very quickly with top yeast. These dextrins are further converted into maltose by the diastase: —

$$mC_{12}H_{20}O_{10} + mH_2O = m(C_{12}H_{22}O_{11}).$$

A complete conversion of the starch into maltose is not desired for beer, since the presence of the unfermentable dextrin imparts fulness of body and nutritive properties, which are increased by the albuminoids, peptones, and amides. These also keep up a slow fermentation after the beer has been drawn into casks or bottles. It is often customary, therefore, to limit the diastatic action by kiln-drying the malt at a high temperature, or by mashing with very hot water at first, or by rapidly heating a part of the mash to boiling.

There are two general processes of mashing: the **infusion method**, generally practised in the United States and in England; and the **decoction method**, usually employed in Europe. By the former process the dry malt is crushed between rolls so that the hull bursts, but it is not ground. It then passes into a large "**mash-tub**," provided with a cover and an effective stirring apparatus. English brewers mix the malt directly with hot water at 75° C., as it saves time and labor, and the extraction of the malt seems to be more complete. But this hot water destroys much of the diastase, and prevents the complete action of the peptase on the albuminoids, thus leaving them in the beer, where they sometimes cause cloudiness.

American brewers usually mix the malt with a little water at 50° to 60° C., and the temperature is kept there for some time, as this is the most favorable temperature for the diastase and peptones to do their work. Then the mash is slowly heated to 70° C., by running in boiling water or free steam. By this slow heating the starch is all converted by the diastase before it is hot enough to form a paste. Some brewers prefer to start with cold water in the mash-tub, and heat slowly to 70°.

The raw cereal used in the mash is generally ground and mixed with a small quantity of the malt in a special tub; then water at about 38° C. is run in, and after about 30 minutes the temperature is raised to 60° C., where it remains another half-hour, the stirrer being in constant operation. Then the mixture is heated to boiling for an hour, and finally the softened raw grain is run into the mash-tub, where the rest of the malt has been wet with water at 38° C., and the mashing process proceeds as above.

Mashing usually takes an hour or more, and the stirrer is kept in constant operation. The product is a liquid called " **wort,**" containing maltose, isomaltose, dextrins, peptones, and amides.

The decoction process yields a more concentrated wort, and is generally used where fuel is expensive, and when a full-bodied, highly extractive beer is desired. The crushed malt is mixed with twice its volume of cold water in the mash-tub, and then the full amount of water desired is made up by adding boiling water, thus raising the temperature of the mash to 38° C. About one-third of the whole mash is then pumped into the **decoction pan** (a boiler heated either by free fire or by steam, and having a good stirrer), where it is rapidly heated to boiling, and at once run back into the mash-tub, where the stirrer is working actively. This raises the temperature of the mash to about 50° C. Again one-third of the contents of the mash-tub is heated to boiling in the decoction pan, and run back, heating the mash to 62° C. Another repetition of this process raises the temperature to 70° to 72° C., when the mash is allowed to stand quietly for 30 minutes.

The wort obtained by either process is filtered from the husks of the malt and other solid residue. When the infusion process is used, the mash-tub generally has a false bottom of perforated copper plate, the holes being sufficiently fine to retain the residue. When the stirrer is stopped, this insoluble matter settles to the bottom, and collecting on the grating, forms a filtering layer which retains the suspended matter, while the wort is drawn off below the false bottom. The first runnings are turbid, and are refiltered. In the decoction process, it is customary to run the mash into a special tub for this filtration. In order to remove all the wort from the residue, a washer called a " **sparger** " is used. This is merely a large Barker's mill with arms extending to within half an inch of the sides of the mash-tub, and with a row of holes one-twentieth of an inch in diameter, and two inches apart, extending along the back of each arm. The flow of water causes the arms to rotate and it is evenly distributed. The process is continued with hot water (75° C.) until the washings reach a density of 1° Tw.

The filtered wort is next run into the **brewing kettle** or **copper**, where it is boiled for some time. This has several objects: —

(*a*) It concentrates the wort, which, by the infusion process especially, is very dilute, and about one-fourth of the water must be evaporated.

(*b*) It destroys the diastase, peptase, and any other ferment which may be present, and thoroughly sterilizes the wort.

(*c*) It coagulates and precipitates most of the albuminous matter remaining in the wort.

(*d*) It affords an opportunity of adding the hops, which are boiled with the wort from one-half an hour to an hour.

Hops are the female flowers (catkins) of *Humulus Lupulus*, L. The leaflets contain tannin, while the yellow powder (lupulin, hop meal, or hop flour), attached to the surface of the catkin, contains hop oil, certain alkaloids or bitter principles, and resins. The oil is volatile, and is present to the extent of 0.25 to 0.30 per cent. It imparts the bitter flavor to the beer. If boiled too long, part of this oil is lost. The alkaloids are supposed to give the narcotic character to hops. The resins contain most of the antiseptic principles, which are protective against the lactic ferment, and, to a less degree, against the acetic ferment; hence more hops are added to lager beer which is stored several months before going to market, than to that intended for immediate consumption. About one pound of hops to 100 gallons of wort is the lowest limit, while as much as 12 pounds per 100 gallons are used for some of the heavy English ales and porters.

The best varieties of hops are raised in Bohemia and Bavaria, but they are also largely cultivated in other parts of Germany, in France, and in the United States.

After boiling the wort from one to six hours, according to the character of the wort, and of the beer desired, the hop catkins are removed by straining the wort through sieves in a vessel called the "**hop-back**." They are then washed, and sometimes pressed, to obtain all the extractive matter.

The hot wort is then pumped through a rose or sprayer into a receiving tank placed in a well-ventilated room. It falls for some distance as a fine mist, and is aerated and cooled some 25° to 30°. It stands in this tank until a sediment deposits. The wort is still hot, and is drawn off and rapidly cooled * to the temperature of fermentation by running over the **Baudelot cooler**, or "**beer-fall.**" † This consists of a series of horizontal copper pipes, about two and one-half inches in diameter, placed, one above the other, to a height of ten or twelve feet, and through which cold water or ammonia circulates; the wort, running over the surface of the pipes in thin films, is quickly cooled to the temperature of the water. Sometimes the flow of wort is inside the pipes, and the water passes over the outside of the beer-fall.

From the cooler, the wort passes to a tank, where it is allowed to settle, and the clear liquid is then drawn into the fermentation butts. These are made of oak, and lined with pitch or asphaltum, and hold from 1500 to 3000 gallons. They are set in underground cellars or, more commonly now, in rooms cooled to a constant temperature by refrigerating machines; or water, cooled to the temperature of fermentation, flows through a coil of copper pipe placed in the butt. A certain amount of pure yeast is added to each tub, the process being called "**pitching,**" and within a few hours the active fermentation begins. In some breweries it is the practice to add the yeast in the settling tanks; after a few hours the wort is drawn from above the sediment (consisting of coagulated albuminous matter, dead yeast cells, hops, and other solid impurities), and passes into the fermentation butts, carrying with it enough young yeast cells to cause active fermentation. According as the temperature of the wort is low (5° to 8° C.) or high (15° to 18° C.) there is a "bottom" or a "top fermentation." The former is used for lager beers, and the latter for ale, porter, and stout.

In the **bottom fermentation** the active fermentation does not begin for 12 to 18 hours after pitching. Then a scum appears on the wort, and is blown into a foam by the escaping carbon dioxide. After three or four days this foam rises to the top, or even several inches above the top of the butt, while its surface is broken by deep cracks. The carbon dioxide escapes over the sides of the butt, and

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* Lactic or acetic fermentation, which would sour the beer, is apt to take place during the cooling. To prevent infection of the wort by bacteria and wild yeasts, systems for ventilating the cooling rooms with filtered or sterilized air are often used.

† This apparatus has generally replaced the old-style, shallow cooling pans in which the wort was exposed to the air in a broad layer only a few inches deep.

falling to the floor is usually carried away by an artificial draught.* Finally the surface of the foam shows a brown color, and in six or seven days the active fermentation diminishes, the temperature falls, and the yeast settles to the bottom. After ten days the active fermentation ceases entirely, and the new beer is drawn into **storage vats,** carrying with it some yeast, which sets up an after-fermentation; the maltose remaining is slowly decomposed, and substances are formed which improve the flavor. These casks are of oak, coated with pitch inside, and usually holding about 1500 gallons. The temperature during this period is kept low, and air is given free access to the liquor. The yeast grows thriftily, and consumes more of the albumins, so that lager beers are lower in these, and are more stable than top-fermentation beers. The time of this storage varies from three to six months. To assist in clarifying it, the beer is usually drawn into "**chip casks,**" in which are shavings of beech wood which have been well cleaned by boiling with sodium carbonate. For the same purpose, isinglass dissolved in tartaric or sulphurous acid is usually added in the chip casks, together with some actively fermenting young beer. The yeast cells attach themselves to the shavings, and the beer is left clear.

Top fermentation is usually employed in England, and largely in this country for ales, etc. The fermentation is very active, usually ending in from three to five days, and the yeast is partly carried to the surface of the wort by the rapid evolution of the carbon dioxide. A certain amount of bottom yeast is also formed. The top yeast is removed by skimming, and the beer is drawn into small casks, holding from two to four barrels each for the after-fermentation. These

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* The amount of carbon dioxide formed is said to be about equal to the weight of the alcohol. Methods have recently been devised to save this gas for use in refrigerating machines, or for carbonating the finished beer. It is evolved rapidly and regularly for some time, and is collected in a hood let down over the fermentation vat to within a few inches of the surface of the liquid. The level of the gas is gauged by means of a toy rubber balloon, filled with air, which floats on the surface of the gas. The carbon dioxide is carefully pumped from the hood so that no air is drawn with it. It is then purified by passing through water, and then through a solution of potassium permanganate, and finally through concentrated sulphuric acid. It is compressed at about 60 atmospheres, and then passed through cooling coils for condensation. The compressed gas is said to be about 99 per cent pure, and is used to some extent to force the beer through the various pipes from the storage cellar to the place where it is drawn into casks or bottles, thus replacing pumps with their contaminations. It is also used in the cooling machines, being circulated through the coils instead of brine or water. It is very satisfactory for this purpose, since the escaping gas does no harm in case there is a leak. About 2200 pounds of liquid carbon dioxide are said to be obtained from 600 barrels of wort. A. Marcet, J. Soc. Chem. Ind., **1894**, 825.

casks are placed in a cold room, and the process goes on until most of the yeast has been forced out of the bung-hole. The cask is then bunged and allowed to stand until the sediment has deposited, when the clear beer is drawn off into barrels for market. Isinglass or gelatine is often added to assist in settling the sediment.

Top fermentation is favorable to the development of other ferments, and a high percentage of alcohol is often depended upon to prevent these growths. In order to increase the alcohol and dextrin without increasing the quantity of malt, it is frequently customary to add sugar or glucose to the wort in the brewing kettle.

During the fermentation the contents of the tub are stirred occasionally to aerate the wort. The progress of the fermentation is judged by the readings of a hydrometer, and as the density of the wort *decreases* as the fermentation advances, the process is called "attenuation." The temperature is carefully watched, and not allowed to rise above 18° C.

In fermentation by the "**vacuum process**,"* the wort is fermented in closed, enamelled iron vessels, from which the carbon dioxide is pumped away as liberated. Thus the time of fermentation and storage is reduced, and wild yeasts and bacteria are excluded. The gases pumped away are led through cooling pipes to condense some of the aromatic flavoring matters, which are returned to the beer after the fermentation is completed. The beer is finally recharged with CO_2 under pressure, just before bottling or barrelling.

Besides alcohol and carbon dioxide, beer contains glycerine, succinic acid, amides, peptones, and dextrins. Phosphoric, acetic, and lactic acids are also present in a small quantity. All the soluble constituents of the beer, except the alcohol and carbon dioxide, and which give it its nutritive qualities, are grouped together under the name of "**extract**." English ales, porters, and stouts are rich in extract, but most German and American beers contain only a moderate amount of it.

Sometimes beer is flavored with bitter substances, such as quassia and gentian root; or ginger or coriander may be added for pungency, but this is prohibited in many countries.

Bottling or **Barrelling**. — Much of the success with which certain beers meet in commerce is due to the care exercised on this point. The barrels are coated on the inside with brewer's pitch, a mixture of rosin and rosin oil which softens at 50° to 60° C. This prevents the beer from soaking into the staves and extracting color or flavor

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* J. Soc. Chem. Ind., **1898**, 1064.

from the wood. All barrels, and especially old ones which are returned for refilling, should be thoroughly scalded and washed out. If this is not done, the beer is liable to sour before it reaches the consumer. It is frequently customary to fume the barrels with sulphur dioxide or to wash them with sulphurous acid or bisulphite of calcium solution. Fluoride of sodium is sometimes used to wash the yeast and in cleaning the fermentation tubs. This prevents the development of injurious ferments. Salicylic acid is often added to improve the keeping qualities, but with doubtful benefit to the consumer.

Bottles must be clean and only the best quality of corks should be used. Bottled beer is usually "Pasteurized" at 60° C. for about an hour. It is essential that both barrels and bottles should be entirely full, for if an air space is left, the beer becomes flat and stale.

The quality of beer depends mainly on the purity of the water and yeast employed, and upon the care taken to keep all parts of the brewery exceedingly clean. All vats, tubs, coolers, and pans must be thoroughly washed and scalded immediately after use, and the floors and walls of the brewery must be perfectly clean.

Various kinds of beers are recognized in commerce, according to the appearance, mode of preparation, flavor, strength of alcohol and of extract, etc.

Ale is a light-colored beer, often rather strong in alcohol, and made by top fermentation with the use of a large amount of hops.

Porter is a dark-colored beer, containing much sugary matter and extract. For this, the malt is kiln dried at such a high temperature that it is partially charred, forming caramel, which colors and flavors the beer.

Stout is similar to porter, but contains more alcohol and extract.

Lager beer is made by bottom fermentation, is rather low in alcohol, and contains a moderate amount of extract. Export lagers are made from stronger worts and contain more alcohol and extract. A special brew made in the spring from very concentrated wort and but little hops is called **bock beer** or **Salvator beer.** It contains much unfermented sugar and will not keep long.

Berlin weiss-bier is made from a mixture of two parts malted wheat to one of barley malt. It is fermented by top fermentation, and is usually bottled before the after-fermentation is ended. Thus it contains much carbon dioxide and foams excessively. It is very light-colored and contains lactic acid.

The following table shows the average composition of beers according to various authors: —

	Sp. Gr. (17.50° C.)	Alcohol	Extract	Acids (Acetic, Lactic, etc.)	Ash
Vienna lager*	1.017	3.70	5.71	0.008	—
Pilsner lager*	1.016	3.43	5.45	0.008	—
Munich export*	1.020	3.94	6.72	0.010	—
Munich Salvator*	—	4.78	10.67	—	—
Berlin weiss-bier*	1.012	2.82	4.21	—	—
Burton pale ale†	—	5.37	5.13	0.16	0.55
Dublin stout XXX†	—	6.78	9.52	0.29	1.40
Milwaukee lager‡	1.010	4.28	4.18	0.057	0.196
Milwaukee Bavarian‡	1.0187	5.06	6.26	0.074	0.346
St. Louis export‡	1.0178	4.40	6.15	0.067	0.312
Philadelphia lager‡	1.0147	4.29	5.22	0.086	0.241

DISTILLED LIQUORS

Distilled liquors are obtained by distilling alcoholic liquids prepared by fermentation. They are essentially mixtures of ethyl alcohol and water in varying proportions with minute quantities of organic ethers and higher alcohols. Pure ethyl alcohol may be considered the representative and chief constituent of these liquors. When first distilled, they contain neither extractive nor mineral matter, and are much stronger in alcohol than fermented liquors.

Alcohol is always prepared on a technical scale by fermenting sugar, which in most cases is derived from starch by conversion with diastase, or from the molasses of the sugar industry. In the United States the materials employed are corn, rye, and barley; in England, barley, rice, corn, and rye are used; while in Germany, the potato and molasses are the principal sources. The products obtained from these several raw materials vary somewhat in their character, flavor, and strength.

Since the largest possible yield of alcohol is desired from a given amount of starchy material, the latter is so treated that the most complete conversion into maltose is obtained with as little dextrin as may be. This is accomplished by treating the starchy material with malt prepared with the view of obtaining all the diastase possible. For this purpose, the germination is stopped earlier and the drying temperature kept lower than in the case of malt for brewing. The preparation of **pure alcohol from corn** is carried on about as

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* Ost, Technischen Chemie, 2te Auf., p. 455.

† Allen, Commercial Organic Analysis, Vol. II, 2d ed., p. 92.

‡ Crampton, U. S. Dep't Agriculture, Bulletin No. 13, part 3, p. 282.

follows: The corn, usually degerminated, is ground to a coarse meal, and a weighed amount of this meal is run into a closed iron digester (called a " cooker ") provided with a stirring apparatus. Here it is mixed with water and heated by steam under two or three atmospheres' pressure for an hour or so. It is then blown out into another vessel; or it may be cooled in the cooker. (The cooling is sometimes hastened by exhausting the vapor from the vessel by a pump.) When the temperature reaches 63° C., the required amount of ground malt, mixed with a little water, is added and the mass well stirred. The temperature should not be above 63° C., in order that the least possible amount of dextrin may be formed. The resulting wort is drawn off through a sieve to remove the grain husks, which are washed with hot water and the washings added to the wort. This is then rapidly cooled (to prevent the development of acetic fermentation) and drawn into the fermenting vats. These are large cylindrical wooden tubs (sometimes 25 feet deep by 20 feet in diameter), one being emptied and another recharged every day. The fermentation of the wort is started by adding yeast, as in brewing; but for alcohol, the quantity of yeast and the temperature of fermentation are regulated with a view to converting all of the sugar into alcohol as rapidly* and completely as possible. Too slow fermentation favors the development of the acetic and lactic fermentations, with resulting loss of alcohol. The temperature is high, being 20° to 25° C., and an active top fermentation is carried on. If the temperature rises much above 25° C., some loss of alcohol by evaporation occurs. During the final part of the fermentation, some of the dextrin in the wort is converted into maltose by diastase still remaining, and this sugar is also fermented by the yeast.

To prevent the development of bacteria and wild yeasts, a little hydrofluoric acid, or alkali fluoride, is often added to the mash, after the conversion of the starch by the diastase. It increases the yield of alcohol by preventing secondary fermentations, and tends to reduce frothing. It is also used as a disinfectant and germicide for general cleaning of the tubs and vats.

When the fermentation ceases, the mash consists of a mixture

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* The legal limits of time within which fermentations must be completed are: For sweet-mash distilleries (where specially prepared yeast is added directly to the wort), 72 hours; for sour-mash distilleries (in which the fermenting agents used are the spent beer, or slop, and barm from a tub previously fermented), 96 hours; and for rum distilleries, 144 hours. At the end of these periods the fermenting tub *must* be emptied; it may be emptied in less time, but cannot be refilled until the full time limit has expired.

of slimy, solid matter, with water, alcohol, fusel oil, acids, etc. The amount of alcohol varies from 10 to 13 per cent by volume, and is separated from the other constituents by distillation. This was formerly carried on in simple stills,* heated by direct firing, and connected with a condensing worm. They were intermittent in action and yielded a very dilute distillate, which had to be repeatedly redistilled to obtain a strong alcohol; thus, *e.g.* from a mash containing 10 per cent alcohol, the first distillate contains about 28 per cent alcohol; by redistilling this distillate, the alcohol percentage is raised to 50 per cent; by another redistillation it is raised to 70 per cent, and this in turn yields an 80 per cent alcohol. By many redistillations, an alcohol of 95 per cent may be obtained, but above this redistillation yields no further separation.

But the principle of fractional condensation is now employed, and improved stills, with dephlegmation and rectifying apparatus, make it possible to obtain concentrated alcohol by two distillations. The old interrupted working has given way to continuous processes, by which the inflow of mash and the outflow of spent mash (slops) are unbroken.

For distilling potato mashes, which are thick and slimy, no continuous-acting still has proved successful, and the intermittent **Pistorius apparatus**, consisting of two connected stills and a dephlegmator, is much used. The **Coffey still** (p. 12) in various modified forms is largely used for grain mashes; the mash† enters the analyzer hot after having passed through the rectifier. From the top plates of the rectifier, the alcohol vapor passes into a copper condensing worm, which empties into a small box with glass sides, through which the density of the liquid may be observed by means of an hydrometer floating in it. The box is locked and sealed by the revenue officer stationed in the distillery, and the distiller has no access to the liquor. It overflows into tanks where it is gauged by the revenue officer as "**high wines.**" It contains some aldehyde and **fusel oil**; the latter, constituting the greater part of the impurities present, imparts a nauseous odor and taste, and is removed by further purification. The raw spirit is diluted with water and run through a wood-charcoal

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* The old pot stills are now used for the distillation of certain drinkable spirits (especially whiskey), but they are uneconomical of fuel and time.

† By its passage through the still, the mash is entirely deprived of its alcohol, but the non-volatile matter, consisting of fats, protein, undecomposed starch, and other non-nitrogenous bodies, flows continuously from the waste pipe of the still. This residue usually contains over 90 per cent water, and is often fed as "slop" to cattle.

filter similar in form to the bone-char filter used for glucose; the charcoal adsorbs* the fusel oil. Another method (that of Bang and Ruffin) is to treat the alcohol with caustic soda and then with dilute sulphuric acid to destroy the aldehydes; the diluted alcohol is then agitated with petroleum distillates boiling slightly above 100° C. The petroleum oil probably absorbs the fusel oil.

The dilute purified alcohol is then rectified in a still provided with a column or dephlegmator tower, similar to the Coupier still or French column apparatus, Figs. 7 and 8. Savalle's apparatus is largely used abroad. Rectification is an intermittent process, the still being entirely emptied and cleaned before a new charge is introduced. The boilers are very large and are usually made of iron.

The products of the distillation are divided according to their character and percentage of alcohol into: —

(*a*) First runnings, consisting of some alcohol, with aldehyde and ethers.

(*b*) Alcohol (cologne spirits) a very pure distillate, with 95 to 96 per cent of alcohol.

(*c*) Commercial alcohol, containing 80 to 95 per cent alcohol.

(*d*) Fusel oil.

These distillates are separated by the revenue officer, who turns the flow from one receiver into the next, according to the densities shown by the hydrometer floating in a glass box similar to that described on p. 458 and through which the distillates pass. First runnings and fusel oil are usually sold to chemical works. The alcohol distillates are marketed directly.

The Coffey still and others on the same principle are well adapted to the direct production, from the mash, of pure alcohol, or, as it is generally called in England, "silent spirit," since it has no special odor nor flavor to distinguish its origin, as is the case with pot stills.

In all countries the manufacture of strongly alcoholic liquors is made a means of raising revenue by the government. Consequently these industries are subject to constant, and often annoying, interferences by the revenue officials, and many burdensome laws are enacted, presumably to prevent fraud. In this country, both the malt and the grain used in the mash are weighed by the revenue officer, the time of fermentation is limited, and the entire process of distillation is conducted under the direct supervision of the inspector. The amount of crude spirit produced is gauged by the officer, and also the quantities of the several grades of rectified alco-

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* J. Am. Chem. Soc., **30** (1908), 1784. W. L. Dudley.

hol produced, and these are run directly from the still into storage tanks in the government storehouse. From these tanks it is drawn into barrels (which must be new), and each cask is at once gauged by the officers, and the number of gallons of alcohol contained in the liquor, and upon which the tax must be paid, is determined. The cask is then put into the bonded warehouse, where it remains until the tax is paid (but not longer than seven years). The tax levied is $1.10 per gallon (231 cubic inches) of "**proof spirit**,"* (or 100 proof alcohol) or $2.08 per gallon of ordinary 95 per cent alcohol. If the liquor is stronger than 50 per cent alcohol per gallon, it is designated as "above proof," and the tax is estimated on the number of gallons of "proof spirit" which can be made from it by dilution. If under 50 per cent strength ("below proof"), no reduction is allowed, and it is taxed as if of "proof" strength. Thus absolute alcohol is rated as "100 above proof," or simply "200 proof"; ordinary commercial 94 per cent alcohol is rated as 188 proof.

This tax was a heavy burden on such industries as use alcohol for manufacturing purposes. Most governments now permit the manufacture of "**denatured**" alcohol for industrial use, and this is free from tax. Various substances may be added to the alcohol for the purpose of denaturing or rendering it undrinkable; for general use 10 gallons of crude methyl alcohol and ½ gallon of benzine are mixed with each 100 gallons of 90 per cent ethyl alcohol; or to each 100 gallons may be added 2 gallons of methyl alcohol and ½ gallon of pyridine bases from bone oil. For various special industries the denaturants used are camphor, nicotine, methyl acetate, and other substances. In England the preparation of "**methylated spirit**," with 10 per cent wood spirits, has long been practised, to avoid the heavy tax of 10*s*. 6*d*. per gallon of proof spirit.*

In Germany a similar provision exists, but in addition to wood spirits, a certain amount of pyridine (bone oil) must also be added. This gives the "denaturated" alcohol a very offensive odor, but does not injure it for many uses.

Besides starch and sugars as raw materials for alcohol making,

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* "Proof spirit shall be held to be that alcoholic liquor which contains one half its volume of alcohol of a specific gravity of seven thousand nine hundred and thirty-nine ten thousandths (0.7939) at sixty degrees Fahrenheit." — U. S. Internal Revenue Laws, Jan. 1, 1900.

By act of the English Parliament, proof spirit is defined as "Alcohol of such strength that 13 gallons of the spirit have the same weight as 12 gallons of distilled water at 10° C. (51° F.)" Proof spirit contains 49.24 per cent of absolute alcohol by weight. The English gallon is the Imperial gallon equivalent to 10 lbs. of water at 62° F. and 30 inches barometric pressure.

cellulose has recently been brought into use for this purpose. According to the process of A. Classen,* sawdust or shavings are treated under 6 to 7 atmospheres' pressure in lead-lined, rotary digesters, with sulphurous acid; the cellulose is partly converted to fermentable sugar. The mass is systematically lixiviated with hot water, and the sugar solution neutralized with calcium carbonate, filtered, and then fermented with yeast. The "mash" is distilled. Yields of 24 to 27 gallons of alcohol per long ton of sawdust are claimed.

The waste liquors from wood-pulp making by the "sulphite process" after treating with hot sulphuric acid contain fermentable sugars;† attempts have been made to neutralize them with calcium carbonate, and then ferment for alcohol. The industry is still in the experimental state.

The **fusel oil** consists mainly of amyl alcohol, with some butyl, propyl, and allyl alcohols. It is always present in crude spirits, and, to a small extent, in the rectified alcohol and liquors. It is generally supposed to have a very destructive action on the health, and its complete removal from liquors has always been insisted upon. But recent experiments ‡ tend to show that, aside from the nauseous odor and flavor which it imparts to the liquor, it has little, if any, injurious effect on the system. The results ascribed to it are probably due to common alcohol. Fusel oil (amyl alcohol) is used largely in the preparation of the so-called "**fruit essences**," organic ethers, which are used in ice cream, soda water, sherbets, etc.

Alcohol is extensively used in the arts as a solvent; for shellac varnishes; in collodion and celluloid; for making transparent soaps; smokeless powders and other explosives; in perfumery; for making various essences, tinctures, and extracts in pharmacy; for vinegar making; and in chemical manufacturing for preparing ether, chloral, chloroform, ethyl nitrite, and various ethyl derivatives, especially for use in the coal-tar dye industry. A considerable amount is used in museums for preserving anatomical and other specimens.

Whiskey is a distilled liquor made from a mash of fermented barley malt, or malt and other cereals. The mash is prepared as described for alcohol (p. 457); after fermentation it is distilled from a pot still (or "copper"), and the distillate condensed in a worm, without dephlegmation. The first product, called "low wines," is

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* U. S. Consular Rep., Feb. 24, **1911**. Trans. Am. Inst. Chem. Eng., **1911**, 111. See also, Metallurgical and Chemical Engineering, **1916** (**14**), 134.

† J. Ind. Eng. Chem., **1912** (**4**), 54.

‡ J. Soc. Chem. Ind., **1891**, 312. A. H. Allen.

redistilled, and yields **foreshots**, **whiskey**, and **feints**, while spent lees are left in the still. The foreshots and feints are redistilled with the next charge, while the whiskey is diluted with water to about 55 per cent of alcohol, and then put in a bonded warehouse to age, or until the revenue tax is paid. During the aging the fusel oil in the liquor is formed into ethers, thus removing the nauseous odor and taste of the raw liquor, and imparting to it a pleasing aroma. This change is slow and the longer the aging, the richer the flavor of the liquor becomes. When first distilled, whiskey is colorless; but it takes coloring matter from the wood of the casks while aging, and acquires a light reddish-brown shade. This color is now generally imitated by adding some caramel.

Scotch whiskey is usually made from malted barley mash, which after fermentation is distilled in pot stills heated by direct fire. The malt used, having been dried over a fire of peat and coke, acquires a *smoky flavor*, which passes into the mash and thence, on distillation, into the whiskey. Frequently some " silent spirit " (p. 459) from a grain mash is mixed with the product of the malt distillation. **Irish whiskey** is made from a mash containing malt and some unmalted grain, especially rye, barley, wheat, or oats. It is distilled in large pot-stills, which have a partial condenser on the neck of the still, so that some distillate is returned to the still, and the whiskey contains about 67 per cent alcohol.

Imitation whiskey is often made by "compounding," *i.e.* diluting grain alcohol with water to about 55 per cent by volume and adding caramel with small quantities of flavoring substances and essential oils, to imitate the color, odor, and taste of the genuine whiskey. An empyreumatic flavor is obtained by adding a few drops of creosote to each cask.

Gin contains about 52 per cent of alcohol, and is made from a fermented grain mash in much the same way as alcohol, but the distilled liquor is left colorless, and is flavored by distilling in pot stills with juniper berries, anise seed, coriander, cardamon seed, calamus root, or fennel. The best gin is made in Holland, at Schiedam, from rye mash, and is distilled only in pot stills, with juniper berries.

Brandy is made by distilling wine, or the fermented juice of other fruit, such as apples, peaches, cherries, blackberries, etc. The best brandy (Cognac) is made by distilling a good quality of white wine, but much inferior stuff is made by distilling low grades of red wine. It is customary to leech the solid residues from wine-pressing with water, and to ferment the liquid so obtained; this is then distilled for inferior brandy. Cheap brandies are distilled directly from the wine, but fine grades are rectified once or twice. The distillate is colorless, but takes color from the casks. It is also customary to add caramel. Brandy contains from 47 to 54 per cent of alcohol, by volume, and owes its peculiar flavor to œnanthic ether. Pot stills are always used in order to preserve the flavors. Cherry brandy is extensively made in southern Germany, where it is called **Kirschwasser.** Some of the pits are crushed and added to the fermented juice, thus flavoring the product with bitter almond and prussic acid. Imitation brandy is made from grain alcohol by diluting and adding various flavoring matters (œnanthic ether, bitter almonds, catechu, etc.), and coloring with caramel.

Rum is made from fermented molasses or *megass* (macerated crushed sugar cane). It is twice distilled, and the new rum is colorless and has a disagreeable odor, which is removed by treating with charcoal and storing for a long time. It is often colored with burnt sugar. It contains about 72 per cent of alcohol, and its flavor is due to ethyl acetate and butrate. Jamaica rum is said to be flavored by putting sugar cane leaves in the still. Ethyl butrate is made on a large scale, and sold as "rum essence," to be used in making imitation rum from grain spirit.

Liqueurs and **cordials** are usually strong alcoholic beverages compounded from grain alcohol, with various flavoring essences. They are usually flavored with sugar cane.

Arrack is made by distilling *toddy,* the fermented juice of the cocoanut palm. It is sometimes flavored with poppy or hemp leaves, or stramonium juice. A distilled liquor made from malted rice and molasses is often sold as arrack.

Absinthe is made in much the same way as gin, but is flavored with wormwood.

VINEGAR

Next to the alcoholic fermentation in technical importance is the acetic fermentation, which is caused by a group of bacteria. These micro-organisms cause the oxidation of the alcohol, probably into aldehyde, and ultimately into acetic acid, thus: —

$$2\ C_2H_5OH + O_2 = 2\ C_2H_4O + 2\ H_2O.$$
$$2\ C_2H_4O + O_2 = 2\ C_2H_4O_2.$$

The specific acetic ferment is *Bacterium aceti,* but the related species, *B. Pasteurianum, B. xylinum,* and *B. Kützingianum,* doubtless cause more or less oxidation of the alcohol. For this oxidation the liquid must not contain more than 10 per cent of alcohol, and certain nitrogenous matters suitable for the nourishment of the ferment must be present.

The materials used for fermented vinegar are cider, wines, decoctions made from malt, beer which has not been boiled with hops, beet sugar solutions, diluted alcohol mixed with malt infusion, and occasionally glucose or molasses. The acetic ferment propagates rapidly in a liquid containing from 2 to 3 per cent of alcohol, nitrogenous matter, and phosphate of potassium, calcium, or ammonium, if the temperature is kept between 20° and 35° C. A thick film, or skin, forms on the surface of the liquid, and finally sinks, owing to its increasing weight, forming the "**vinegar mother**"; then the formation of acid ceases. If the fermentation is very active after the alcohol is all converted, the resulting acetic acid may itself be attacked and decomposed into water and carbon dioxide. This, however, does not take place if a fresh supply of alcoholic liquor is added. Under the most favorable conditions the ferment cannot live in a liquid containing much more than 13 per cent of acetic acid.

In the **Orleans process** of making vinegar from wine, oak casks of about 300 litres' capacity are used. The cask is filled about one-third full of strong vinegar containing some ferment, and about 10 litres of wine (previously filtered through beechwood shavings until clear) are added, and the whole allowed to stand at a temperature of from 25° to 30° C. After about eight days the wine has soured, and another portion of 10 litres of wine is added. This process is repeated until the cask is about half full, when about one-third of the vinegar is drawn off, and the process of adding fresh wine is resumed. This goes on, under favorable circumstances, for several years, until the cask becomes too full of sediment; then it is emptied, and thoroughly cleaned by washing and scalding with hot vinegar. The casks have openings at the top for the admission of air, and the fermentation is largely spontaneous.

The action of the ferment may be checked if the temperature falls too low; or if the wine added is very low in alcohol, it may not support the ferment, and the vinegar is decomposed into water and carbon dioxide. The ferment may also be weakened or destroyed by the presence of vinegar eels, *Anguillula aceti*, a species of microscopic worm, which deprives the ferment of the oxygen needed for its propagation.

The Orleans process is slow, but the resulting vinegar has a fine flavor and aroma.

Pasteur suggested a modification of the above process, in which the ferment is cultivated in a suitable liquid, and the alcoholic liquid is added regularly when the " mother " is well started. When the acid formation becomes slow, the " mother " is collected and washed, and used to start a new fermentation.

The " **quick vinegar process** " is now generally practised for fermenting malt decoctions, diluted alcohol, or the extract from any fermented mash. The liquid should be clear, and free from any sediment or slime. The fermentation is carried on in tall vats, or casks, about 12 feet high by 5 feet in diameter. These have perforated false bottoms, on which rests the filling of beechwood shavings, reaching nearly to the top of each cask. Over the shavings, a few inches below the cover of the cask, is a perforated wooden plate, through the holes of which short pieces of twine are drawn; 4 or 5 glass tubes are set in this plate, to permit the upward passage of the air. The beech shavings are boiled in water, and then soaked in strong vinegar, before filling into the vat. Their purpose is to spread the liquid into thin films, so that the oxidation may be rapid. They also serve as points of attachment for the ferment. The liquid to be fermented, a mixture of dilute alcohol and vinegar, is fed in a slow stream on to the top of the cover, through which it percolates, dripping from the ends of the twine upon the shavings. It comes in contact with the ferment on the shavings, and with the current of air passing up through the mass, and the alcohol is rapidly oxidized into acetic acid. The temperature within the vat rises, causing the air to rise and escape through the openings in the top, while fresh air enters through holes in the sides of the vat, just on a level with the false bottom, thus causing a continual circulation of fresh air within the vessel. The temperature is shown by a thermometer, and is kept as near 30° C. as possible, by regulating the temperature of the air admitted into the cask. If allowed to go too high, much alcohol is lost by evaporation, and the vinegar is weak. Too rapid an air current also evaporates much alcohol. The vinegar formed collects under the false bottom, and flows out through a siphon.

If the liquor does not contain more than 4 per cent of alcohol, it may all be converted by one passage through the vat, but the resulting vinegar is weak. Hence it is customary to add more alcohol, and run the liquor through the cask again. Or, as is often done, it flows through a series of vats.

Exact regulation of the strength and flow of alcoholic liquid, and of the amount of air admitted, is essential to successful working. Pure air and good ventilation of the room are also necessary. Considerable alcohol is lost by evaporation, amounting, even in good work, to about 15 to 20 per cent of that in the original liquid. The air leaving the converters is often washed with water to recover the vaporized alcohol and acetic acid. On an average, the vinegar produced contains about 6 per cent acetic acid, which may be increased to 10 or 12 per cent by proper regulation of the process; there is, however, a consequent diminished yield of vinegar. The time required to produce finished vinegar is from 8 to 12 days. The amount of alcohol added must be so regulated that the liquid leaves the vat still containing a small percentage of unchanged alcohol, for, if it is all converted, the oxidation extends to the acetic acid, and some may be lost through decomposition into water and carbon dioxide. Many accidents cause the process to go wrong, and much care is necessary to secure regularity of product and yield. If vinegar eels appear, it is customary to kill them by adding hot vinegar until the temperature of the vinegar running out of the cask has risen to 50° C.

The vinegars made from different sources vary in color, taste, specific gravity, and other properties.

Cider vinegar is usually made by spontaneous fermentation of cider in barrels with open bungs. Sometimes "mother" is added to hasten the action. It is yellow or brown in color, has an odor resembling apples, and contains malic acid.

Wine vinegar is light yellow or red, according as it is made from white or red wine, that made from the former being considered the better. It contains tartaric acid, and some acid potassium tartrate, with other matters derived from the wine, some of which influence the flavor of the product. It has a particularly agreeable aroma and taste, and is considered the finest for table use.

Malt and **beer vinegars** are brown in color, and contain dextrin and protein, and other extractive matters, together with acetic ether, which impart peculiar odors and flavor to them. They also contain phosphates and other mineral matter.

Spirit vinegars, made from diluted alcohol, are nearly colorless, and since they contain little or none of the extractive matter present in fruit or malt vinegars, they lack much of the flavor and odor of these. Sometimes they are colored with caramel, and are often flavored with one or more of the characteristic ingredients of cider, wine, or malt vinegars, and sold under these names.

Very weak vinegar will not bear much agitation nor handling without decomposition; it is often the practice to add a certain amount of sulphuric acid, under the pretence of preserving the vinegar when shipped. Good vinegar, however, is never treated in this way by reputable makers.

Imitation vinegar is often made from dilute acetic acid derived from wood distillation. This is colored with caramel, and generally flavored with acetic ether; but usually contains no phosphates, tartrates, nor other substances characteristic of true vinegar. Traces of empyreumatic matter are often present, which may give it a disagreeable flavor.

Vinegar is chiefly consumed as a condiment, or used for making pickles.

LACTIC ACID

A fermentation of some technical importance is that produced by certain bacteria, especially *Bacterium acidi lactici*, by which sugars are converted into lactic acid: —

$$C_6H_{12}O_6 = 2\ C_2H_4(OH)COOH.$$

These ferments are generally distributed on the surface of grains, fruits, and malt, thus finding access to mashes and worts; under favorable circumstances they grow exceedingly rapidly, and cause souring of the liquid. But since they cease to propagate after the liquid contains about 1 per cent of lactic acid, and as this acid is a good protection against the development of other bacteria, while it has but little effect upon yeast, it is often customary to allow the lactic fermentation to take place in connection with the alcoholic, especially in grain mashes for alcohol.

Lactic acid, $CH_3 \cdot CH(OH) \cdot COOH$, is prepared by fermenting a sugar solution, and neutralizing the acid, as soon as formed, with calcium carbonate. The solution of calcium lactate is concentrated, and the salt decomposed with sulphuric acid.

Lactic acid forms a syrupy liquid which is now used in dyeing and calico printing as a substitute for tartaric and citric acids, and for deliming skins previous to tanning. Antimony lactate is used in place of tartar emetic in mordanting.

REFERENCES

The Chemistry of Wine. G. J. Mulder. Translated by H. Bence Jones. London, 1857. (Churchill.)
Lehrbuch der Gährungs Chemie. Adolf Mayer, Heidelberg, 1874.
On Fermentation. P. Schutzenberger, New York, 1876. (Appleton.)

Traité general des Vins et de leurs Falsifications. É. Viard, Paris, 1884.
Die Bereitung, Pflege und Untersuchung des Weins. J. Nessler, Stuttgart, 1889.
The Micro-organisms of Fermentation. A Jörgenson. Translated by H. T. Brown. London, 1889.
Traité pratique de l'Art de Faire le Vin. Frederic Cazalis, Paris, 1890.
L'art de Faire le Vin avec les Raisins secs. J. F. Audibert, Paris, 1891.
Études sur la Bière. M. L. Pasteur, Paris, 1876. (Gauthier-Villars.)
Lehrbuch der Bierbrauerei. Carl Lintner, Braunschweig, 1878. (Vieweg.)
Gährungs-Chemie für Praktiker. Josef Bersch, Berlin. (Wiegandt, Hempel, und Parey.)
  Vol. I. Die Hefe und die Gährungs Erscheinungen. 1879.
  Vol. II. Fabrikation von Malz, Malzextract und Dextrin. 1880.
  Vol. III. Die Bierbrauerei. 1881.
The Brewer, Distiller, and Wine Manufacturer. John Gardner, Philadelphia, 1883. (Blakiston, Son & Co.)
The Theory and Practice of Modern Brewing. Frank Faulkner. 3d ed. London, 1888. (F. W. Lyon.)
Handbuch der Bierbrauerei. Conrad Schneider u. Gottlieb Behrend, Halle, a. S., 1891. (W. Knapp).
Chemistry in the Brewing Room. Chas. H. Piesse, London, 1891.
Manual of Brewing. E. G. Hooper. 4th ed. London, 1891.
A Textbook of the Science of Brewing. E. R. Moritz and G. H. Morris, London, 1891. (E. & F. N. Spon.)
La Bière. L. Lindet, Paris, 1892 (?).
Les Distilleries. M. Désiré Savalle, Paris, 1881. (G. Masson.)
A Practical Treatise on the Raw Materials and the Distillation and Rectification of Alcohol. Wm. T. Brannt, Philadelphia, 1885.
L'Alcool. Albert Larbaletrier, Paris, 1888. (Bailliere et Fils.)
A Treatise on Alcohol, with Tables of Spirit-Gravities. Thomas Stevenson, London, 1888. (Gurney & Jackson.)
Traité de la Distillation. J. Fritsch et E. Guillemin, Paris, 1890.
La Fabrication des Liqueurs et des Conserves. M. Ch. Girard, Paris, 1890.
Nouveau Manuel complet de la Distillation des Grains et des Mélasses. Albert Larbaletrier et M. F. Malepeyre, Paris, 1890.
Les Appareils de Distillation et de Rectification. Émile Barbet, Paris, 1890.
Traité de la Fabrication des Liqueurs et de la Distillation des Alcools. P. Duplais, 2 vols., 7me éd., Paris, 1900. (Gauthier-Villars.)
Das Flussäureverfahren in der Spiritusfabrikation. M. Maercker, Berlin, 1891.
La Rectification de l'Alcool. E. Sorel, Paris, 1894 (?). (G. Masson.)
Chemie du Distillateur. M. P. Guichard, Paris, 1895. (Bailliere.)
Industrie de la Distillation, Levures et Alcools. M. P. Guichard, Paris, 1897.
Études sur le Vinaigre. M. Pasteur, Paris, 1868.
Acetic Acid and Vinegar, etc. John Gardner, London, 1885. (Churchill.)
A Treatise on the Manufacture of Vinegar. Wm. T. Brannt, Phila., 1890.
Die Essigfabrikation. J. Bersch. 5te Auf. Wien, 1901.
The Principles and Practice of Brewing. W. J. Sykes, London, 1897.
The Laboratory Text-Book for Brewers. L. Briant, 2d ed., London, 1898.
The Soluble Ferments and Fermentation. J. Reynolds Green, Cambridge, 1899.
Les Fermentations Rationnelles, par Georges Jacquemin, 1900.
Micro-organisms and Fermentation. Alfred Jorgensen. Trans. by Alex. K. Miller and A. E. Lermholm. 3d ed., London, 1900. (Macmillan & Co.)
Ferments and their Actions. Carl Oppenheimer. Trans. by C. Ainsworth Mitchell. London, 1901. (Griffin & Co.)
Manual of Alcoholic Fermentation. By Chas. B. Matthews, London, 1901.
Enzymes and their Applications. By J. Effront. Trans. by Samuel C. Prescott, New York, 1902. (Wiley & Sons.)

Handbuch der Spiritusfabrikation. M. Maercker. 8te Auf. 1903.
The Chemical Changes and Products resulting from Fermentations. R. H. A. Plimmer, London, 1903. (Longmans, Green & Co.)
Manufacture and Exportation of Alcoholic Beverages and Canned Goods. H. W. Wiley. Bul. No. 102, Bureau of Chemistry, U. S. Dep't of Agriculture, 1906.
Regulations and Instructions concerning the Tax on Distilled Spirits. No. 7, Revised Sept. 16, 1908. U. S. Internal Revenue.
The Nature of Enzyme Action. W. M. Bayliss, London, 2d ed., 1911.
Alcoholic Fermentation. Arthur Harden, London, 1911.

EXPLOSIVES

Explosives are chemical compounds or mechanical mixtures which are capable of very rapid decomposition or combustion, upon the application of a shock, or of a small amount of heat. Through the agency of chemical action they *suddenly* generate large volumes of gas, which is heated to a high temperature at the moment of liberation. Explosives comprise gases, liquids, and solids. Explosive gas mixtures will not be considered here, since, except in gas-engines, they have no technical application, though often introducing dangerous complications in certain technical processes. Finely divided organic matter, or oxidizable substances (*e.g.* magnesium powder) suspended in air, may if ignited cause violent "dust explosions," which constitute a serious danger in various manufacturing processes. Liquid explosives, excepting only nitroglycerine, which is seldom used in the liquid condition, have little or no industrial importance, since being extremely sensitive to shocks and heat, they are too dangerous to handle or transport; for the same reasons many endothermic bodies, such as the halogen compounds of nitrogen, and the diazo-bodies are not employed.

When the combustion takes place under such conditions that the gases formed cannot readily escape, a very high pressure is suddenly developed, owing to the great amount of heat generated. Some explosives can be fired by heat or ordinary shock, but others require the sudden and excessive pressure developed by certain violent explosives called "**detonators,**" such as the fulminates of mercury or silver, and the azide of lead. Detonators have extreme shattering power. Detonation is necessary to initiate the complete break-down of certain relatively stable molecules; it is not unlikely that detonation produces atomic vibrations in the molecule itself sufficient to start an excessively rapid disintegration.

The energy of an explosive is mainly determined by the amount of gaseous products formed by its decomposition, the rapidity of their evolution, and the temperature to which these gases are heated. It has been calculated that the explosion of one kilogram of dynamite in the form of a cube, measuring 9 cm. on the side, occupies $\frac{1}{50000}$ of a second, while the same weight of ordinary black powder requires $\frac{1}{100}$ of a second. But the volume of gas set free by the dynamite is about 530 liters when reduced to 0° C. and at 760 mm. pressure;

while the gas from gunpowder, under the same conditions of temperature and pressure, amounts to about 270 liters. Moreover, the temperature of the gas from the dynamite is very much higher than is that from gunpowder.

Nearly all explosions caused by chemical action are merely rapid oxidations of substances containing carbon, hydrogen, or nitrogen. The slower the oxidation the weaker the explosion, while for the most energetic action the combustion must be practically instantaneous. The speed of the oxidation depends largely on the size of the particles of the explosives, and also upon their composition. Chemically homogeneous substances are usually more powerful explosives than the most carefully prepared mixtures, since in the former the combustion is propagated from molecule to molecule more rapidly.

Explosives which decompose suddenly cause a very different result than those which are slow-burning. The former, even when exploded in the open air, have a shattering action upon any substance with which they are in contact. They are used in hard-rock blasting, especially where large pieces of the stone are not desired, or when the rock is full of cracks or seams; fewer drill holes are needed, and the rock is shattered for some distance away from the blast. But for military purposes, for quarrying and blasting in soft rock or coal, slow-burning powder is preferable to the more powerful dynamite.

Gunpowder is a mechanical mixture, and is the oldest and a very important explosive. A doubtful tradition assigns its discovery to Berthold Schwartz, a monk at Freiburg, Germany, in the fourteenth century. It was used at the battle of Crécy in 1346, and again at Augsburg in 1353. It was probably derived from the formula of the "Greek fire" of the Orient. Its constituents are potassium nitrate, sulphur, and charcoal. Since these must be pure, the manufacturer generally purifies them. Only roll brimstone is used, and this is sublimed in Dejardin's, or other similar apparatus. The flowers of sulphur, which first distil over, are contaminated with sulphur dioxide, and are redistilled with a new portion of sulphur. The purified brimstone is finely ground in ball-mills, disintegrators, or under edge-runners, sometimes with the addition of a part of the charcoal. Bronze balls are used in the mill; the dust is carefully sifted.

The nitre is purified from chloride, or sodium nitrate, by several recrystallizations from pure water, the solution being stirred while cooling in order to separate fine crystals. These are washed with water while in the centrifugal machine, or on a draining platform. They are not usually dried before mixing.

Carbon for gunpowder is best obtained from charcoal prepared from light, soft woods, such as willow, poplar, alder, or buckthorn. Young trees cut in the spring when full of sap are preferred. The bark is removed, and the wood stored for about two years until thoroughly dried. It is then carbonized in sheet-iron cases, which are heated in retorts, from which the products of distillation may be collected or not, as desired. The temperature of the carbonization depends upon the kind of powder to be made. For black powder it ranges from 350° to 500° C.; for brown powder it does not exceed 280° C. When the carbonization is ended, the cases are removed and allowed to cool before they are opened. The charcoal is then sorted to secure uniformity in the product, and is stored for some time before grinding, to allow it to absorb all the oxygen possible; otherwise spontaneous combustion of the powdered charcoal is liable to occur.

Charcoal for black powder contains about 80 to 90 per cent carbon, 5 to 7.5 per cent oxygen, and 2 to 3 per cent hydrogen. That for brown powder contains about 70 to 75 per cent carbon, 20 to 35 per cent oxygen, and 4.5 to 5 per cent hydrogen. The residue, in each case, is ash.

The ground materials are weighed, due allowance being made for the moisture in the nitre, and then put into the **mixing machine**; this consists of a gun-metal cylinder revolving around a horizontal shaft, which turns in a direction opposite to that of the cylinder, and carries arms which stir up the mass as they revolve. After mixing, the "green charge" is sifted again, moistened with from 5 to 6 per cent of water, and spread on the bed of the **incorporating mill**. This is an edge-runner, having iron or stone rolls, which travel on a bed of bronze or stone. The rollers are usually about 15 inches wide, and weigh 3 to 4 tons each. They make 7 or 8 revolutions per minute, and the usual time of grinding a charge is from 3 to 6 hours. Travelling wooden scrapers push the charge from the sides of the bed into the path of the rollers. The charge is kept moist during the incorporating, but explosions, the causes of which are not easy to discover, occur frequently. Consequently, the mill is arranged to run as nearly automatically as possible, and the workmen leave the building during this process.

The "mill-cake" coming from the incorporating mill is lumpy, and is reduced to fine powder by passing through the "**breaking-down**

machine." This consists of two sets of gun-metal rolls, placed one over the other, the upper set being corrugated and the lower pair smooth. These rolls are set in movable bearings, which allow them to separate slightly, in case of any excessive pressure. The mill-cake is thus reduced to a fine meal, containing from 1 to 4 per cent of moisture. This is put into wood-lined metal frames, and pressed in an hydraulic press to the desired density, usually 300 to 450 pounds pressure per square inch being applied. The press-cake so formed may be as thick as desired, for special purposes, but is usually about one-half an inch thick. For common powder, this compact, dense press-cake is put through the **granulator**, which consists of two or three pairs of grooved or toothed rolls of gun-metal; between them are inclined oscillating sieves, which sift the material from one pair of rolls and deliver the coarse particles to the next pair, where they are again crushed. Under the whole series of rolls are two sieves, the upper having a No. 10 mesh and the lower having a No. 20 mesh. These remove the coarse particles, and the fine grains are run over several finer meshed sieves, to obtain various grades of sporting powder, and dust. The grains thus separated are **glazed**; *i.e.* the powder is placed in revolving wooden drums, in which, by rubbing against each other, the sharp corners and edges are worn off. Powder which has been heavily pressed is hard and dense, and takes considerable polish. For common grades, it is customary to add about one ounce of graphite to every 100 pounds of powder in the glazing drum. This coats the grains and fills the pores, thus protecting them from moisture and atmospheric influences.

After glazing, the dust is removed by sifting, and the powder is dried. It is spread in wooden frames having cloth bottoms, and these are placed in racks in a room through which a current of warm air is circulating, and which is kept at a constant temperature of 35° to 60° C., according to the nature of the powder. The temperature is raised slowly, and, after drying, the powder is cooled slowly, the entire process requiring about 24 hours. Sometimes the powder is dried in a stream of cold air which has been passed over calcium chloride, sulphuric acid, or quicklime, to dry it before it enters the dry-room. Many schemes have been devised for drying powder in vacuum, but they have not proved practical. After drying, the powder is given a final glazing, and is sifted to remove the dust, and is then ready for use.

Special forms of powder are used for particular purposes. The coarse grains are used for blasting, the fine grains for small arms, while the fine dust is not desirable for any purpose, except in fireworks. **Pebble** and **prismatic powders** are chiefly used for ordnance. The press-cakes of the "green charge" are cut into pebbles, which are glazed and dried like common powder, but the drying must be slow. For the prismatic powder, the green charge is pressed in hexagonal moulds to form short prisms, from $\frac{5}{8}$ to $1\frac{3}{4}$ inches in diameter. With the solid prism the burning surface continually diminishes as the combustion progresses, thus *decreasing* the rapidity of the gas evolution. For use in heavy ordnance, it is best that the evolution of gas (*i.e.* the combustion) shall be slow at first, until the inertia of the projectile is overcome, and then an increasing evolution of gas is desired. By perforating the prism with one or more holes, the combustion extends along the perforations into the interior, hollowing out the grain and continually increasing the burning surface, with consequent increased evolution of gas. Thus less strain is exerted on the gun, and greater velocity imparted to the ball. Fine-grain powders burn much more rapidly than do coarse-grain, and the strain on the gun is proportionately greater.

The United States army standard black powder is composed of: —

Potassium nitrate, 75 per cent by weight.
Carbon (as charcoal), 15 per cent by weight.
Sulphur, 10 per cent by weight.

The combustion of this powder in an unconfined state may be represented as follows: —

$$2\ KNO_3 + 3\ C + S = 3\ CO_2 + N_2 + K_2S.^*$$

But when exploded in a confined space under pressure, the reaction becomes very complex, and many other substances are formed. According to Debus,† it is represented by the following equation: —

$$8\ KNO_3 + 9\ C + 3\ S = 2\ K_2CO_3 + K_2SO_4 + K_2S_2 + 7\ CO_2 + 4\ N_2.$$

According to Guttmann,‡ some fifteen products are formed by the free burning of powder, of which the chief are potassium sulphate, potassium carbonate, carbon dioxide, nitrogen, and carbon monoxide.

The products of the combustion consist of about 57 per cent solids and 43 per cent gases, by weight. The pressure exerted by the

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[*] C. E. Munroe, Rec. U. S. Naval Institute, **4**, 21.

[†] Annalen der Chemie und Pharmacie, **265**, 312.

[‡] Industrie der Explosivstoffe, p. 309.

explosion of powder entirely filling a closed space is about 44 tons per square inch, or nearly 6400 atmospheres.

Brown or **cocoa powder** used for military purposes, especially for heavy guns, has slower combustion and less dense smoke than black powder. It contains about the following ingredients: —

Potassium nitrate	79	per cent
Sulphur	2 to 3	" "
Carbonaceous matter	18	" "
Moisture	0 to 1	" "

The carbonaceous matter is partially charred rye straw, which, it is supposed, is carbonized by exposing it to superheated steam until it takes on a light brown (chocolate) color. Owing to incomplete carbonization of the straw, the charcoal is readily combustible, and can be used with a small proportion of sulphur.

Mining powders of several grades are made by varying the proportion of nitre, sulphur, and charcoal, according as a quick- or slow-burning explosive is desired. These are generally coarse-grained, and are cheaper than the finer rifle powders. Sometimes they are made with sodium nitrate instead of with potassium nitrate, but this salt is somewhat hygroscopic and may absorb sufficient moisture to damage the powder. Potassium chlorate has been used instead of nitre, but it is more expensive and more dangerous in mixing and handling, owing to its sensitiveness to shocks. A **white gunpowder** was formerly made from potassium chlorate, potassium ferrocyanide, and sugar. It possessed no special advantages over common black powder. Barium and ammonium [*] nitrates have been used to replace the potassium salt, but being more costly, find no general use. A so-called "**amide powder,**" made in Germany, consists of ammonium nitrate with some potassium nitre. It forms little smoke or flame.

Gunpowder ignites at about 300° C., and the rapidity of combustion increases with the increase of pressure. Hence the importance of "tamping" in blasting.

Nitrocellulose, or **gun-cotton**, is prepared by treating cellulose fibre in a mixture of concentrated nitric and sulphuric acids. Its constitution was formerly considered to be that of a true nitro-body, having the formula, $C_6H_7O_5 \cdot (NO_2)_3$, but it is now regarded as a nitrate of cellulose. Eder,[†] assuming the formula of cellulose to be

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[*] Ammonium nitrate is used in mining powders to lessen the flame and high temperature of the explosion. Such powders are used in mines where fire-damp occurs.

[†] Zeitschr. f. angew. Chemie, **1901.**

$C_{12}H_{20}O_{10}$, concluded that the highest degree of nitration was found in the hexanitrate and proposed $C_{12}H_{14}O_4 \cdot (NO_3)_6$ as the formula for gun-cotton, and that the formation took place thus: —

$$C_{12}H_{20}O_{10} + 6\ HNO_3 = C_{12}H_{14}O_4 \cdot (NO_3)_6 + 6\ H_2O.^*$$

The decomposition on explosion is represented thus: —

$$C_{12}H_{14}O_4 \cdot (NO_3)_6 = 7\ CO_2 + 5\ CO + 3\ N_2 + 3\ H_2O + 4\ H_2.$$

Vieille † found eight different types of nitrocellulose, and proposed $C_{24}H_{40}O_{20}$ as the cellulose formula; his highest nitration product contained 13.47 per cent of nitrogen corresponding to the formula $C_{24}H_{29}O_9 \cdot (NO_3)_{11}$.

The amount of gas set free from one kilogram of gun-cotton is 982 litres (water as vapor) and the heat liberated is 1074 Cals.; ‡ the temperature of the explosion has been estimated as 6000° C.

Gun-cotton was discovered by Schoenbein in 1846, and attempts were made in several countries to use it for military purposes. But several spontaneous explosions of magazines occurred, which soon caused it to be given up. Von Lenk in 1849–1853 proved these explosions to be due to incomplete conversion in the nitration and the presence of free acid, left within the fibre. Cotton fibre is a long, hollow tube, much twisted and shrunken, into which the acid penetrates and is only removed with great difficulty, unless the fibre is cut and ground to a fine pulp. In 1865 Abel improved the process of manufacture by pulping and compressing the gun-cotton, and now, when properly made, it is considered one of the safest of explosives.

The cotton used § is the short fibre ("linters" ‖) removed from the seed husk after ginning, which has been carefully purified from the grease, dirt, and natural oil by a long "soda boil" (p. 505) followed by washing in hot water. After drying, the cotton is run through a "picker machine," to loosen the fibres, and then dried at 225° F. until the moisture is less than 0.5 per cent. It is then placed in sealed cans to cool. The nitration is effected with a cold mixture of 3 parts of pure sulphuric acid of sp. gr. 1.842, and 1 part of pure nitric acid of sp. gr. 1.52. The nitrating may be done in a cast-iron tank (*dipping pot*) cooled by a water-jacket. The apparatus will hold

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* Guttmann, Industrie der Explosivstoffe, 318.

† Moniteur scientifique, **1897**.

‡ Berthelot.

§ Met. Chem. Eng. **1915** (XIII), 361.

‖ For some purposes wood pulp, or pure tissue paper especially prepared, may be used for nitration instead of cotton.

from 120 to 250 lbs. of mixed acid, and about 2 lbs. of cotton (introduced in several small portions) are treated at one time. Each portion of cotton as introduced is quickly submerged in the acid by means of an iron or aluminum fork. After soaking 15 to 30 minutes, the cotton is raked out of the acid and drained on an iron grid, against which it is pressed by an iron plate connected with a lever, the excess acid flowing back to the tank. The cotton absorbs about 10 to 11 times its weight of acid, and this amount of fresh acid mixture is added to the tank before the next dipping. The gun-cotton is transferred to a centrifugal machine having a steel or earthenware basket and whizzed for a few minutes to remove as much acid as possible. The gun-cotton is then removed from the centrifuge, in small quantities at one time, with steel forks, and quickly plunged into a large vat full of cold water, and well stirred to dissipate the acid and keep down the temperature. Very often this washing is carried on in a hollander machine (p. 559), the drum of which is furnished with beaters instead of knives. When the cotton is no longer acid to litmus, it is boiled for about 48 hours, in wooden vats, heated by steam coils; the coils are surrounded by fine wire gauze, to prevent the gun-cotton from touching the hot pipes. The water is changed several times during the boiling, but the gun-cotton persistently retains traces of acid. To remove this acid the fibre is then pulped in hollanders having drums set with knives, as for paper making (p. 560). Often a little calcium carbonate is added towards the end of the pulping, to neutralize any remaining traces of acid. The pulp is then separated from the excess water in cloth-lined centrifugals, or in drainer vats having cloth laid on the perforated bottom. The wet pulp is then pressed to reduce the water content to the desired degree and to increase the density of the pulp. Well-made gun-cotton should not contain much more than 4 per cent of collodion cotton (soluble in alcohol-ether mixture).

For military purposes the gun-cotton pulp is compressed very heavily to form cakes of suitable size and shape for charging torpedoes and mines. The moist gun-cotton is safer to handle and transport, but will explode by detonation with a mercury fulminate cap. To prevent loss of the moisture, the blocks after compression may be coated with paraffine wax, or varnished with an acetone or ethyl acetate solution of nitrocellulose, which forms an impervious film; they are then enclosed in zinc or metal canisters.

Nitration in centrifugal machines is commonly practised and is more rapid and convenient than the use of dipping tanks and pots. An ordinary iron centrifugal is so constructed that the outlet pipe may be closed and the casing filled with mixed acid, submerging the perforated basket. A cover is provided with a large pipe, through which the fumes pass to the draught flue and fan. The perfectly dry cotton is introduced in single handfuls and worked into the acid with an iron prong or bar, while the basket is slowly rotated. When from 12 to 20 pounds of cotton have been introduced, the apparatus stands half an hour or more until nitration is completed. Then the outlet pipe is opened, the acid drawn off, and the basket set in rapid rotation, until the cotton is free from adhering acid. The gun-cotton is then quickly removed from the basket in small masses, by a pair of tongs, and at once submerged in a large tank of water. The subsequent washing and pulping of the gun-cotton are essentially as described on p. 477.

If a drop of water or oil falls into the gun-cotton in the centrifugal, decomposition of the whole mass ensues, with copious evolution of nitrous fumes, but as a rule there is no explosion, and only the loss of the cotton results.

Nitration by the **displacement process** of Thomson has been substituted for the centrifugal and dipping methods in some works. In this are used earthenware vessels, having a perforated false bottom, and a drain-cock below, through which the mixed acid is introduced into the vessel, and also drawn off at the end of the nitration. The vessel is covered with an aluminum hood from which the fumes evolved are drawn away by suction. The cotton is introduced in small portions until about 20 lbs. are in the apparatus and is left in the acid for two or more hours; a perforated iron or aluminum plate is then laid on top of the cotton, compressing it slightly, and finally water is run over the perforated plate in a slow stream, while the drain-cock is cautiously opened to allow the mixed acid to escape slowly at a rate corresponding to the inflow of water above the plate. Thus little diffusion of water into the acid takes place, and most of the acid is drawn off in a concentrated state suitable for re-inforcing with more strong acid. The temperature is also kept low, and there is less risk of decomposing the nitrated cotton. The washing and pulping of the cotton are similar to the previous processes.

Well-made gun-cotton is insoluble in water, alcohol, ether, and chloroform. It is somewhat soluble in acetone and in ethyl acetate, and swells to form a jelly-like mass with nitrobenzene. It resembles the original cotton in appearance, but is slightly harsher to the touch. It is not exploded readily by shocks, but explodes with great violence when detonated. When unconfined, it burns rapidly with a large flame. When not washed entirely free from acid, it is liable to spontaneous decomposition and explosion.

Lower cellulose nitrates are prepared as **collodion-cotton** or **pyroxyline**, for making smokeless powder, gelatine dynamite, blasting gelatine, etc. These collodion-cottons also enter into the composition of **celluloid** and various other plastics, photographic films, artificial silk, waterproof varnishes, and surgical dressings. Collodion-cotton is readily soluble in alcohol-ether mixture, and is made by immersing the cotton for one or two hours in a mixture of concentrated sulphuric acid with nitric acid of 1.45 sp. gr. The strength of the acid and the temperature and time of nitration influence the solubility of the collodion considerably.

Nitroglycerine, $C_3H_5(NO_3)_3$, was discovered in 1847, but no attempt to make practical use of it was made until about 1864, when Nobel established a factory and began its production on a large scale. But very soon a number of explosions occurred when handling and transporting the liquid, and means were at once sought to render it less dangerous. In 1866 Nobel invented **dynamite**, by absorbing the liquid nitroglycerine in diatomaceous earth, and this is now the form in which most nitroglycerine is utilized.

The name nitroglycerine is a misnomer which was given under the erroneous supposition that it contained the nitro group NO_2, but its true constitution was later shown to be glyceryl trinitrate. It is easily made by the action of concentrated nitric acid on glycerine: —

$$C_3H_5(OH)_3 + 3\ HNO_3 = 3\ H_2O + C_3H_5(NO_3)_3.$$

A mixture of 250 parts of nitric acid (98 per cent HNO_3) with 350 parts of sulphuric acid (96 per cent H_2SO_4) is used for each 100 parts of glycerine (sp. gr. 1.262, see p. 385). Nitroglycerine is somewhat soluble in both nitric and sulphuric acids, but is not dissolved by the mixture; hence, better separation is obtained after the nitration. The nitrating vessel is an iron or lead-lined, water-jacketed, covered tank, containing lead coils through which cold water is circulated. A rotating stirrer, or perforated pipe through which cold, dry air can be introduced, serves to keep the mixture agitated during nitration. In the bottom of the tank are large taps, leading to a vat beneath, containing a large volume of cold water. In case of dangerous rise of temperature during nitration, the entire charge can be quickly emptied into this "drowning tank," which stops further action.

The entire amount of mixed acid is put in the nitrator, and glycerine (at 20° to 25° C.) added in numerous fine streams from a perforated pipe, or sprayed in by an air-blown injector. The tank is covered, and a pipe carries away the fumes. The temperature * of the reaction, as shown by thermometers, must not rise above 30° C.; it is regulated by the rate of inflow of the glycerine, and by compressed air agitators or mechanical paddle stirrers. After the reaction is over, the entire charge is run into a separator tank, where it stands until the nitroglycerine, being lighter than the acid, all rises to the top. It is drawn off by an adjustable skimmer, which delivers it into a tank of water that is not colder than 15° C., lest the nitroglycerine freeze. The product is washed several times with water, and then with dilute sodium carbonate solution, to remove all traces of acid. The yield from 100 lbs. of glycerine is about 220 lbs. of product. Single charges of 2500 lbs. or more of glycerine are often nitrated in this way. The spent acids, further separated from any traces of nitroglycerine by standing a day or two, are then *denitrated* by treating with steam and air, or they may be used in the nitric acid retorts with sodium nitrate. Sometimes they are "revivified," by adding the required amounts of fuming sulphuric and nitric acids.

On explosion, nitroglycerine decomposes about as follows: —

$$2\ C_3H_5(NO_3)_3 = 6\ CO_2 + 3\ N_2 + 5\ H_2O + \tfrac{1}{2}\ O_2.$$

The volume of gas at 100° C. thus produced is about six times as great as from gunpowder, and the actual temperature of the explosion is much higher than that of gunpowder, being about 3000° C. as calculated by Wuic (quoted by Guttmann). The volume of gas produced by one liter of nitroglycerine is about 1135 liters. According to Ost,† the temperature of the explosion, as calculated from the observed heat of the explosion and the specific heat of the products of the combustion, is 6980° C. This temperature is probably too high, due to the use of low values for the specific heats of the gases and to disregard of the dissociation at high temperatures. Neglecting these factors, the pressure developed would be about 31,400 kilograms per square centimeter.

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* For better control of the process, Boutmy and Faucher mix the glycerine with part of the sulphuric acid, and cool the resulting sulphoglyceric acid, $C_3H_5(OH)_2 \cdot (HSO_4)$, or $C_3H_5(HSO_4)_3$. The nitric acid is mixed with the rest of the sulphuric, and after cooling, the sulphoglyceric acid is added; nitroglycerine is thus formed with much less heat evolved than when nitrating the glycerine directly. When using this process, several explosions occurred which were difficult to explain, and it has been generally abandoned.

† Lehrbuch der technischen Chemie, 5te Auf., 182.

Nitroglycerine is a heavy oily liquid of a pale yellow color and sweet taste. Its specific gravity is 1.60. It is insoluble in water, but dissolves in ether, benzene, methyl alcohol, and chloroform. It freezes at about 8° C. and thaws at about 12° C., though there is some variation in these points in different samples, according to their purity. It explodes when heated to 180° C., but burns in the open air without explosion, if in small quantities. It is very sensitive to shocks and may readily be detonated by a sharp blow. This sensitiveness is reduced by the addition of nitro-naphthalenes, and these are also claimed to prevent the freezing of dynamite.* When pure, it keeps indefinitely in a dark place, but exposure to sunlight increases its sensitiveness and may cause spontaneous explosion. Taken internally, it is very poisonous and is a powerful medicinal agent, somewhat resembling strychnine in its physiological effects; ten grains are said to be a fatal dose, while smaller quantities cause headache and vertigo; even when only in contact with the skin, it is said to cause violent headache. It is used as a remedy in *angina pectoris*, and is injected into the blood in cases of poisoning by carbon monoxide, or water-gas.

As an explosive, it is only used in the liquid state for "torpedoing" oil and gas wells (p. 338). When frozen, it is much less sensitive to shocks, and may be transported and handled with safety. But before use, it should be thawed by standing in a room warmed to about 20° C. It is one of the ingredients of a large number of high explosives which, although not so powerful as the nitroglycerine itself, are much safer and more convenient to handle. These explosives may be divided into two classes: (*a*) those in which the nitroglycerine is absorbed in some inert, non-explosive material, and (*b*) those in which it is mixed or combined with substances which are in themselves explosive. The most important example of the first class is **dynamite**; in this the nitroglycerine is absorbed in infusorial earth, white clay, pulverized mica, wood pulp, sawdust, or powdered charcoal. The chief requisite of a good absorbent or "dope" is that it shall hold the nitroglycerine without any oozing or dripping, otherwise the liquid spreads in thin films over the outside of the package, and becomes extremely sensitive to shocks, and very dangerous. Infusorial earth, often known by its German name, *Kieselguhr*, is much used in Europe as an absorbent. It is a white clay, containing a large amount of the frustules* of diatoms, which are chiefly minute tubes, into which the nitroglycerine is drawn by capillary attraction, and permanently held. The kieselguhr is calcined to dry it, and to

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* J. Soc. Chem. Ind., **1897**, 933.

* a siliceous shell

destroy organic matter, and is then mixed by hand with the requisite amount of nitroglycerine and a little calcined soda, to destroy any acidity. With three parts of nitroglycerine to one of kieselguhr, the dynamite is plastic, and contains 75 per cent of its weight of nitroglycerine. In America, wood pulp to which some sodium nitrate is added is commonly used as "dope." This will absorb about 75 per cent of nitroglycerine, and forms the **dynamite No. 1**, or **giant powder.** Weaker dynamite with 60, 40, or 20 per cent nitroglycerine is prepared for use where the No. 1 grade would cause too much shattering. Dynamite is packed into tubes of paraffined paper, and compressed by hand to form cartridges of convenient weight. It is not very sensitive to shocks, but is readily detonated by an explosive cap. In cold weather the nitroglycerine congeals, and such frozen dynamite does not give good results. It is best thawed by placing in a warm room for some time before use. Special water-jacketed warming pans are also used for thawing dynamite. It should never be heated over a stove or fire, as prolonged heating to 70° or 80° C. has caused explosions.

Most of the nitroglycerine explosives employed contain an active dope such as mixtures of sulphur, with sodium, potassium, or ammonium nitrate and powdered charcoal, wood fibre, or other carbonaceous matter. Examples of these are the various brands called Atlas, Forcite, Hecla, Hercules, Judson, and Vulcan powders, and carbonite, lithofracteur, stonite, vigorite, etc. The ammonium nitrate powders are much used in coal mining, where gas or dust explosions may follow a blast. Ammonium nitrate may be detonated, and as the temperature of its explosion is low (about 1100° to 1200° C.) it produces little flame, while absorbing some heat from the gases produced by the explosive with which it is mixed. Such powders containing ammonium nitrate, or salts with water of crystallization (Epsom salts, etc.), are often called "*safety explosives.*"

As typical examples of these explosives, the following will serve: —

ATLAS POWDER			JUDSON POWDER		FORCITE	
	Grade A	Grade B				
Sodium nitrate . .	2	34	Sodium nitrate . .	64	Potassium nitrate .	18
Wood fibre . . .	21	14	Sulphur	16	Gelatinized cotton	7
Magnesium carbonate	2	2	Cannel coal . . .	15	Nitroglycerine . .	75
Nitroglycerine . .	75	50	Nitroglycerine . .	5		

Forcite is a plastic mass, resembling rubber, impervious to water, and safe to handle. It is made by treating finely pulped cotton with high-pressure steam until the whole mass is converted into a jelly, which is then mixed with nitroglycerine at a temperature of 40° C., and powdered nitre is then added.

Nitrogelatine or **blasting gelatine** is made by dissolving soluble nitrated cellulose (collodion) in nitroglycerine. The latter is warmed to about 35° C., and the collodion slowly stirred in, until 7 or 8 per cent has been added. After a time the mass becomes viscous, and is formed into cartridges. It is not very sensitive to shocks, and may be made less so by adding 3 or 4 per cent of camphor. It is not affected by water and hence may be used for submarine work. It keeps well when stored, and is a more powerful explosive than dynamite.

Gelatine dynamite consists of blasting gelatine, mixed with wood pulp (4½ per cent) and potassium nitrate (26 per cent), together with a little sodium carbonate.

An explosive somewhat similar to blasting gelatine is **cordite**, a "smokeless powder," which has been adopted by the English government as a military explosive. This was patented by Abel and Dewar, and consists of: —

Nitroglycerine	58	parts.
Gun-cotton	37	"
Vaseline	5	"
Acetone	19.2	"

The nitroglycerine and gun-cotton are mixed by hand, the acetone is added, and the paste worked in a kneading machine for 3½ hours. The vaseline is then added, and the whole kneaded for 3 hours more. The paste is then forced through a spaghetti machine to form threads, which are wound on drums and dried at 40° C. for several days to evaporate off the acetone. The threads are then cut into convenient lengths for use in cartridges.

Smokeless powders are important for military and sporting purposes. They are probably too expensive for blasting and mining. The base of these powders is nitrated cellulose, which has been treated in various ways to render it slower in burning than gun-cotton, and also less sensitive to heat and shocks. As a rule, they are less inflammable than gun-cotton, and require stronger detonators. Since metallic salts cause smoke, they are not used in these powders. There are three general classes of smokeless powders now in use: (*a*) Those consisting of mixtures of nitroglycerine and nitrated cellulose, which have been converted into a hard, horn-like mass, either with or without the aid of a solvent. To this group belongs **ballistite**, containing 50 per cent nitroglycerine, 49 per cent nitrated cellulose (collodion), and 1 per cent diphenylamine;* also, **cordite** (see above), **Leonard's powder**, and **amberite**. This last contains 40 parts nitroglycerine and 56 parts nitrated cellulose. (*b*) Those consisting mainly of nitrated cellulose of any kind, which has been rendered hard and horny by treatment with some solvent, which is afterwards evaporated. These are prepared by treating nitrated cellulose with ether or benzene, which dissolves the collodion, and when evaporated leaves a hard film of collodion on the surface of each grain. Sometimes a little camphor is added to the solvent, and, remaining in the powder, greatly retards its combustion. (*c*) Those consisting of nitro-derivatives of the aromatic hydrocarbons, either with or without the admixture of nitrated cellulose; to this group belong **Dupont's powder**, consisting of nitrated cellulose dissolved in nitrobenzene; **indurite**, consisting of cellulose hexanitrate (freed from collodion by extraction with methyl alcohol) made into a paste with nitrobenzene, and hardened by treatment with steam until the excess of nitrobenzene is removed; and **plastomenite**, consisting of dinitrotoluene and nitrated wood pulp.

Another class of explosives which are not, however, much employed are the **picrates** and **picric acid**. By treating phenol, $C_6H_5 \cdot OH$, with concentrated nitric acid, tri-nitrophenol or picric acid, $C_6H_2(OH) \cdot (NO_2)_3$, is formed. The alkaline salts of this body (called picrates) are powerful explosives, but are too dangerous for use.

The salts of **fulminic acid**, $C_2H_2O_2N_2$, called **fulminates**, are exceedingly dangerous, being easily exploded by shocks or blows. The silver and mercury fulminates are the most important. The former is too dangerous for general use, but the latter is largely used as the "primer" in percussion caps. It is made by mixing a solution of mercuric nitrate and nitric acid with alcohol. It is a very dangerous explosive when dry.

Lead azide and other heavy metal salts of hydrazoic acid (N_3H) also find use as detonators, being stronger than the fulminates.

In order to avoid danger in shipping and handling, a class of explosives has come into use in which the ingredients, in themselves

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* Nitroexplosives tend to decompose slowly with evolution of nitrous acid; the acidity renders the explosive unstable. The diphenylamine serves to eliminate the nitrous acid as soon as formed.

non-explosive, are mixed immediately before use. These are called **Sprengel explosives**, from the name of the inventor; they are very powerful in many cases, and some of them are extensively used. **Roburite** consists of dinitrochlorbenzene, or possibly dinitrobenzene alone, mixed with ammonium nitrate. It does not explode by friction or shock, but is readily detonated. It yields hydrochloric acid in the combustion gases, and hence is disadvantageous in mining. **Bellite** and **securite** are somewhat similar to roburite. **Romite** contains nitronaphthalene, paraffine, potassium chlorate, and ammonium nitrate, in various proportions. **Ammonite** contains nitronaphthalenes and ammonium nitrate. **Rack-a-rock** is made from potassium chlorate soaked in nitrobenzene, or in the "dead oil" from tar. It is very powerful, and moderate in price. It was largely used in the removal of Hell Gate in New York Harbor. **Panclastite** is a liquid consisting of carbon disulphide with liquid nitrogen peroxide. **Hellhoffite** consists of nitro- and dinitro-benzenes dissolved in nitric acid.

Military explosives must be very stable against accidental shock. They comprise two classes, the propellants or explosives used in guns to drive the projectile, and high explosives used for shells, torpedoes, etc. The latter must be sufficiently stable against shock to be unaffected by the discharge of the gun, but capable of explosion by detonation. The basis of most propellants is nitrocellulose, the speed of explosion of which is controlled by the admixture of modifying substances, and by the shape and density of the grain, *e. g.* smokeless powders, p. 484. For shells the chief substances are picric acid and trinitrotoluol (T N T); the latter especially is stable to all influences except detonation and has the advantage of high density.

Melinite is a mixture of picric acid with collodion, or in one form is supposed to be fused picric acid alone, which has been melted in a carefully regulated oil-bath. It is used in France for a military explosive for shells, by the English Government as **lyddite**, and by the Japanese under the name "**shimose**."

In coal mines, especially where "fire damp" is prevalent, **lime cartridges** are sometimes used. These are made by compressing quicklime into cylinders, leaving a small hole down the middle. They are put into drill holes, and tamped with sand. Water is poured into the hole, and, passing into the perforated cylinder, wets the lime, which swells greatly on slaking, and exerts great pressure. The coal is broken down without any flame or concussion, and hence there is no danger from the gas.

REFERENCES

Tri-Nitroglycerine as applied in the Hoosac Tunnel. Geo. M. Mowbray, New York, 1874. (Van Nostrand.)
Notes on Certain Explosive Agents. Walter N. Hill, Boston, 1875.
Researches in Explosives. Captain Noble and F. A. Abel.
Part I. London, 1875. Part II. London, 1880.
Dynamite, ihre ökonomische Bedeutung und ihre Gefährlichkeit. Isador Trauzl, Wien, 1876.
Coton-poudre, nitroglycerine et dynamites. M. Pellet, Paris, 1881.
Zur la Force des Matieres explosives d'après la Thermochimie. M. Berthelot. 2 vols. Paris, 1883.
Die neuen Sprengstoffe. Isador Trauzl, Wien, 1885.
Les Explosifs modernes. Paul F. Chalons, Paris, 1886.
Manuel du Dynamiteur. La Dynamite de Guerre et le Coton-poudre. M. Dumas-Giulin, Paris, 1887.
A Dictionary of Explosives. J. P. Cundill, London, 1889.
Die gepresste Schiesswolle. Franz Plach, Pola, 1891. (E. Scharff.)
Explosives and Ordnance Material, etc. Stephen H. Emmons. Reprint from Vol. **17**, Proc. U. S. Naval Institute, Baltimore, 1891.
The Dangers in the Manufacture of Explosives. Oscar Guttmann, London, 1892.
Blasting. Oscar Guttmann, London, 1892.
Les Explosifs industriels. J. Daniel, Paris, 1893. (Bernard et Cie.)
Index to the Literature of Explosives. Chas. E. Munroe, Baltimore, 1893.
Die Industrie der Explosivstoffe. Oscar Guttmann, Braunschweig, 1895.
Die Explosiven Stoffe. Franz Boeckmann. 2te Auf. Wien, 1895.
Nitro-Explosives. P. Gerald Sanford, London, 1896. (Lockwood.)
A Handbook on Modern Explosives. M. Eissler, London, 1897.
Smokeless Powder, Nitro-Cellulose, etc. J. B. Bernardou, New York, 1901.
Lectures on Explosives. W. Walke, 3d ed., New York, 1902.
The Manufacture of Explosives. O. Guttmann. 2 vols. London.
Military Explosives. E. M. Weaver, New York, 1906.
Nitro-explosives. P. G. Sanford, London, 1906.
Die Explosivstoffe. R. Escales, 1908.
Nitrocellulose Industry. 2 vols. E. C. Worden, New York, 1911.
Journal of the Society of Chemical Industry: —
1890, 265. **1890**, 476. McRoberts. Blasting Gelatine.
1893, 1056. Sanford. Nitroglycerine.
1895, 507. Blomén. Nitroglycerine.

TEXTILE INDUSTRIES

FIBRES

Textile fibres are divided, according to their source, into vegetable, animal, and mineral. Of these only the first two will be considered here, since mineral fibres, consisting of asbestos, slag-wool, glass-wool, metallic wires, etc., are never subjected to any of the processes of bleaching, dyeing, or chemical treatment which come within the scope of this book, though they are sometimes used for packing, lagging, or filtering purposes in chemical works.

Vegetable fibres are plant cells of rather simple structure, usually forming a part of the plant itself. They are capable of withstanding high heat, and are not readily attacked by dilute alkalies to cause disintegration or weakening. They consist essentially of cellulose $(C_6H_{10}O_5)_n$, which may be pure, or mixed with its alteration products; in a few instances, the fibre as actually employed consists entirely of cellulose derivatives obtained by chemical means. Concentrated caustic alkalies form alteration products with vegetable fibre; free sulphuric, or hydrochloric acid, if strong, quickly destroys the fibre, but nitric acid forms nitrates, or oxidized derivatives.

Animal fibres are essentially nitrogenous substances (protein matter) often containing sulphur. They may consist of complex cell structures, or bundles of cells enclosed in a single envelope, or they are solid filaments formed from a liquid secreted by caterpillars, spiders, or certain mollusks. They are readily destroyed by hot alkalies, but withstand the action of mineral acids very well. They are much more easily injured by dry heat than are the vegetable fibres.

VEGETABLE FIBRES

Vegetable fibres are divided into two groups, — **seed hairs**, consisting of single cells, and **bast fibres**, consisting of bundles of fibre-cells joined together to form filaments of greater or less length. The most important vegetable fibres are cotton, flax (linen), hemp, jute, China grass, and esparto.

Cotton fibre consists of the seed hairs of several species of *Gossypium,* plants belonging to the *Malvaceae,* or mallow family. The most important commercial varieties are *Gossypium barbadense,* L. (Sea Island cotton), *G. herbaceum,* L., or *G. hirsutum,* L. (upland cotton of the southern states), *G. arboreum*, L. (Indian and Egyptian), and *G. Peruvianum*, Cav. (Brazil, Peru, and neighboring countries). The varieties are distinguished by difference in the length and fineness of the fibre or *staple*. The following table * shows the average length and diameter in inches of the principal commercial grades: —

	Length of Staple			Diameter of Staple
	Max.	Min.	Average	
Sea Island	1.80	1.41	1.61	.000640
New Orleans	1.60	.88	1.02	.000775
Upland	1.06	.81	.93	.000763
Egyptian	1.52	1.30	1.41	.000655
Brazilian	1.31	1.03	1.17	.000790
Indian	1.02	.77	.89	.000844

Thus it will be seen that the longest fibres have the least diameter; they are also silkier, and can be spun into the finest threads.

The fibres are attached thickly to the surface of the seed, and as they develop a mass of lint is formed which ultimately bursts the enclosing pod or boll. Each fibre consists of a single long cell; but as it grows the cell walls become thinner, and finally collapse to form a flat tube. After the boll bursts the liquid cell content solidifies by exposure to the sun and air, the dissolved matters are deposited somewhat irregularly on the different parts of the cell wall, and, consequently, the fibre twists into a spiral shape. Thus, as seen under the microscope, cotton fibre appears as an irregular, twisted, and flattened tube, tapering to a point at one end. The unripe fibres are comparatively straight, but if made into yarn they twist and curl, and are of little value; being difficult to dye, they cause specks in the dyed goods.

Cotton fibre consists essentially of cellulose enclosed in a film or outside skin of modified cellulose. On the surface is a deposit of wax and oily matter which protect it from the action of moisture, and which is removed in the bleaching process before dyeing or printing the cotton goods. The cellulose of the fibre is scarcely affected by cold dilute mineral acids, but if allowed to dry on the fibre the acid quickly attacks it. Concentrated sulphuric acid converts cotton into a gelatinous mass, from which water precipitates a starch-like body called **amyloid**.† By longer action of the strong acid, cotton is

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* Walter H. Evans, Bulletin No. 33, U. S. Dept. of Agriculture, p. 77.

† Parchment paper is produced by the short action of strong acid on paper, whereby a layer of amyloid is formed on the surface.

converted into a soluble compound (cellulose sulphuric acid), then into dextrin, and finally into dextrose.

Boiling in dilute alkalies has no injurious action on cotton if the air is excluded; otherwise there may be more or less formation of oxycellulose, which may weaken the fibre. When treated with caustic soda solution at 50° Tw.*, the fibre becomes rounded, swollen, and semi-transparent, and the interior cavity almost disappears, while a marked shrinkage in length takes place. It gains in weight and in strength, while its affinity for coloring matter is much increased. The fibre probably enters into combination with the alkali to form a compound of the formula $C_{12}H_{20}O_{10} \cdot Na_2O$, or $C_{12}H_{20}O_{10} \cdot 2\,NaOH$, which decomposes with water to form hydrocellulose, $C_{12}H_{20}O_{10} \cdot H_2O$. This action was discovered by John Mercer, hence the name "**mercerized cotton**" applied to fibre which has been so treated.

Mercerizing is extensively employed for producing a high lustre on cotton goods, so that it has a silky appearance. The material is held under tension on a frame while being treated with the caustic soda and until the caustic is washed out; or tension may be applied after the alkali treatment and before the caustic is washed away. Stretching after washing does not produce a lustre. The tension prevents, to a great extent, the shrinkage which would otherwise occur, but excessive stretching is said to decrease the lustre; apparently, less force is required to keep the cotton at its original length during mercerization than to draw it back to its first length afterward. The cotton is thoroughly wet out before mercerizing, to insure even action on the fibre. Special machines are used for yarn, warps, and cloth, the object of each being to prevent contraction and give even impregnation.

The time of washing is shortened by rinsing in water, then relieving the tension and washing with dilute acetic or sulphuric acid, at 0.5° Bé., while the temperature is raised to about 50° C.

Lange * describes the cotton fibre, mercerized under tension, as a straight, translucent tube, and he supposed the lustre to be caused by the parallel reflection of light rays from the smooth surfaces. Hübner and Pope † hold that the mercerizing liquid causes first a swelling and then an untwisting of the natural folds of the fibre; the ends being more or less firmly held, the untwisting of the swollen fibre produces the appearance of a "gelatinous straight rod, in which a series of pieces of corkscrew-like windings are visible," thus forming

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* Färberzeitung, **1898**, 197.

† J. Soc. Chem. Ind., **1904**, 410.

* sp. gr. 1.250

spiral ridges, with rounded edges, on its surface, which reflect the light falling on them from any direction.

The compound $C_{12}H_{20}O_{10} \cdot 2\ NaOH$ is called **alkali cellulose**; when exposed to the action of carbon disulphide fumes, a cellulose thiocarbonate or xanthate is formed. This body, when beaten with water, forms a thick solution called "**viscose**," which is easily decomposed by heat or certain salts, producing cellulose hydrate and free alkali, and liberating carbon disulphide. By squirting viscose through fine capillary tubes and causing this decomposition, a thread of cellulose having a silky lustre is produced. This viscose silk is very tender when wet, but is brilliant and takes dyes well. Viscose is also used for paper sizing, as a fixing agent in textile printing, and as a cement.

By treating cellulose with acetic anhydride in the presence of a little phenol-sulphonic acid at 80° C., cellulose tri-acetate is produced. It dissolves in chloroform, and acetylene tetrachloride, but is insoluble in water, and is used for films, waterproofing, insulation, and other purposes.

Flax or **linen** is the bast fibre of the flax plant, *Linum usitatissimum*, L. The individual fibres are long cylindrical cells, pointed at the ends, and having thick walls with a narrow central cavity. Each fibre is marked with transverse bands, and has a glistening surface. The average length is from 2 to 4 cm.; the individual cells are united in bundles, firmly glued together, consequently linen is much less elastic than cotton fibre, next to which it ranks in importance among vegetable fibres. In warm countries flax is raised chiefly for the seed. (See Linseed Oil, p. 357.) That grown in temperate climates has much the better fibre. It is pulled up by the roots before the seeds ripen, and is immediately subjected to the process of "**rippling**," *i.e.* it is drawn through the teeth of a coarse comb to detach the seeds. To separate the bast fibre from the rind, woody tissue, and pith, the flax is "**retted**." This may be done in five different ways: —

(*a*) Retting in stagnant water is practised in Ireland and to some extent in Russia. The flax is put into pools of soft water and left until bacterial action sets in; this softens and partly destroys the gummy and resinous matter cementing the fibres to the ligneous tissue. Great care is necessary that the bast fibres themselves are not attacked. The fermentation is often very offensive. When it has gone far enough, the flax is exposed to the action of the air and sunlight for several days ("grassed").

(*b*) Retting in running water is extensively practised in France and Belgium. The flax is put into crates and submerged in streams. The fermentation takes place as above, but requires a longer time. The coloring matter is washed away, and a lighter colored product is obtained.

(*c*) Dew retting consists in exposing the damp flax to the weather for several weeks. The fermentation takes place much as above.

(*d*) Retting in water at 30° to 35° C. hastens the fermentation greatly, so that it is generally complete in about three days. The flax is often passed between squeeze rolls, to assist in detaching the woody fibre. By treating the flax with water and steam under pressure, it is rapidly retted, and the fibre has a silky lustre.

(*e*) Mineral acids are sometimes used in stagnant-water retting, to prevent the offensive odor. By digesting the flax in very dilute hydrochloric acid, followed by a weak alkali bath, the retting is quickly finished.

Various mechanical processes are employed to detach the ligneous matter from the fibre after retting. **Breaking** consists in crushing the flax with grooved rolls; after this it is "scutched," *i.e.* the crushed mass is pounded by hand in a machine, to remove the loosened matter. **Heckling** is a combing process to draw the fibres parallel and make them suitable for spinning.

Linen fibre is not so pure cellulose as cotton, but, in general, acts like the latter. It is stronger, has more natural lustre, is more difficult to bleach and dye, and, being a better conductor of heat, feels cold to the touch.

Hemp is the bast fibre of *Cannabis sativa*, L., which is largely cultivated in Russia and Italy. The fibres are separated from the wood and pith of the stalks in the same general way as flax. They are stronger and coarser than flax, and, being more deeply colored, are mainly used for rope, coarse canvas, and bagging.

Jute is the bast fibre of several species of *Corchorus*, of which *C. capsularis*, L., is the most important. The plants are indigenous to India, and their cultivation is mainly confined to India and Ceylon, though some has been raised in Louisiana and Mississippi. The fibre is obtained by simple retting in water. It is very long, sometimes reaching two meters, but the fibre cells are short, and the filaments are not so strong as those of flax or hemp. The fibre is light yellow, and has a high lustre. It is quite susceptible to the action of acids and alkalies, and is easily destroyed by mineral acids. Much care is required to bleach it with bleaching powder, since the weakening of the fibre is excessive. Sodium peroxide gives the best bleach on this material; or potassium permanganate, followed by sulphurous acid, may be used. It differs in its chemical composition from cotton and flax. Its cellulose is all combined with lignified tissue, forming *bastose*. Jute resembles cotton which has been mordanted with tannin, and can be dyed directly with basic dyes.

China grass, or **ramie**, is a bast fibre derived from *Bœhmeria nivea*, Gaud., a species of nettle cultivated in China and Eastern Asia. The fibre is difficult to detach from the ligneous matter; retting usually divides it into its component cells, which cannot then be separated from the stem and bark. It is customary to separate the fibres by crushing the green stalk and washing away the woody matter with running water, but this method is expensive. The fibre has a brilliant lustre (which dyeing is liable to injure), and is easily bleached. It is very strong, and is nearly pure cellulose.

Esparto is a grass with tough fibre, cultivated in Spain, and chiefly used for cordage and paper making.

Manila hemp and **sisal** are used as substitutes for hemp. The former is obtained in the Philippine Islands, from the leaves of a wild plantain, *Musa textilis*, Née., and, being tough and light, is much used for cordage and ropes. Sisal is obtained from an agave plant, *Agave rigida*, Mill., and *A. Americana*, L., in Central America and the West Indies. It is chiefly used for burlap as a substitute for jute.

Other vegetable fibres of small importance are **cocoanut fibre**, from the husk of the cocoanut, used for brushes, mats, and cordage; **New Zealand flax**, a long fibre prepared from a New Zealand plant, *Phormium tenax*, Forst., and chiefly used for ropes; **Sunn hemp**, an Indian plant, furnishes a fibre suitable for ropes and cordage.

ANIMAL FIBRES

Of animal fibres, only silk and wool are of much technical importance. **Silk** fibre forms the cocoon of the silkworm, *Bombyx mori*. The worm has two glands, situated on either side of its body, each connected by a duct with a capillary opening (spinneret) in the worm's head. These glands each appear to secrete two transparent liquids; the one, **fibroine**, $C_{15}H_{23}N_5O_6$,* constituting from one-half to two-thirds of the whole secretion, forms the interior and larger part of the silk fibre; the other, **sericine**, $C_{15}H_{25}N_5O_8$,* also called **silk glue**, is yellowish in color and is readily dissolved in boiling water, hot soap solutions,

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* According to Mulder.

or by alkalies. It forms the outer coating of the fibre. As soon as discharged into the air, the fluids from the spinnerets solidify, and coming in contact with each other at the moment of discharge, are firmly cemented together by the sericine; hence, under the microscope the fibre shows two separate structureless filaments. The cocoon is made up of one continuous fibre, from 350 to 1200 meters long, with an average diameter of .018 mm.

Silkworms are raised from eggs kept in an incubator from twelve to eighteen days, while the temperature is slowly raised from 18° to 25° C. The caterpillars have a prodigious appetite, and are fed regularly on mulberry leaves (*Morus alba*, L.) for about thirty days, during which time they grow rapidly, casting their skins every five or six days, and attaining a length of about 8 cm. Then they cease to eat, and crawl upon twigs, where they spin their cocoons. This spinning requires about three days, when the worms are killed by heating the cocoons in an oven at 60° to 70° C. for three hours, or by steaming them for 10 or 15 minutes. After sorting, the cocoons are reeled. This is an entirely mechanical process requiring much skill. The cocoons are soaked in water at 60° C., until the silk glue is softened. Then the operator catches the loose ends of several fibres on a small brush, and passes them through the agate or porcelain guides of the reel, where they are twisted to form threads of sufficient size for weaving. Two threads are formed simultaneously on each reel, and are made to cross and rub against each other to remove kinks and to straighten them, and also to rub the softened silk-glue coverings together, so that the fibres adhere and form solid, uniform threads, — **raw silk**. There is considerable waste, consisting of short and tangled fibre from the exterior of the cocoons, and from those which have been opened by the moth in escaping. This is worked up as floss, and for making spun silk.

Raw silk is exceedingly hygroscopic, and, under favorable circumstances, will absorb as much as 30 per cent of its weight of moisture, and still seem quite dry. It is, therefore, customary to determine the moisture in each lot at the time of sale. This is called "**conditioning**," and must be done with great care, usually in official laboratories. A sample is taken from each bale, and, after careful weighing, is dried in a current of air in a special apparatus, at a temperature of 110° C., until the weight becomes constant. From the average of several tests the absolute amount of dry silk is determined, to which the legal amount of moisture permissible (11 per cent) is added, and the result taken as the weight of the raw silk.

Raw silk consists of about 25 per cent sericine, the remainder being pure fibroine, and has a harsh feel and is stiff and coarse. Before it is made into yarn or cloth, it is usually subjected to various treatments to make it soft and glossy. The first process is called **discharging, stripping, or ungumming**, and its purpose is to remove more or less of the silk glue (sericine) from the fibre, according to the kind of goods desired. The hanks of silk are suspended on wooden sticks in a vat filled with soap solution at 95° C. This is made by dissolving Marseilles, or olein soap to the amount of 30 per cent of the weight of the silk, in soft water, free from lime. The hanks are turned several times by hand in this liquor, during a period of from one to one and a half hours; the fibres swell, become sticky, and finally the sericine dissolves, leaving the silk glossy and soft. The soap bath is not boiled, as that would tangle the fibres and cause the yellow color often present in the sericine to become fixed on them; also long boiling weakens silk. For very fine work, two or three soap baths are employed, the raw silk being first put into that which has been longest in use and which is therefore strongly charged with dissolved sericine;* there the glue is softened and partly removed; the hanks are transferred to the succeeding baths in order, finally leaving the one most recently prepared. This yields soft, white silk, which is rinsed in a warm dilute sodium carbonate solution and then wrung. That which is to be sold as white silk or dyed a very light shade is then subjected to a second discharging process, in which the hanks are tied in several places with tape, enclosed in linen bags, and boiled in a 15 per cent soap solution from one-half to three hours, to remove all the glue. This product, called "**boiled-off silk,**" has lost from 20 to 30 per cent of its original weight. In order to reduce this loss of weight, raw silk is often treated in a weak soap bath until the waxy matters have been partly removed, and is then washed and sometimes bleached by exposure to sulphur dioxide vapors. The product, called "**ecru silk,**" is harsh to the touch, but has lost only about from 2 to 4 per cent of its original weight; it is chiefly used in the warp of black silk and for the back of velvet.

Another process † of treating raw silk for dyeing, while leaving a large part of the sericine on the fibre, is employed for producing **souple silk**. The hanks are first scoured in a 10 per cent soap solu-

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* The soap liquor finally becomes heavily charged with sericine and is drawn from the tank as "boiled-off liquor." It is used in making up the dye bath for silk dyeing, pp. 532, 534, and 536.

† Chemische Technologie, Wagner.

tion for an hour or two at 25° to 35° C. to soften and swell the fibres. They are then bleached by working for 10 or 15 minutes in very dilute *aqua regia*. The bleached silk is then exposed to sulphur fumes for several hours, until sufficiently white. It is then *soupléd*, *i.e.* worked for an hour and a half in a solution of cream of tartar or magnesium sulphate, 3 or 4 grams to the liter. This swells and softens the fibre, which was left harsh by the bleaching process. Soupléd silk has lost only 6 or 8 per cent of its original weight, but is weaker than boiled-off silk.

Concentrated mineral acids, especially hydrochloric, dissolve silk completely. Very dilute acids are absorbed by it, thus increasing the lustre and imparting a peculiar feel to the fibre, which when compressed emits a curious rasping sound called "**scroop.**" The property of scroop may be given by treating the silk in a bath of dilute acetic, or tartaric acid, and drying without washing. Caustic alkalies in strong solution rapidly destroy silk if heated; but in cold solution, caustic soda of 50° Tw. has little action on the fibre and may be used to produce on mixed cotton and silk goods the crinkled appearance shown by seersuckers. Ammonia has little or no action on the fibroine but dissolves the sericine. Alkaline carbonates are less destructive than caustic, but attack the fibre slowly. Borax dissolves sericine without material injury to the fibroine, but is not so good as soap for ungumming raw silk. Lime-water swells the fibre, makes it brittle, and dulls the lustre. Chlorine destroys silk as do other oxidizing agents unless used very dilute and with much care. When soaked in solutions containing metallic salts, especially iron, aluminum, tin, lead, or copper, silk absorbs some of the salt and a precipitation of basic salt within and upon the fibre occurs. On this fact depends the weighting of silks (p. 515).

Besides the cultivated silks, certain kinds of wild silks are of some commercial importance. The most important is **tussah silk**, obtained from the cocoons of Indian and Chinese moths, *Antherœa mylitta* and *A. pernyi*. The fibre is double and somewhat flat, each filament being composed of a number of fibrillæ. It is brown in color, is stiffer and coarser than ordinary silk, and differs in its chemical composition, containing less carbon and nitrogen and more oxygen. It is more resistant to the action of alkalies and acids and to bleaching agents. It is difficult to bleach and dye, and is chiefly employed in making pile fabrics, such as velvets, plush, and imitation sealskin. Other wild silks are **muga silk** from *Antherœa Assama*, and **eria silk** from *Attacus ricini*, both found in India; **yamamai silk**, from *An-*

theræa yamamai of Japan; sea-silk or byssus, produced by a mollusk, *Pinna nobilis,* found in the Mediterranean Sea. The fibre of sea-silk is brown and very soft, and is not easily affected by acids or alkalies.

The following analyses from Hummel's Dyeing of Textile Fabrics are of interest.

Composition of the cocoons: —

Moisture	68.2
Silk	14.3
Floss	0.7
Chrysalis	16.8

Composition of raw silk: —

	Yellow Italian Silk	White Levant Silk
Fibroine	53.37	54.04
Gelatine	20.66	19.08
Albumin	24.43	25.47
Wax	1.39	1.11
Coloring matter	0.05	0.00
Resinous and fatty matter	0.10	0.30
	100.00	100.00

The ultimate analysis of silk fibroine is shown in the following table: * —

	Tussah Fibroine	Mulberry Fibroine (Calculated for $C_{15}H_{23}N_5O_6$)
Carbon	47.18	47.78
Hydrogen	6.30	6.23
Nitrogen	16.85	18.90
Oxygen	29.67	26.04
	100.00	98.95

Artificial silk is made from cellulose by several processes, and also from gelatine or casein, but only the cellulose products are now important.

(*a*) The *Chardonnet-Lehner process* uses collodion (p. 479) containing about 15 per cent of pyroxyline in solution in alcohol-ether mixture, amyl acetate, or acetylene tretrachloride. The filtered solution is forced, under 60 atmospheres pressure, through capillary glass tubes, into a chamber where it meets a current of air to evaporate the solvent and coagulate the pyroxyline, which forms filaments closely resembling natural silk fibre in appearance; several of the filaments are twisted into a fibre, which after washing in water is "denitrated" by treatment with a cold dilute solution of ammonium or sodium sul-

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* Manual of Dyeing, Knecht, Rawson, and Loewenthal, p. 55.

phide. This reduces the nitrate forming hydrated oxycellulose, which retains the silky lustre, and is no more inflammable than cotton. The fibres, after washing and drying, are combed and spun into yarn, which has less strength than natural silk, however.

(*b*) The *Pauly-Fremery process* uses a solution of mercerized cotton in ammoniacal copper oxide liquor. The filtered solution is squirted through capillary glass tubes into dilute (18° Bé.) sulphuric acid, or a 5 per cent caustic soda liquor, which precipitates hydrocellulose. After washing and drying the fibre possesses a very high lustre.

(*c*) *Viscose silk* is made by forcing a thick solution of cellulose thiocarbonate (p. 490) into ammonium sulphate liquor, which precipitates hydrocellulose as a fibre. After washing free from alkali, the material is spun into yarn having a high lustre. It is somewhat cheaper than the other varieties and its use is increasing rapidly. The viscose solution is made directly from wood pulp.

(*d*) *Cellulose acetate silk* is made by squirting a solution of cellulose acetate (p. 585) in acetylene tetrachloride, to form fine filaments which are spun into yarn. It is not very inflammable and has high lustre, but is not readily dyed in aqueous baths.

Artificial silk fibres can be fused together to form artificial horsehair and bristles, which are now of considerable commercial importance.

Much **mercerized cotton** (p. 489) is now prepared to imitate silk.

Wool is the hair of the sheep, but that of certain goats, such as the alpaca, cashmere, and mohair, as well as that of the camel, is also classed with wools. Wool differs from true hair only in its physical structure, being covered with minute overlapping scales and having a twisted or curled fibre. The character of wool varies with the breed, food, and care of the sheep, and the climate and nature of the soil on which the food is grown. The fibre varies from short, fine, and wavy, to long, coarse, and straight in different breeds. The length ranges from 1 inch to 10 inches in different varieties, even reaching 16 inches in the case of certain cashmeres and mohairs. The wool cut from one animal is called a fleece, and the different grades in each fleece are separated by hand, that from the neck, back, and shoulders being the longest and best quality. The long staple wools have a silky appearance and are often called lustre wools. They are generally used for *worsted* goods, while the short, fine wools are made into *woollen* goods. Mohair, obtained from the Angora goat, has a high lustre and is soft and fine, as are also the alpaca, vicuna, and llama wools derived from South American goats.

Sheep pelts are often soaked in "milk of lime," or sodium sulphide, to loosen the wool before making leather from the skin. Such wool is known as "**pulled wool**," and is of inferior quality.

Wool is very hygroscopic, and may contain from 8 to 12 per cent of moisture in hot, dry weather, up to 50 per cent in very damp air. On an average, it contains about 18.25 per cent, and this is the legal limit in most European countries, and is generally determined in "conditioning laboratories," as in the case of silk. The temperature of drying is kept between 105° and 110° C., since above this temperature there is danger of injuring the fibre. At 100° C. wool becomes plastic, and after cooling retains the shape into which it may have been formed while hot.

Each wool fibre is covered with a layer of broad scales, projecting in the same direction and overlapping much like shingles on a roof, the outer edges being more or less free. When the approximately parallel fibres are moved upon each other by rubbing or "milling," the scales interlock and cause "felting." The interior substance of the fibre is composed of narrow cells tapering towards each end. Some wools also have a central or medullary part, made up of cells of different shape, and which usually contain the coloring matter of the fibre. Such wools are stiff and brittle, and resemble hair in their properties; the best wools are free from such medullary cells.

The internal cells appear to have more attraction for dyes than do the outer horny scales, and much of the effect of acids and other additions to the dye-bath is supposed to be due to the raising of these scales by their action, thus permitting the access of the dye to the interior substance. Diseased and dead fibres, known as "kemp," do not color well, since they have a very impenetrable layer of these scales; moreover, they do not felt properly, and are dull in lustre.

Pure wool fibre, consisting for the most part of **keratine**, the characteristic constituent of horn, feathers, etc., is not of constant chemical composition, varying in different qualities and kinds. The approximate composition of keratine from wool is: —

Carbon	49.25*
Nitrogen	15.86
Hydrogen	7.57
Sulphur	3.66
Oxygen	23.66

The presence of sulphur is characteristic of wool, and often causes difficulties in mordanting and dyeing. The ash of the fibre averages less than 1 per cent of the weight of the wool. When heated to 130°

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* Hummel, Dyeing of Textile Fabrics.

C., with water under pressure, and dried, wool is rendered very brittle. Dilute acids have no apparent action on it, but a small percentage is absorbed and cannot be readily removed by washing; concentrated mineral acids destroy the fibre. By treating mixed cotton and wool goods with a dilute sulphuric or hydrochloric acid, and drying at 110° C., the cotton is "carbonized" (p. 501), and when heated crumbles to dust and falls away from the unchanged wool. The same result is obtained by treating the goods with hot, dry hydrochloric acid gas. Alkalies attack wool energetically, the caustic alkalies and lime being most destructive, especially in boiling solution, by which the fibre is completely destroyed. Alkaline carbonates are much less injurious, and are used in dilute solution for scouring wool. Ammonia and ammonium carbonate have little tendering effect on it, and are best for washing, for which soap, borax, and sodium phosphate are also used. When strong and allowed to act for some time, oxidizing agents cause the fibre to become tender. Very dilute solution of potassium bichromate is largely used in mordanting wool, but care is necessary to prevent "over chroming." When moist, chlorine is taken up by wool, and the fibre made very tender, but a slight treatment with it makes the wool more susceptible to certain dyes; dry chlorine is said to have no action. Wool is colored yellow by hypochlorous acid, hence bleaching powder is not used to bleach the fibre. When boiled in solutions of various metallic salts, it absorbs a considerable amount of them, and it is often so treated when mordanting before dyeing. The nature of the reactions occurring is not clear, but apparently there is a direct union between the fibre or some of its constituents and the salt. Wool has great affinity for many dyes, and the colors produced are generally faster than when dyed on cotton or silk.

Before it can be subjected to any manufacturing process, raw wool must be washed and scoured to remove impurities, which are present to the extent of from 30 to 80 per cent of the total weight. These consist of: (*a*) **yolk** or **wool grease,** and (*b*) **suint,** which exude from the body of the animal with the perspiration; and (*c*) dirt mechanically mixed with them or entangled among the fibres.

The wool grease is soluble in ether, benzene, or carbon disulphide, and is made up of bodies, consisting largely of solid alcohols, especially cholesterine and isocholesterine, together with the oleic, palmitic, and stearic acid esters of those alcohols. These substances are not easily saponified with alkali, but can be emulsified with soap solution, and thus easily removed from the fibre.

Suint is soluble in water, and consists mainly of potassium salts of oleic, stearic, valeric, and acetic acids, together with sulphates, chlorides, and phosphates, and nitrogenous bodies.

These are generally removed by washing in a solution of soap. A soft soap, made from Gallipoli oil (p. 363), is preferred for the best qualities of wool, but usually a cheaper soap, containing some sodium carbonate, is employed. The washing is done in machines, and care is taken not to entangle the fibre any more than need be. There are usually three tanks, placed *en cascade*, and so arranged that the wool may be automatically passed from one to the next, while the liquor is drawn from one to the other in a direction opposite to the movement of the wool. The raw wool is introduced into the soap liquor containing more or less impurity from its previous use in the other tanks. The temperature should be from 35° to 40° C. The wool is submerged and pushed forward a short distance by prongs or forks which work automatically. At each stroke, a portion of the wool is pushed between squeeze-rolls, which expel the liquor; it then passes into the next tank, where it is washed in the same way with cleaner soap liquor, and then goes through squeeze-rolls into the last tank, containing clear water or fresh soap liquor. The wash liquor, aided by the free alkali added and the potassium oleate, etc., in the *suint*, emulsifies and dissolves the wool grease and *suint*, loosening the mechanical impurities, which sink to the bottom. After washing in clean water, the wool is "centriffed," and then dried on wire netting by a current of warm air. The foul-smelling, dirty brown liquor from the first tank is drawn off, and may be evaporated directly and calcined to recover the potash, which amounts to from 1 to 8 per cent of the weight of the wool. Or it may be treated to recover the wool grease, sometimes called **Yorkshire grease**; it is settled to remove coarse dirt, and then sulphuric acid is added in slight excess, to decompose the soaps and set free the fatty acids, which rise to the surface, carrying the wool grease with them. The water is drawn off from the magma, which is pressed, hot, in canvas bags. The grease is kept in a liquid condition until all sediment deposits, when it is drawn into casks, where it solidifies on cooling. It is used as a lubricator, and in leather dressing.

By passing the clarified wash liquor through a machine similar to a cream separator, the grease is very neatly separated from it. For the preparation of lanolin from this grease, see p. 370.

Wool is often treated by methods intended to recover the yolk and *suint* separately. This is usually done by extracting first with a volatile solvent (carbon disulphide or petroleum spirit) to remove the wool grease, and then washing the wool in water to remove the *suint.*

The washed wool is harsh and brittle, and before being manufactured must be softened by oiling. Pure olive oil is best for this, but lard, colza, hemp, peanut and mineral oils, and sometimes "red oil" (oleic acid) are also used. This in turn must be removed by scouring before dyeing.

Wool containing much straw, burrs, or other vegetable matter is often cleaned by **carbonizing**. The raw wool is submerged in a solution of aluminum chloride of about 8° Bé. for 25 to 30 minutes; it is then lifted out, "centriffed," and at once put into a hot room, where the absorbed aluminum chloride is decomposed, and the hydrochloric acid formed attacks the vegetable matter, making it so friable that it falls to dust when the wool is passed through a beating machine. Instead of aluminum chloride, a solution of sulphuric acid may be used for carbonizing.

A similar process is used to separate wool fibre from cotton or other vegetable fibre in rags which are to be made into "shoddy."

BLEACHING

Natural fibres, either vegetable or animal, always contain coloring matters, which, even though present in very small quantities, impair the purity of the white desirable in most uncolored fabrics. And there are always certain gums, resins, waxes, and oily matters on the fibres, either natural to it or added to facilitate spinning and weaving. In woven goods there is more or less sizing, *i.e.* starch, china clay, metallic salts or oxides, etc., put upon the fibre to assist in weaving or to improve the appearance or weight of the cloth. These substances prevent the proper action of mordants and dyes, or detract from the appearance of those fabrics to be sold undyed, and the bleacher must remove them and decolorize the fibre.

In general, the bleaching process is divided into two stages, the washing or scouring and the bleaching proper or chemical treatment which varies with the different kinds of fibres.

COTTON BLEACHING

Cotton is commonly bleached in the yarn or woven piece, since there is no special demand for bleached cotton-wool.

Yarn bleaching. — If the cotton is to be dyed in dark colors, it is customary to give it a thorough boiling in water alone, or with the addition of some soda-ash, to remove the grease, wax, and resinous matters. After washing, it is at once dyed. But for white yarn, or that to be dyed any light shade, the bleaching process is more complicated. The hanks of yarn are linked together to form a chain, and then loosely packed into a closed iron vessel, called a "**kier,**" where they are boiled for several hours with caustic soda or soda-ash, under a low pressure (5 pounds per square inch), or even in open vessels. The kier has a false bottom, upon which the yarn rests. A vertical pipe passes up through the centre of the kier, to within a few inches of the top. Across the upper end of this pipe is a dome-shaped bonnet, and at the lower end is a steam injector which forces the liquor collected under the false bottom up through the pipe against the bonnet, which distributes it over the yarn, through which it percolates, collecting under the false bottom. Thus a constant circulation of the liquor is maintained in the kier. On an average about 4 per cent (of the weight of the goods) of soda-ash is used in the lye.

The yarn is then washed with clean water and is treated with a cold dilute bleaching powder solution, called the "**chemick.**" This is about 2° Tw., and is pumped over the yarn as it lies in a wooden tank having a false bottom. After 5 or 6 hours the yarn is removed, squeezed, and washed in water for a few minutes. It is then "**soured**" by plunging into a tank containing a dilute sulphuric or hydrochloric acid of about 1° Tw. Chlorine is thus liberated from the bleach absorbed in the fibre, and sets free oxygen from the water, which at once attacks and destroys the coloring matters, the yarn becoming pure white. This process requires about 15 to 20 minutes; then the yarn is thoroughly washed in water and passed into a hot soap solution, to which a little bluing (ultramarine) has been added, if the yarn is to be sold uncolored. The soap is worked into the yarn by squeeze-rolls, until the fibres are uniformly blued; then the excess of soapy water is removed in a centrifugal machine, and the yarn is dried.

The **Haubold machine** for yarn washing consists of a circular tub containing a rotating central shaft from which square bobbins radiate. On these the hanks are hung, and as they are carried slowly forward, a suitable gearing imparts to the bobbins an intermittent forward and backward rotation on their own axes. The tank is divided by a radial partition, on one side of which fresh water enters, while on the other the dirty water flows out. The hanks are moved against the current of water, and are taken out when they come to the partition on the side where the clean water enters.

In other washing machines, the yarn is pounded by heavy wooden hammers driven by power. Or, as shown in Fig. 119, the hanks tied together to form a chain are washed by passing through squeeze-rolls (A, A) and under a stretching roller (B), placed in the bottom of the wash tank. The yarn thus passes down and up under the rollers and between the squeeze-rolls several times.

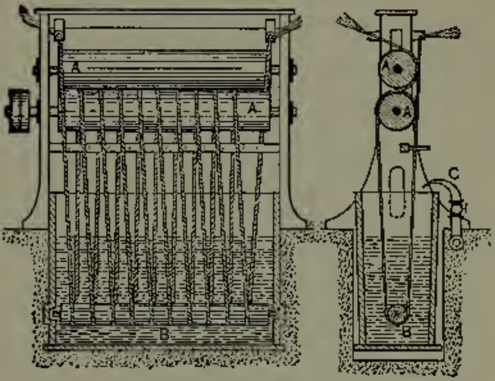

Fig. 119.

Improved apparatus is now employed, in which the lye-boiling, chemicking, souring, and washing are all carried on in one wooden vessel. The yarn is not moved during the process, and the various liquors are pumped through the apparatus in their order, and the labor is thus much reduced.

Cloth bleaching is done by one of three methods: the **market bleach** for goods to be sold as white muslin; the **Turkey-red bleach**, for goods to be dyed red with alizarin; the **madder bleach** designed for cloth which is to be printed with various mordants and then dyed in a bath of alizarin. The latter leaves the cotton white and almost pure cellulose. It is necessary to remove every impurity which can attract the dye or prevent its taking the fibre. If the cotton is not chemically clean before printing, the pattern will not be clear and sharp, nor the background a pure white.

The **madder bleach** is carried out as follows: The separate pieces of goods are marked on the ends for future identification, and then stitched together, end to end, to form a continuous web, which is first "**singed**" to remove the lint, floss, and loose hairs, as these would prevent the printing of sharp designs. This may be done by passing the cloth, opened to its full width, over one or two red-hot copper plates, slightly curved and set in the roof of a furnace; it is difficult to keep these evenly heated, owing to the cooling effect of the rapidly moving cloth, and the singeing is liable to be imperfect in places. Consequently a revolving hollow roll is sometimes used, which is kept red hot by passing the flames of the furnace through it on their way to the chimney. Or the cloth may be passed over a row of Bunsen gas flames. Directly over these is a small roller, under which the cloth passes at sufficient tension to cause the "nap" to stand out well as it comes into the flame. As soon as the cloth passes the hot plate or flame it is plunged into a trough of water, to extinguish any sparks.

The goods are then thoroughly wet in water (the "**gray-wash**"), and much of the sizing and dirt is removed. The cloth is then usually piled in a heap and left overnight, to thoroughly soften the gums and starchy matters left in it. It is then given the "**lime-boil,**" with milk of lime under pressure preferably in the injector kier. The cloth is passed through a trough of milk of lime, of which it absorbs about 4 or 5 per cent of its own weight. Without wringing, it is passed into the kier, which is filled nearly full, and packed by boys, who tread the cloth down evenly, so that the liquor will be forced to pass through it, and not through channels between the folds. Water is introduced, and then steam is blown in until the air is expelled and the kier is hot, when the cover is screwed down and the boiling continued under from 10 to 70 pounds pressure, for several hours. The **kier** (Fig. 120*) is made of boiler plate, and is from 6 to 10 feet high by 4 to 6 feet in diameter; it will hold from 600 to 3500 pounds of cloth. Steam is admitted through (A), and passing the injector (G), draws the limewater through (B) and delivers it through (C) to the nozzle (N), which sprays it over the goods. The pressure in the upper part of the kier forces the liquor through the goods, and it collects among quartz pebbles in the bottom, whence it is drawn through (B) to the top of the kier. If needed, water is admitted through (D) and milk of lime through (E). At the end of the operation the waste liquor is drawn off through (F).

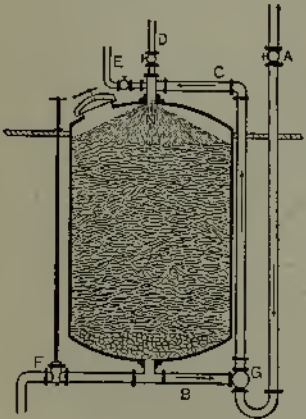

Fig. 120.

The object of this lime-boil is to convert the fatty matters into lime soap, to dissolve the starch and other soluble substances, and to so change the natural impurities chemically, that they, together with the lime soap formed, are readily removed in succeeding operations.

The cloth is usually darker after this treatment than before. It is next washed in machines similar to that shown in Fig. 119, to remove excess lime, soluble matters, and loose dirt. The rope of cloth is thus passed through the water and between the rolls (A, A) several

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* After Knecht, Rawson, and Loewenthal, Manual of Dyeing.

times, while it is sprayed by a heavy stream of water from the pipe (C) as it comes up to the squeeze-rolls.

It now passes to the **first-sour**, or **gray-sour**, where it is treated with dilute sulphuric or hydrochloric acid at 1° or 2° Tw.; this decomposes the lime soap, and removes any iron stains and other metallic oxides. The goods are then passed through squeeze-rolls, to remove the excess of acid, and are thoroughly washed to prevent the acid from rotting the fibre, as it would on long exposure to the air.

The **lye-boils**, of which there are two or three, are also carried on in the injector kier. In the first boiling the goods are treated with 1 per cent soda-ash * for about 3 hours; in the second about 3.6 per cent soda-ash, 0.8 per cent caustic soda, and 1.6 per cent of rosin are used, and the whole boiled for 12 hours; the third lye-boil is with soda-ash alone, and continues for 3 hours. These boilings remove the remaining fats and oils from the lime soaps, and extract much of the brown coloring matter. The addition of rosin is a characteristic of the madder bleach, and is supposed to remove certain substances from the cotton which readily attract the dye.

After a thorough washing, the next process is the "**chemicking,**" or treatment with bleaching powder, which is done in a machine similar to the squeeze-rolls used in the souring. The cloth while still wet is passed through a clear, cold solution of bleaching powder at ½° to 2° Tw. It is then piled in a heap and left for some hours. The bleach is partly decomposed by the carbon dioxide of the air, and hypochlorous acid is set free; this decomposes in the presence of organic coloring matter, liberating oxygen, which destroys the color. If the bleach liquor is too strong the cotton is attacked and oxycellulose formed, which is objectionable.

After the chemick, the cloth is piled for a few hours; then it is next subjected to the "**white-sour.**" It is treated with dilute mineral acid, to complete the liberation of chlorine from the bleach remaining in the fibre. Hydrochloric acid is the best for this, since it renders the lime more soluble. The cotton is completely decolorized, and after about three hours is thoroughly washed. It is passed through squeeze-rolls, and then opened out smooth and passed over large copper drums, heated by steam, to dry it thoroughly. The whole time necessary for the madder bleach is about five days.

For 24,000 kilos of cloth the following scheme is given by Hummel: † —

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* These percentages are calculated on the weight of the goods.

† Dyeing of Textile Fabrics, p. 77.

1. Wash after singeing.
2. Lime-boil: 1000 kilos lime; boil 12 hours; wash.
3. Lime-sour: hydrochloric acid, 2° Tw.; wash.
4. Lye-boils: —

    1st: 340 kilos soda-ash ($1\frac{1}{4}$ per cent ash): boil 3 hours.

    2d: $\left.\begin{array}{l}\text{860 kilos soda-ash (= 3.6 per cent).}\\ \text{380 kilos rosin (= 1.6 per cent).}\\ \text{190 kilos solid caustic soda (= 0.8 per cent).}\end{array}\right\}$ Boil 12 hours.

    3d: 380 kilos soda-ash (= 1.6 per cent); boil 3 hours; wash.

5. Chemicking: bleaching powder solution, $\frac{1}{4}$° to $\frac{1}{2}$° Tw.; wash.
6. White-sour: hydrochloric acid, 2° Tw.; pile 1 to 3 hours.
7. Wash, squeeze, and dry.

The **Turkey-red bleach** is employed for cotton which is to be dyed a full color with alizarin red. It is essential that the fibre shall not be singed nor exposed to chlorine,* since the development of a brilliant red would be thus prevented. The process is therefore simpler, the outline for 2000 kilos of cloth being as follows: † —

1. Wash.
2. Boil 2 hours in water; wash.
3. Lye-boils: —

    1st: 90 liters of caustic soda solution, 70° Tw. (= $4\frac{1}{2}$ per cent of weight of goods); boil 10 hours; wash.

    2d: 70 liters of caustic soda solution, 70° Tw. (= $3\frac{1}{2}$ per cent of weight of goods); boil 10 hours; wash.

4. Sour: sulphuric acid, 2° Tw.; steep 2 hours.
5. Wash well, and dry.

The **market bleach** differs from the madder bleach chiefly in that the singeing and rosin-boil are omitted and the cloth is starched and blued slightly before drying. An outline of the process is about as follows: —

1. Gray-wash.
2. Lime-boil: 8 to 12 hours; wash.
3. Lime-sour: hydrochloric acid, 2° Tw.; steep 2 to 4 hours; wash well.

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* The injurious action of the chlorine is supposed to be due to the formation of oxycellulose. J. Soc. Dyers and Colorists, 1886, 29.

† Hummel, Dyeing of Textile Fabrics, p. 85.

4. Lye-boils: —

   1st: 1½ to 3 per cent soda-ash; boil 3 to 12 hours.

   2d: 1½ to 3 per cent soda-ash; boil 3 to 12 hours; wash well.

5. Chemick: bleaching powder solution, ¼° to ½° Tw.; pile 6 to 12 hours.
6. White-sour: hydrochloric acid, 2° Tw.; pile 3 hours; wash.
7. Starched and blued.
8. Calendered.
9. Tentered and folded.

Much care is taken in the finishing operations. The bluing is generally mixed with the boiled starch, and after passing through squeeze-rolls, the lightly starched cloth goes to the calender machine. Here it is heavily pressed between hot, polished steel rolls to give it a smooth and glossy surface. Next it goes to the tentering machine, which consists of a travelling frame with parallel sides, carrying clips or hooks, to which the cloth is fastened by the selvedges. The side rods of the frame have an intermittent backward and forward movement which stretches and draws the cloth in the direction of its width. Beneath are a number of flat steam-boxes, the heat from which rapidly dries the cloth. Finally, it goes to a folding machine, by which the cloth is laid in folds one yard in length; the number of yards required for a bolt is then cut off.

Various modified bleaching processes have been devised, chiefly with the view of saving time, labor, and wear on the goods. That of Horace Koechlin has been introduced in some works. The lime-boil is abolished, and a single caustic soda and rosin-boil is substituted for the lye-boils. A special horizontal kier is used, into which cars packed with the cloth can be run. The boiling here is not essentially different from that in the ordinary form, but the cars are run out and others immediately run in, without material cooling of the kier; thus much time is saved. The chemicking, souring, and washing are carried on in the usual way.

In the **Mather-Thompson process** * the same kier is used as in the Koechlin process, but a special apparatus is employed for the subsequent chemicking, followed by a soda-boil and a second chemicking. After passing through the bleaching powder solution the cloth is exposed to the action of carbon dioxide gas to set free the hypochlorous acid; this hastens the bleaching.

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* For details of this process, see Thorpe's Dictionary of Applied Chemistry (Revised Ed.), Vol. I, 472.

The **Hermite bleaching process** [*] depends upon the electrolytic decomposition of magnesium or aluminum chloride, to form bleach liquors consisting of hypochlorites of these metals; the liquors are employed instead of bleaching powder for chemicking.

Peroxide of hydrogen used in conjunction with soap, magnesia, and caustic soda in a boiling bath gives an excellent bleach on cotton. But its cost is yet too great to allow of its general use for this purpose.

Permanganate of potassium, in slightly *acid* solution, gives a very good bleach on cotton which has been boiled in caustic soda to remove gums and oily matters. Alkaline permanganate must be avoided, as it forms oxycellulose. When removed from the permanganate bath, the goods are colored a deep brown, but a pure white is produced by passing them into a bath of sodium bisulphite or sulphurous acid. The process is worked cold and the goods must be thoroughly washed after bleaching.

LINEN BLEACHING

Linen contains more than 25 per cent coloring matter and other impurities (chiefly pectic acid, so-called), and the bleaching process is more difficult and tedious, although essentially similar to that used for cotton. Linen is more readily attacked by alkalies, acids, or chlorine, and more care and time (from 3 to 6 weeks) are needed to prevent injury to the fibre. The liquors are much weaker and the processes are usually repeated several times. It is also customary to "**grass**" linen for a week; *i.e.* to expose it to the sun and dew by spreading it on the grass. It is frequently moistened to assist in the bleaching. It is supposed that the ozone in the air is here the active agent.

Linen is bleached in the form of thread, yarn, or cloth. According to the degree of whiteness, it is said to be quarter, half, or three-quarters bleached, but the strength of the fibre diminishes as the purity of the white increases. The following outline of the **Irish process** for yarn bleaching is according to Hummel [†]: —

1. Lye-boil: 10 per cent soda-ash in solution, boil 3 to 4 hours, wash and squeeze.
2. Chemick: reel one hour in bleaching powder solution at ½° Tw.; wash.
3. Sour: steep one hour in sulphuric acid at 1° Tw.; wash.

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[*] Hurter, J. Soc. Chem. Ind., **1887**, 337.

[†] Hummel, Dyeing of Textile Fabrics, p. 88.

4. Lye-boil (scald): boil one hour with 2 to 5 per cent soda-ash in solution; wash.
5. Chemick: reel again as in (2); wash.
6. Sour, as in (3); wash well and dry.

This gives a half bleach; for three-quarters bleach, repeat Nos. 4, 5, and 6, but after the lye-boil (4), grass for a week; and in (5), instead of reeling the yarn, steep it in the bleach liquor 10 to 12 hours.

Linen piece goods* are bleached similarly to cotton cloth, but the details vary. There are the same lime-boil, sour, and several lye-boils with caustic soda, then a grassing for several days, followed by a chemick, sour, and third soda-boil, another grassing, and a second chemick. If not white, the goods are rubbed between rubbing boards with a strong soap solution, to remove mechanically the fine black specks called "sprits" adhering to the fibre. This is followed by a third grassing, chemick, sour, and washing.

Potassium permanganate has been recommended for linen bleaching in conjunction with sulphurous acid or hydrogen peroxide. These substances act rapidly and reduce the time of bleaching to a few days.

Jute is bleached by treatment with sodium hypochlorite or bleaching powder solution, followed by a sour and thorough washing. Sodium hypochlorite liquor containing about 1 per cent of available chlorine is recommended for cloth, the presence of the soda preventing the formation of chlorinated products. Yarn is commonly treated with bleaching powder solution, three baths being used; these vary in concentration from about 20 per cent (on the weight of the goods), down to 5 per cent of bleaching powder in the last bath. The yarn is hung in each bath for half an hour or more, at a temperature of 48° C.; it is then washed, treated with sulphuric acid at 1° Tw. for half an hour, again washed and dried. (In the presence of water, chlorine may combine with the jute, forming yellow chlorination products.)

Potassium permanganate, followed by treatment with sulphurous acid, yields a good bleach but is expensive; sodium peroxide also gives a good bleach and is used to some extent.

Hemp is not often bleached, since its chief use is for cordage and twine, where the color is of no consequence. It is sometimes partially bleached by boiling in sodium silicate, washing and treating with bleaching powder solution for some hours, then souring in dilute acid and washing thoroughly.

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* Herzfeld, Handbuch der Färberei, p. 375. Also see Hummel.

WOOL BLEACHING

The preliminary operations of washing and scouring the loose wool have already been described on p. 499. After spinning, the yarn is left greasy, and a second scouring is necessary before bleaching or dyeing.

Wool yarn, especially when tightly twisted, shows a decided tendency to curl and shrink when wet in warm water. As this would cause tangles and felting in the scouring and dyeing, the yarn is stretched on a strong frame carrying a number of projecting arms. A hank of yarn is hung over two of these arms, and is stretched tight by means of screws which separate the arms. When filled, the frame is submerged in boiling water for half an hour. It is then taken out, and the yarn allowed to cool while stretched. The hanks are then shifted so that the portion that was in contact with the arms now comes *between* them, and the entire process repeated. This removes all the "curl," and the yarn is ready for scouring, which may be done by hand or in machines. In the first method, the hanks are suspended from wooden rods in the tank containing the hot scouring liquor (soap solution), and are swung to and fro, with frequent turning of the rod, to wet all parts of the hank. They are then washed by swinging them in a tank of water. An effective scouring machine for yarn consists of a pair of squeeze-rolls placed over a tank filled with soap liquor, and containing several rollers, under and over which the hanks, tied together in a chain, are passed.

Woolen cloth may be scoured in a scouring machine called a "**dolly**"; the cloth is passed as a rope through the soap liquor, and then between squeeze-rolls. But goods which are liable to crease must be scoured in the **open-width scouring machine.** The cloth is then sprayed with clean water, returned to the soap bath, and again put through the squeeze-rolls. The dirty soap liquor expressed is caught in a special trough, and is run off. The cloth is finally washed with water to remove all the soap.

Mixed goods, called "**unions,**" composed of cotton warp and wool weft, or goods made of two kinds of wool, will "cockle" or wrinkle when wet, owing to unequal shrinkage. They are consequently "**crabbed,**" to take the stretch out of the fibre. The cloth is passed through a bath of boiling water, and at once rolled tight and smooth on a roller or beam. After cooling *on the roll,* it is again passed through hot water, and rewound on a second beam. The process is repeated a third time, using cold water, and rolling the cloth under heavy pressure, obtained by a weighted roller resting on top of the beam. In order to stretch the goods under higher temperatures than they will be subjected to in the subsequent dyeing, they are next steamed by rolling them on a perforated iron cylinder, into which steam at 40 pounds pressure is admitted and forced through the whole thickness of the cloth. After cooling, it is rewound on another perforated roll, and steamed again. This rewinding brings those portions of the cloth which were on the outside of the roll into the centre and nearer the steam entrance, so that the effect of the high temperature is made more even throughout the piece. The goods may now be scoured and dyed without shrinkage, provided that the temperature in these processes does not exceed that obtained in the crabbing and steaming.

Wool cannot be bleached by any process similar to that used for vegetable fibre, since it would be dissolved by the lye-boils, while chlorine would combine with the fibre without destroying the natural yellow color. The bleaching agent most generally used is sulphur dioxide, or its solution in water as sulphurous acid. It is almost always used as gas, and the operation is called "**stoving**," sulphuring, or gas bleaching. It is carried on in a closed brick chamber, or "stove," about 6 × 10 × 6 feet, the wooden lining of which is made fast by wooden pegs, so that all metal (especially iron) is excluded. The washed and scoured hanks are hung on wooden rods, for 6 or 8 hours, in contact with the sulphur fumes produced by burning sulphur in a pot in the bottom of the stove. Thin cloth is stoved by passing it, in the open width, in a zigzag course up and down many times over rollers at the top and bottom of the chamber, which it finally leaves through the same narrow slit at which it enters. It may be passed through the chamber several times, until sufficiently bleached.

Sometimes the goods are soaked for 24 hours in a solution of sulphurous acid, or sodium bisulphite with mineral acid, and then wrung and washed.

The action of sulphur compounds in bleaching wool is not entirely clear. By some authorities, the sulphur is supposed to decompose the water present, liberating hydrogen, which, in turn, unites with the color to form a colorless body. By others it is thought that the sulphur enters into combination with the coloring matter to form a colorless sulphite compound. But whatever the actual reaction, the bleach is not permanent, and after some time the yellow color gradually returns, especially if the goods are washed with soap or alkalies.

Hydrogen peroxide is an effective but expensive bleaching agent for wool. Since it affords a permanent bleach, the coloring matter is probably oxidized and destroyed. The goods are soaked at 15° C. for 24 hours in a 3 per cent solution of hydrogen peroxide, containing 2 per cent of ammonia (sp. gr. 0.910). Increasing the temperature hastens the process. Hydrogen peroxide is also used for bleaching hair, furs, and feathers.

SILK BLEACHING

The boiling off and discharging of **raw silk** has already been considered (p. 494). It is often subjected to various mechanical treatments to increase its lustre, *e.g.* "stretching," in which the hanks are given a series of violent jerks while suspended from a fixed peg; "glossing," in which they are twisted very tight; or "lustreing," by steaming them while in a state of great tension.

Silk is bleached with sulphur dioxide, or with hydrogen peroxide, or with potassium permanganate and sulphurous acid. The stoving process, similar to that used for wool bleaching, is repeated several times, the silk being washed after each stoving. It is then tinted with a trace of some blue or other coal-tar dye to make it appear a clearer white.

Tussah silk is hard to bleach, and cannot be decolorized by stoving. A bath of barium peroxide in water, followed by dilute hydrochloric acid, is recommended by Tessie du Motay. Ammoniacal hydrogen peroxide may also act on silk as on wool. But, at best, tussah silk can only be bleached a light cream color.

MORDANTS

A **mordant** is a substance used in textile dyeing and printing, either to fix or to develop the color on the fibre. In the first case, it combines with the fibre, and forms a body having affinity for coloring matter; in the second, it becomes an essential constituent of the color when deposited on the fibre. Metallic mordants are abstracted from aqueous solution, wholly or in part, by the fibre, upon which they generally deposit metallic hydroxides or basic salts, which form color lakes in the dyeing process.

Mordants are either of mineral or of organic origin. The former comprise the common mineral acids, and salts of aluminum, chromium, iron, copper, antimony, and tin, and to a lesser degree those of manganese, cobalt, nickel, uranium, vanadium, and tungsten. The organic mordants are certain organic acids, especially acetic, oxalic, tartaric, citric, lactic, the sulphated ricinoleic and oleic acids forming Turkey-red oil, and tannin substances, mainly derivatives of gallic or protocatechuic acids. Only the most important of these mordants can be mentioned here.

Aluminum mordants are chiefly the acetate or "red liquor" (p. 308), sulphate (p. 282), and the alums (p. 285). The chlorides and nitrates are rarely used. Aluminum salts are used for mordanting cotton, linen, and wool, but seldom for silk. Alum and normal sulphate do not readily yield alumina to cotton. Basic sulphates are generally used, and deposit over 50 per cent of their alumina on the fibre, when it is steeped in them, and then dried and aged in a warm atmosphere. Sometimes the fibre is first soaked in some such substance as tannic acid, Turkey-red oil, or stannate of soda, which forms insoluble compounds with the alumina of the basic sulphate, or precipitates it as such in an insoluble form. The acetate is only used for Turkey-red, and the alumina is fixed by the evaporation of acetic acid during the aging.

Alum and neutral sulphate are much used for wool, the fibre decomposing these solutions when boiled in them, and retaining the alumina in an insoluble form. The wool fibre is both acid and basic in character, dissociating these salts, and combining with both the acid and the base of the salt. This reaction is most complete at a boiling temperature; but for the best results the salts must not be decomposed until they have had time to penetrate into the fibre. Decomposition is retarded by using tartrates or oxalates in conjunction with the aluminum sulphate; these probably form aluminum tartrate or oxalate by double decomposition, and the aluminum is slowly given up to the fibre. Acid potassium tartrate (cream of tartar) has the best effect, but free sulphuric, hydrochloric, or oxalic acids also retard the decomposition.

Silk is very seldom mordanted in this way, as the lustre would be injured.

Chromium salts, which react similarly to the aluminum salts, are used for cotton, linen, and wool. With these are included the chromates and bichromates, but in all cases chromic oxide, Cr_2O_3, is fixed on the fibre. Chromic acid and its salts act here as oxidizing agents, and are themselves reduced to chromic oxide before deposition.

Cotton and linen are difficult to impregnate with chromium salts. The sulphates, nitrates, and acetates are much used in calico printing, while bichromates and alkaline solutions of chromium hydroxide are used in dyeing and printing. The most successful method of mordanting cotton with chromium salts is that proposed by H. Koechlin. The cotton is soaked in the solution of chromium salt (preferably basic salt), dried and passed through *boiling* soda solution; the process is repeated until the goods are sufficiently mordanted.

Another process is to prepare the goods with tannin, or with Turkey-red oil, and then soak them in the chromium solution; the fixing is done in cold limewater. A solution of basic chromium acetate is used for cotton; after steeping some hours, it is dried and steamed in a closed chamber, to fix the chromium oxide on the fibre.

Wool is mordanted with chromium fluoride, chrome alum, or bichromate (chromic acid). Chrome alum yields the largest quantity of chromium to the fibre, but in dyeing, the result is less satisfactory than with bichromates. The addition of cream of tartar to chrome alum is an improvement. Chromium fluoride mordants wool very well, being easily but slowly decomposed, without the use of tartrates. A little oxalic acid is generally added. The chromic acid thus deposited on the fibre does not affect the feel or spinning qualities of the wool, while the hydrofluoric acid set free appears to have no injurious action on the dye or goods.

Potassium bichromate is the most generally useful mordant for wool, yielding fast and brilliant colors on dyeing. The mordant bath contains potassium bichromate to the amount of 2 to 4 per cent of the weight of the wool, dissolved in water equal to 50 to 100 times the weight of the wool. The goods are boiled in this for one or one and a half hours, and washed, and are then ready for dyeing. Sulphuric acid is sometimes added to the mordant bath in small amounts, but better results are obtained with oxalic acid or cream of tartar, which reduce part of the bichromate to chromium hydroxide on the fibre; by treating the chromed wool in a bath of sodium bisulphite the reduction is more complete. An excess of chromic acid in the fibre oxidizes the color, deadening it when dyed, and also weakens the fibre. Such "overchromed" wool is said to be greatly improved by reduction of the bichromate in the fibre before dyeing.

The nature of the changes which take place in mordanting wool with bichromate has been much studied, but is not yet clearly proved. The work of Knecht,* and of Kay and Bastow,† indicates that the

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* Journal of the Society of Dyers and Colorists, **1888**, 104; and **1889**, 186.

† *Ibid.*, **1887**, 118.

potassium bichromate is partly dissociated into neutral chromate and chromic acid: —

$$K_2Cr_2O_7 = K_2CrO_4 + CrO_3,$$

the latter being absorbed by the fibre, while the neutral chromate remains in the bath. This chromic acid is subsequently reduced during the dyeing.

Silk is sometimes mordanted with basic chromium salts, and potassium bichromate is occasionally used as an oxidizing agent in dyeing catechu browns and logwood blacks.

Iron salts are largely used, both in dyeing and printing, and on all fibres. Both ferrous and ferric salts are employed, the most important being sulphates, basic sulphates (nitrate of iron), acetates, and nitrates. They are not only applied as mordants, but also as oxidizing and weighting materials to modify the shades of color, or to increase the stiffness and density of the goods. With most dyes, iron salts tend to " sadden " or darken the shade, and are therefore chiefly used for dark colors, especially browns and blacks. In mordanting, the iron is usually fixed on the fibre as hydroxide or tannate.

Cotton is treated with ferrous sulphate (copperas, p. 279), after having been previously steeped in tannin, thus precipitating tannate of iron on the fibre. Ferrous acetate (pyrolignite of iron, p. 309) is used by impregnating the fibre with the solution, drying, and aging, or the goods may be passed through limewater. It is also used with tannin-prepared cotton. Nitrate of iron (basic sulphate, p. 148) is generally used for cotton, which is merely saturated in the solution, and then passed into limewater or sodium carbonate solution, the process being repeated until sufficient hydroxide has been deposited on the fibre. **Iron buff** is produced in this way. Sometimes the goods are prepared with tannin, passed through the limewater to form calcium tannate, and then into the iron solution. This produces ferric tannate, varying in color from brown to black.

Wool is sometimes mordanted by boiling with oxalic acid and copperas, the latter chiefly to sadden the color; but other iron salts are not used.

Silks are extensively treated with iron salts in dyeing blacks. The pyrolignite of iron is chiefly used on raw silks which have been previously prepared with tannin, preferably chestnut extract. The silk is worked in a warm (60° C.) pyrolignite of iron solution, exposed to the air for a short time, and then washed. By sufficient repetition of this treatment the weight can be increased by 20 to

150 per cent of the original weight of the silk. Hard water greatly assists this process. The color produced is a bluish black; the lustre is dulled, but is restored by a bath of very dilute hydrochloric acid, to which a little olive oil has been added.

Boiled-off silk is weighted and dyed by the use of **nitrate of iron**, the silk being worked in the iron liquor, washed, and put into a boiling soap solution composed of "boiled-off liquor" (p. 494), olein soap, and a little soda crystals. This precipitates the ferric hydroxide. The silk is then washed with hard water (which helps fix the iron), and the whole process repeated until sufficient iron has been deposited on the fibre. With each operation, the weight of the silk is increased about 4 per cent, and the color becomes dark brown, though the lustre is preserved. This weighted and mordanted silk is then dyed black.

Raw silk is also weighted with nitrate of iron and has greater affinity for the iron salt than has boiled-off silk.

Copper salts are chiefly used as oxidizing materials in mordanting, acting as carriers of oxygen. Copper sulphate (blue vitriol, p. 280) and acetate (verdigris, p. 237) are most used.

Copper sulphate is used in producing logwood blacks and cutch browns on cotton. On wool, it is used together with aluminum sulphate and copperas for logwood blues and blacks, and also with potassium bichromate. Copper salts act as saddeners for logwood blacks on silk.

Antimony salts used as mordants are tartar emetic (potassium antimony tartrate), double oxalates of potassium and antimony, and fluorides of antimony and sodium. They are always used after tannin mordanting on vegetable fibre, where they form antimony tannates. They are not used for silk or wool. Tartar emetic is generally employed, and its application is simple; the tannin mordanted cotton is passed at once into a cold bath of the salt, and then thoroughly washed before drying.

Tin salts are valuable mordants, yielding especially brilliant shades. The salts chiefly used are stannous chloride (tin crystals, $SnCl_2 \cdot 2\,H_2O$), stannic chloride, $SnCl_4$, sodium stannate ("preparing salt," Na_2SnO_3), and stannous nitrate, $Sn(NO_3)_2$ (known only in solution). "*Tin spirits*" is a general name for a number of tin solutions of various composition, made with nitric, sulphuric, or oxalic acid. By dissolving granulated tin in concentrated hydrochloric acid, a solution of stannous chloride is formed, which is sold as "*muriate of tin*"; or tin crystals are separated from it, and the mother-liquors, containing a large amount of tin chloride, are often sold as muriate of tin, single or double, according to the strength. "*Pink salt*" is a double stannic-ammonium chloride, $SnCl_4 + 2\ NH_4Cl$, formerly much used as a mordant. Various solutions of stannic salts were much used under such names as Cotton Spirits, Pink Cutting Liquor, Oxymuriate of Tin, Solution of Tin, etc.

Cotton and linen are not often mordanted with stannous salts, but being powerful reducing agents, they (especially tin crystals) are used by the calico printer in "discharges," or "resists." Stannous chloride reduces iron salts and is used to neutralize the effect of iron impurities in calico printing. Stannic salts are used as mordants on cotton and linen, when these are dyed with natural dye-stuffs, such as camwood, barwood, fustic, etc., and for some of the aniline dyes. Tannic acid is used before the tin, and stannic oxide or stannic tannate is fixed on the fibre. Stannate of soda is also used to mordant cotton and to prepare it for printing; the goods are steeped in the solution and then passed into a bath of dilute mineral acid or aluminum sulphate, which precipitates stannic hydroxide on the fibre.

Wool is often mordanted with stannous chloride by entering it in a cold bath of about 4 per cent tin crystals (calculated on the weight of the wool) and 2 per cent oxalic acid or cream of tartar. This is then slowly heated to boiling. Too much tin salt makes the wool harsh and prevents proper felting in the milling process. Stannic chloride is not a suitable mordant for wool, but impure mixtures of stannic and stannous salts are often used as mordants for cochineal scarlets on wool. Wool is sometimes prepared with sodium stannate for printing, followed by treatment with dilute sulphuric acid.

Black silks are weighted with stannous chloride together with catechu, on fibre which has already been weighted with iron. For weighting light-colored silks, stannic chloride (tin spirits) is often used. The raw fibre is steeped in a solution of tin salt until impregnated, and the tin hydroxide is fixed by treatment with cold dilute soda solution, or by merely washing in water. The silk is then "boiled-off" in soap liquor to remove the harsh feel. The weight is increased about 25 per cent by this process. But stannic chloride has an injurious action on the fibre if too strong (over 50° Tw.) and shrinks it very much, besides destroying certain dyes which may be afterwards used.

Acetic acid (p. 308) is largely used in dyeing and printing, but more as an assistant than a mordant. It neutralizes many bases without affecting the dyeing process, and it does not attack vegetable fibre. Crude pyroligneous acid contains reducing substances, and because of this is used where oxidation is to be prevented.

Oxalic acid, $H_2C_2O_4 \cdot 2\,H_2O$, forms crystals readily soluble in water. It is largely used in dyeing, mainly as an addition to the dye-bath to retard the deposition of the color, and for a fixing agent in mordanting wool with bichromate, aluminum sulphate, or copperas.

Tartaric acid, $C_2H_2(OH)_2(COOH)_2$, is often used as an addition to the mordant bath for wool, and to the dye-bath to retard the dyeing, and in clearing and brightening the color on silk after dyeing; also as a "resist" and "discharge" in calico printing. The most important tartrates are cream of tartar, $C_4H_4O_4(OH) \cdot (OK)$, and tartar emetic, $C_4H_4O_6K \cdot (SbO) + \frac{1}{2}\,H_2O$.

Citric acid, $C_3H_4(OH)(COOH)_3$, and **lactic acid,** $C_2H_4(OH)COOH$ (p. 467), are used somewhat in place of tartaric acid, but more especially as resists, etc., in calico printing.

Turkey-red oil (p. 326), or **soluble oil,** is used as a mordant on cotton for dyeing with basic dyes and Turkey-reds, and for preparing cloth for calico printing.

TANNINS

Tannins, many of which are used in tanning, are important mordants, their value depending on the fact that they are absorbed by cotton, linen, and silk, while they retain their property of precipitating insoluble metallic compounds in the fibre, and also of uniting with the basic dyes. Tannins from different sources are possibly not of the same composition and any particular sample may not be homogeneous. Some of the tannins are glucose esters * of gallic and digallic acids; tannins of this type have been produced synthetically, and it is not impossible that all the more characteristic tannins are glucosides. **Tannic acid,** the most important of the tannins, is probably an ester of glucose with five molecules of *m*-digallic acid, *i.e.* a penta-gallate of glucose. It is soluble in six parts cold water, and is obtained by extracting powdered gall-nuts with water, alcohol, and ether. On evaporation the aqueous solution yields the tannin as a colorless, or light yellow, amorphous, scaly, or vitreous mass. Tannic acid is precipitated from aqueous solution by dilute sulphuric, or hydrochloric acid, by alkalies, chlorides, etc., but not by nitric acid or Glauber's salt. Gelatine or untanned hide removes it completely from solution. It is a weak acid, but will decompose alkali carbonates. It is easily oxidized, and reduces many metallic salts, Fehling's

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* Ber. **46** (**1913**), 3253.

solution, and permanganates. It forms a blue-black precipitate with ferric salts, which is the basis of many kinds of writing ink.

The tannins occur in numerous plants, being found in the roots, bark, wood, leaves, flowers, fruit, seed-pods, or in excrescences on the plant. The chief commercial sources are gall-nuts, sumach, oak and hemlock bark, mimosa bark, chestnut wood, cutch (catechu), gambier, myrabolans, valonia, divi-divi, kino, quebracho, and canaigre.

Galls, or **nut-galls**, are excrescences on various kinds of oak trees, produced by the sting of the female gall wasp, *Cynips gallæ tinctoriæ*, Oliv., and in which the eggs are deposited. Young nut-galls, from which the insect has not yet escaped, are greenish or bluish in color, and are rich in tannin; afterwards they become yellow, and the percentage of tannin is much decreased. The best qualities come from Persia, but the Levant galls, from Smyrna and Tripoli, contain from 55 to 60 per cent tannic acid and some gallic acid. Poorer grades come from Italy, France, Germany, and Austria.

Japanese and Chinese galls are caused by the sting of an insect (plant louse) on the leaves of plants (*Rhus semialata*, Murr.) of the sumach family. These galls are irregular in shape, and are light and hollow, but contain 70 per cent tannin, or even more.

Sumach of commerce consists of the leaves and young twigs from various plants of the *Rhus* family, especially *Rhus Coriaria*, L.; poorer grades are derived from *R. Cotinus*, L. These shrubs are found in many countries, but Italy, Spain, Greece, and Virginia furnish the better grades. Sumach is largely used in mordanting, since it contains very little coloring matter to stain the goods. Good samples contain from 15 to 20 per cent of tannin, and are sold as a fine powder, or as leaves, mixed with twigs and stems. Much is now sold as "extract," a thick brown liquid obtained by evaporating the aqueous solution, usually in vacuum.

Catechu, or **cutch** (*terra japonica*), is obtained from the wood and pods of *Acacia Catechu*, Willd., and from the betel nut, the fruit of the *Areca Catechu*, L., a species of palm-tree. Both plants are natives of India. Cutch appears in commerce as dark brown, irregular lumps, which dissolve in water, forming a dark brown solution. It contains a tannin called catechu-tannic acid, and another body, catechin. It is extensively used as a brown dye on cotton, for calico printing, and also in the weighting of black silks. It is a good mordant for certain basic coal-tar dyes, when employed in dyeing compound shades. On cotton, copper salts should always be used in conjunction with cutch.

Gambier is extracted from the leaves of an Indian shrub, *Uncaria dasyoneura*, Korth. It has a yellow color, and is used somewhat as a pigment and as a yellow dye. It is slightly soluble in cold water, and very readily so in hot water. In commerce it appears as small cubical blocks, containing about 40 per cent tannin, chiefly as catechu-tannic acid. Gambier is used in silk and cotton dyeing, much in the same way as catechu. It is extensively used in tanning Morocco leather.

Myrabolans are the dried fruit of certain Indian and Chinese trees, *Myrobolanus Chebula*, Gært. They appear in commerce as dried and shrivelled nuts about an inch long, containing about 30 per cent tannin (ellagitannic acid), and also a brownish coloring matter. They are used in place of tannic acid, for some purposes in mordanting cloth, and also in weighting black silks.

Valonia is the acorn cups of an oak, *Quercus Ægilops*, L., native of Greece, Asia Minor, and France. The cups are very large, and covered with coarse hair, or "beard," which is especially rich in tannin. They are drab in color, and contain a yellow coloring matter. Good valonia contains about 30 per cent of true tannic acid.

Divi-divi is the fruit of a West Indian tree, *Cæsalpinia coriaria*, Willd. It forms very thin pods about three inches long, and often folded and twisted, and containing about 30 per cent of ellagitannic acid, with some gallic acid. The color of the pods varies from light brown to black, and considerable coloring matter is present, which stains the goods. It is used for mordanting blacks on cotton and silk.

Chestnut, *Castanea sativa*, Mill., furnishes a tannin extract, the composition of whose tannin is unknown. The extract is a black solid, or a brown syrup, forming turbid solutions with water. It is extensively used in weighting black silk.

Kino is the dried sap of certain trees, *Pterocarpus Marsupium*, Roxb., *Butea frondosa*, Roxb., and *Eucalyptus rostrata*, Schlecht. It forms small garnet-red angular grains, slightly soluble in water, and contains a large quantity of kinotannic acid, a substance of unknown composition. The chief supplies come from India, Africa, and Australia. It is chiefly used in medicine, and resembles catechu.

Oak and hemlock bark are rich in tannins, containing about 15 per cent, but they are contaminated with certain anhydride substances which are slightly soluble in water, and color the goods a deep brown or red, and hence are unsuitable for mordants. These anhydrides are called *phlobaphenes*, and are much like the tannins in their action, combining with fibre and precipitating gelatine, ferric salts, etc.

These barks are extensively used for making leather, especially the heavy and strong kinds.

Mimosa bark (Wattle) is obtained from several species of *Acacia* in Australia, Natal, and South America. It contains from 24 to 40 per cent tannins.

Quebracho is an extract made from hardwood trees, *Aspidosperma Quebracho*, Schlecht, and *Quebrachia Lorentzii*, Griseb., natives of South America. It contains about 25 per cent of tannins, contaminated with red coloring matter.

Canaigre is obtained from the roots of a species of dock, *Rumex hymenosepalus*, Torr., a native of Arizona and New Mexico. It is now extensively cultivated in the southwestern part of the United States. It contains about 30 per cent of tannin, together with a bright yellow coloring matter, much resembling gambier. It is always sold as extract.

Extracts are now prepared from nearly all of the above tannin substances, by treating them with water and evaporating the tannin solution to a thick syrup, or even to dryness, generally by the aid of vacuum. These extracts are much more economical to ship, and more convenient to use, but are frequently adulterated with glucose or other matter.

COLORING MATTERS

According to their origin coloring matters may be classified broadly into three groups: (1) Natural Organic Dyestuffs (Vegetable and Animal); (2) Artificial Organic Dyestuffs; (3) Mineral Dyestuffs. For practical purposes, however, a classification based upon the method of application to the fibres (p. 531) is more convenient.

NATURAL DYESTUFFS

Natural dyestuffs have been employed for textile coloring since prehistoric times. They are soluble in water and have more or less tendency to combine directly with the fibres. Many of them are not in themselves dyes, but form color lakes by combination with mordants. In recent years they have been very generally replaced by the more brilliant and readily applied artificial colors.

Indigo is one of the oldest known dyes, and probably originated in India. It exists in the indigo plant, *Indigofera tinctoria*, L., and in woad, *Isatis tinctoria*, L., in the form of a glucoside, *indican*, $C_{26}H_{31}NO_{17}$, which is decomposed by acids to form the coloring principle indigotine, $C_{16}H_{10}N_2O_2$, and a sugar. To isolate the coloring matter, the stems and leaves of the plant are put into a cemented cistern and covered with water. A fermentation soon begins, causing a rise in the temperature, while the indican is decomposed and the sugary matter destroyed; at the same time, the indigo is reduced to indigo white, $C_{16}H_{12}N_2O_2$. This dissolves to form a greenish-yellow liquid, which is drawn off into vats and violently stirred and splashed by the workmen for several hours, in order to thoroughly aerate and oxidize the indigo white. The blue pigment precipitates, and after settling, the liquor is drained off. The magma is repeatedly washed and finally boiled, to prevent any further fermentation, and is filtered, drained in cloth-lined frames, and finally pressed into cakes; these are carefully dried, away from the sunlight. The yield is about 0.2 to 0.3 per cent of the weight of the plant.

The indigo of commerce forms dark blue cubical cakes having a matt, earthy appearance on the fractured surface. Its content of pure indigo varies from 20 to 90 per cent and averages about 45 per cent. It contains indigo red and indigo brown, which affect the shade of the blue; also moisture and mineral and glutinous substances. Indigo is tasteless, odorless, insoluble in water, alcohol, ether, dilute acids or alkalies. By careful heating it sublimes. If very finely powdered, concentrated and fuming sulphuric acid dissolve it to form mono- and disulphonic acids, the latter being soluble in water. The sodium salts of these indigo sulphonic acids constitute the **indigo extract, soluble indigo,** or **indigo carmine** of commerce. These are obtained by neutralizing the sulphuric acid solution of indigo with sodium carbonate, and precipitating the indigo carmine by adding common salt. True indigo carmine is the sodium salt of the disulphonic acid, and is dyed on animal fibres as an acid dye, p. 535; when sold as a dry powder it is called "**indigotine.**"

The vegetable indigo industry is now greatly diminished through competition by the artificial product.

Artificial indigo has almost entirely replaced natural indigo since about 1910, its successful production on a commercial scale being the result of long series of investigations and experiments. But none of the various syntheses proposed were feasible, until the discovery that naphthalene could be used as raw material.

Naphthalene is oxidized to phthalic anhydride by fuming sulphuric acid in the presence of mercury bisulphate to moderate the reaction; the sulphur dioxide liberated is recovered for use in the "contact sulphuric acid process." The phthalic anhydride is converted into phthalimide, which by oxidation with chlorine yields anthranilic acid. This by treatment with monochloracetic acid yields phenylglycine-o-carboxylic acid, which by fusion with caustic potash* forms indoxylic acid and indoxyl; these are converted into indigo by oxidation with air.

For methods of indigo dyeing, see p. 541.

Logwood is the heart wood of a tropical tree, *Hæmatoxylon Campechianum*, L., native in Central America. It is brought into commerce in the form of logs, chips, and extract. The chromogen (p. 527) in the wood is *hæmatoxylin*, $C_{16}H_{14}O_6$, which forms nearly colorless crystals when pure; it exists in the wood as a glucoside and partly in the free state. It is readily oxidized, especially in the presence of an alkali, to form hæmatein, $C_{16}H_{12}O_6$, which is the real dyestuff. This forms colored lakes with metallic bases, yielding violets, blues, and blacks with the various mordants.

The logs are chipped or rasped to form a coarse powder, which does not contain much hæmatein when fresh, the dyestuff being formed by "curing" or oxidizing. The rasped wood is fermented by moistening with water and exposing in heaps to the air. To control the temperature and give better exposure, the heap is shovelled over and sprinkled with water at frequent intervals, until the chips assume a deep, reddish-brown color, or even develop a bronze shade. Alkalies, potassium nitrate, chalk, or ammonium chlorate are sometimes added to hasten the process. The cured chips yield a decoction which is rapidly taken up by the fibre in dyeing operations. The amount of water in cured chips is nearly double that contained in the fresh wood.

Most "**extract**" of logwood is now made from chips which are not cured. They are put into an extractor, an iron vessel provided with a false bottom and a perforated steam coil. The extractors are often set in batteries, so arranged that the liquor from one flows into the next more recently filled vessel, finally leaving that containing the freshest wood. Pressure extraction is often used, but an increase of over 15 pounds is liable to cause decrease in the coloring power of the product. After settling to separate wood fibre and resin, the liquid from the extractors is evaporated in vacuum pans, the Yaryan being often used for the dilute liquors. When it becomes thick, the evaporation is continued in a common vacuum pan (strike pan) until a density of about 50° Tw. is reached for liquid extract; or it may be continued until a solid extract is obtained on cooling.

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* Better yields are obtained if sodamide is used instead of caustic potash for the fusion, but its price is relatively high.

Throughout the process, precautions are taken to prevent access of air and consequent oxidation of the product. The use of chemicals to develop the color in the extract itself is of doubtful value, as this development should only take place in the dye-bath. The yield of solid extract is about 20 per cent with pressure, and without pressure about 16 per cent.

Logwood extract is frequently adulterated with glucose, molasses, and chestnut, hemlock, and quercitron extracts. Logwood is chiefly used with a chrome or iron mordant for blacks on wool and cotton.

Red woods of commerce are **Brazil wood,** *Cæsalpinia Brasiliensis,* L., and **Pernambuco wood** (*C. Crista,* L.), from Brazil, West Indies, and Bahama; **sappan wood,** *C. Sappan,* L., from China, Japan, and Siam; **Lima wood,** *C. bijuga,* Sw., from Central America; and **peach wood,** *C. echinata,* Lam. These contain the chromogen *brazilin,* $C_{16}H_{14}O_5$, which is chemically related to hæmatoxylin. Brazilin is colorless, but dissolves in alkalies, forming a red solution which oxidizes on exposure to the air, forming brazilein, $C_{16}H_{12}O_5$; this combines with alumina to form red lake similar to alizarin red, but more fugitive.

Another class of red woods contains *santalin* ($C_{15}H_{14}O_5$). These resemble Brazil woods in color, but are heavier and of harder texture. The more common ones are **sandal wood,** *Pterocarpus santalinus,* L., from Madagascar and the East Indies; **barwood,** *Baphia nitida,* Lodd., and **camwood.**

Madder is the pulverized root of *Rubia tinctorum,* L., a plant formerly largely cultivated in Europe and Asia Minor. It contains glucosides which are decomposed by fermentation, forming **alizarin,** $C_{14}H_6O_2(OH)_2$, and **purpurin,** $C_{14}H_5O_2(OH)_3$, which are identical with di- and trioxyanthrachinon. Madder extract is prepared by fermentation and evaporation of the filtered solution, yielding "**garancine**" and "**madder flowers.**"

Madder has been used for ages in dyeing Turkey-red on cotton, affording one of the brightest and fastest colors. But in 1868, Græbe and Liebermann made artificial alizarin from anthracene derived from coal-tar. In consequence of this discovery, the madder industry has nearly disappeared.

Alizarin is made from anthracene by oxidizing the latter with chromic acid, to form anthraquinone. This is treated with fuming sulphuric acid, which converts it into a monosulphonic acid, soluble in water. By neutralizing with caustic soda, the difficultly soluble sodium salt is precipitated from the solution. The sodium salt is mixed with caustic soda and an oxidizing agent ($KClO_3$) and heated for two days in an autoclave at 180° C., whereby the sulphonic group is replaced by hydroxyl, and another hydroxyl group is introduced in the ortho position to the first. By dissolving the fused mass in water and adding sulphuric acid, the alizarin is precipitated as a nearly insoluble yellow mass, which is brought into commerce as a wet paste containing about 20 per cent of coloring matter. Other methods of preparation without sulphonation are also in use.

Archil or **orseille** (cudbear) is an important dyestuff derived from certain lichens, *Roccella tinctoria,* D. C., *R. fuciformis* (L.) D. C., indigenous in Madagascar, Zanzibar, Azores, Ceylon, and France, and *Lecanora tartarea,* Achar., from Sweden. They contain mixtures of phenols and phenol acids, which, when treated with ammonia and exposed to the air, yield *orcein,* a violet powder sold as "cudbear." It is either a paste or powder prepared by evaporating the aqueous extract to dryness in vacuum. The powder dissolves in alkalies and forms colored lakes with heavy metals and lime. It was formerly much used in wool dyeing, yielding violet and red shades.

Litmus is obtained by treating the above-mentioned lichens with ammonia and potash, and fermenting the mass. The dyestuff forms a red color-acid, whose alkali salts are blue. The commercial article consists of calcium carbonate, or sulphate, which is mixed with the coloring matter and formed into small cubes. It is not used as a dye, but is interesting because of its use as an indicator.

Cochineal consists of the dried bodies of the female insects, *Coccus cacti.* These insects live on certain cactus plants in Mexico, Central America, Algeria, and the East Indies; they are collected, and killed by placing them in ovens or in hot water, or by steaming them. When killed by dry heat, the cochineal is coated with a silvery gray powder, consisting of a wax, *coccerin;* but if boiled or steamed, the cochineal is "black," and of less tinctorial power. The silver gray is often imitated by dusting the black cochineal with powdered stearic acid or talc. The coloring principle is *carminic acid,* $C_{17}H_{18}O_{10}$, a glucoside, soluble with a deep red color in water, and forming scarlet lakes with alumina and tin salts. Cochineal contains about 10 per cent carminic acid. The dye is chiefly used on wool. Cochineal yields the pigment carmine (p. 245).

Lac dye is also obtained from an insect, *Coccus lacca,* which exudes the lac resin (p. 396). The collection and preparation of the resin involve the preparation of the dye. The latter is very similar to carminic acid, and is prepared by extracting the gum with sodium carbonate,

Kermes is similar to cochineal, and consists of dried insects, *Coccus ilicis*, from northern Africa and Spain. It is seldom used in dyeing at the present time.

Fustic is the heart wood of *Chlorophora tinctoria*, Gaud., or *Maclura tinctoria*, native in West Indies and tropical South America. It yields a coloring principle, *morin*, $C_{15}H_{10}O_7 \cdot 2\ H_2O$, which forms lemon yellow lakes with alumina. It is sold as chips, and as an extract, and is chiefly used for wool dyeing, especially for modifying the shade of logwood and other dyes.

Young fustic is the heart wood of a sumach, *Rhus Cotinus*, L., native in Spain, Italy, Hungary, and the Levant. It yields an orange-colored lake with alumina and tin. The color principle is *fisetin*, $C_{15}H_{10}O_6$.

Quercitron is the powdered bark of the North American tree, *Quercus coccinea*, var. *tinctoria*, Gray. It contains a dyestuff, *quercitrin*, $C_{21}H_{20}O_{11} \cdot 2\ H_2O$, which is converted by dilute acid into *quercetin*, $C_{15}H_{10}O_7$, and isodulcit, $C_6H_{12}O_5$. Quercetin dissolves in alkali with a yellow color, and forms yellow lakes with alumina and tin. By extracting the bark with alkali, and neutralizing the extract with sulphuric acid, a mixture of quercitrin, quercitin, and isodulcit is obtained, which appears in commerce as " **flavine**." Both the bark and the extract are used in wool dyeing and calico printing.

Persian berries are the dried fruit (berries) of certain buckthorn (*Rhamnus*) species, growing throughout southern Europe. The coloring principle is a glucoside, which is decomposed by acids into isodulcit and *rhamnetin*, $C_{16}H_{12}O_7$, the latter being the dyestuff. It forms yellow and orange shades with alumina and tin, and is mainly used in calico printing.

Curcuma, or **turmeric**, is the dried root of various species of *Curcuma* of Central Asia. The dyestuff is *curcumin*, $C_{14}H_{14}O_4$, or $C_{21}H_{20}O_6$, which yields a tolerably fast yellow on cotton. It is also used to color oils and wax.

Annatto (*arnotto*) is obtained from the fruit of the West Indian and South American trees, *Bixa Orellana*, L. It contains the orange dye, *bixin*, $C_{28}H_{34}O_5$, and comes in commerce as a thick paste, or dry cakes. It is mainly used for coloring butter and cheese.

Cutch is described on p. 519.

ARTIFICIAL DYESTUFFS

The artificial organic dyestuff industry originated in England with the discovery of the lilac color, *mauve*, by Perkin, in 1856.

This was obtained by direct oxidation of aniline containing toluidine. In 1859 Verguin made magenta, or fuchsine, and each following year other colors were discovered, until at the present time there are several thousand dyes on the market, and a stupendous industry has arisen in their manufacture. Because the first artificial dyes were prepared from aniline, the colors were known as "aniline dyes," a name still applied to them, but they are now more properly called "coal-tar dyestuffs." They are made from various aromatic substances largely derived from coal-tar, especially the benzene hydrocarbons, phenols, and pyridine bases.

The relation of the color to the constitution in the coal-tar dyes has been explained by Witt.* He shows that the introduction of certain groups (called chromophores) into *colorless* aromatic hydrocarbons produces colored substances called chromogens. The chromogens possess very slight coloring power in themselves, but are converted into dyestuffs by the addition of certain salt-forming (auxochromous) groups, such as hydroxyl (OH), or the amino group (NH_2). Thus benzene is colorless, but the introduction of chromophor groups, such as the nitro group (NO_2), or the azo group ($-N=N-$), forms the colored chromogens, mono-, di-, and tri-nitrobenzene, or azobenzene. The chromogens may take on the auxochromous groups (OH) or (NH_2), and form dyestuffs such as picric acid, $C_6H_2(NO_2)_3(OH)$, or amino-azobenzene, $C_6H_5N=NC_6H_4 \cdot NH_2$. If the auxochromous groups are converted into salts, the color is much intensified; thus sodium picrate is a deeper yellow than picric acid. But the sulpho-group, SO_3H, and the carboxyl group, CO_2H, are not auxochromous, notwithstanding that they form salts, and they impart little tinctorial power to the chromogens. From this Witt drew the following conclusions: —

(1) The simultaneous occurrence of a chromophor and an auxochromous group is essential to the development of tinctorial properties in an aromatic substance.

(2) The chromophor exerts a greater color-generating influence in the saltlike derivatives of the dyestuff than in the free compounds.

(3) In the case of dyes of similar constitution, the one having the more stable salts is the better.

A classification of the synthetic dyestuffs according to their constitution, with reference to Witt's theory, may be made, but for

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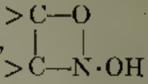
* Ber. d. deutsch. Chem. Gesel. **9** (1876), 522.

practical uses a grouping according to the methods of application to the textile fibres is more useful (see p. 531).

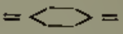
Classified according to structure the following groups * are distinguished: —

I. Nitroso- or Quinoneoxime derivatives; chromophor, 

$$\begin{array}{l} >C-O \\ \;\;|\quad\;\;| \\ >C-N\cdot OH \end{array}$$

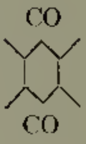
II. Nitro derivatives; chromophor, $-NO_2$

III. Azo dyestuffs; chromophor, $-N=N-$

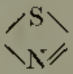
IV. Triphenylmethane dyestuffs; chromophor, 

V. Pyronine dyes; chromophor, 

VI. Acridine dyestuffs; chromophor, 

VII. Oxyketone dyestuffs; chromophor, 

VIII. Oxazine dyes; chromophor, 

IX. Thiazine dyes; chromophor, 

X. Azine dyes; chromophor,  or 

XI. Miscellaneous dyestuffs.

The limits of this book will not permit a full consideration of the individual dyestuffs, and for them recourse must be had to the handbooks mentioned in the list of references.

Dyestuffs are often called **substantive** and **adjective**; the former will color fibres directly, the latter will only color with any permanence when used in conjunction with a mordant. Nietzki designates † the two classes as **direct dyes** and **mordant dyes**. Hummel divides ‡ coloring matters into **monogenetic**, or those which produce only one color under any condition; **polygenetic**, those which produce several colors, according to the mordant used.

DYEING

Dyeing is the process of precipitating coloring matter upon, or within, the substance of a body which is to be colored. Dyestuffs are distinguished from pigments by the fact that they are soluble in

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* After Gardner in the Dictionary of Applied Chemistry, 2d ed., Vol. II, 282.

† Farber-Zeit., 1889–90.

‡ Dyeing of Textile Fabrics, p. 147.

water, or in the liquid of the dye-bath, from which solution they are abstracted by the material to be dyed. In the majority of cases dyes are applied to textile fibres or fabrics, but occasionally natural products, such as straw, feathers, horn, leather, ivory, bone, or wood may be dyed. The substance is immersed in a hot or cold aqueous solution of the dyestuff, except in a few rare cases where other solvents than water may be used, or the solution applied as a spray. The solution may be acid, alkaline, or neutral, according to the nature of the material and of the dyestuff; thus alkaline or neutral baths are generally used for cotton and vegetable fibres, neutral or acid baths for wool, and acid or alkaline baths for silk.

Several theories concerning the nature of the dyeing process have been proposed. The **mechanical theory** assumes the coloring to be due to mechanical absorption of the dye within the capillary tubes and pores of the fibres. The inability of many dyes to color all fibres equally well is ascribed to the different size of the pores of the fibres, relative to the size of the dye molecules. Also the size of the pores may be affected by heat, or by the action of certain chemicals, as astringents.

The **chemical theory** * supposes a chemical combination to take place between the coloring matter and some, or all, of the constituents of the fibre.† It has been shown that silk and wool, when brought into reaction with many dyes, will set free the acid united with the color base; also that the colorless rosaniline base in the dye-bath will color wool by the formation of a salt with the constituents of the fibre. The action of silk and wool towards acids and bases is in general similar to that of amino-acids, of which these fibres are condensation products. The relative fastness of a color on different fibres is also in accord with the chemical theory.

The **solid solution theory**, advanced by O. N. Witt in 1889, supposes that dyeing consists in the formation of a solid solution of the dye, or of the mordant in the case of mordant colors, in the fibre, analogous to the solution of metallic oxides in colored glass. The coloring substance is withdrawn from its liquid solution in the dye-bath and passes into the fibre, the fibre substance acting as the solid solvent; this action is similar to the extraction of a substance from its aqueous solution, by ether or other solvent in which the body is more readily soluble than it is in water.

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* See Knecht, Jour. Soc. Chem. Ind., **1889**, 457.

† This applies to animal fibres but is difficult to reconcile with the chemical inertness of cellulose.

Recent investigations * indicate that dyeing is due to **adsorption** of the **colloidal coloring substance** on the surface of the fibre, and that the amount of color deposited from solution, on any kind of fibre, depends on the same laws that control the adsorption of gases, or of dissolved substances, upon the surface of adsorbing media, such as bone-black, etc. It has been found experimentally, that in adsorption processes, the amount of substance condensed on the surface of the adsorbing agent is a power function of the concentration of the adsorbed material, whether this exists as a gas, or in solution, and furthermore, it has been shown that the removal of many dyestuffs from solution by such diversified substances as cotton, silk and wool fibres, bone-char, precipitated silica, metallic hydroxides, etc., follows this law; and also that the constants of the adsorption equation are of the same order of magnitude for the different adsorbing agents. Thus according to Freundlich, and others, dyeing phenomena obey the formula $\frac{x}{m} = K \cdot C^{\frac{1}{n}}$, where x denotes the weight of color taken from solution; m is the weight of fibre dyed; C is the final concentration of color in the dye-bath; and K and $\frac{1}{n}$ are constants.

This last hypothesis seems to throw more light on the nature of the dyeing process than any of the others, and while in some cases chemical action with the fibre and the mordant undoubtedly plays a part, in the following the facts given will in general be interpreted in terms of the adsorption theory.

The methods of dyeing and composition of the dye-bath vary with the nature of the fibre and of the dye. Silk and wool are often dyed directly, although mordants are frequently used; cotton and linen have much less affinity for coloring matters; dyes of the benzidine class and the sulphur colors are used for these fibres directly, but basic and mordant colors require the fibre to be mordanted.

The character of the water is very important in dyeing. Iron is the most injurious impurity, since it dulls (saddens) the shade of most colors. Hard water containing lime or magnesium salts should generally be purified before use, but in a few cases, as in dyeing Turkey-reds, and with logwood, a little lime is beneficial. Suspended dirt must be removed.

The tanks used for dyeing are usually made of iron; but for

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* Müller and Slassarski. Krafft, J. Soc. Dyers and Col., **1899**, 211. Biltz, *ibid.*, **1904**, 145.

certain delicate colors, especially on silk, they are made of wood, so put together that no metal comes in contact with the dye-liquor. The pipes and coils used for heating are generally copper.

Loose cotton and wool are dyed by submerging in vats filled with the dye-liquor. Or the mass of fibre may be compressed into a closed vat having a false bottom, the liquor being circulated through the mass by pumping from below the false bottom, and returning it to the top. An apparatus similar to that shown in Fig. 120 is sometimes used.

Hanks of yarn are often dyed by suspending from sticks, or rods, laid across the top of the open dye-vat, which has a false bottom, under which the heating steam is introduced. Turning the hanks by hand involves much labor, and machines have been devised in which the hanks, weighted at the lower end by rollers to keep them straight, are suspended on rollers of wood or porcelain, which are rotated by driving gears. Or the hanks are fixed on rods, on the periphery of a rotating drum, which is partly submerged in the dye-bath; the rods are revolved slightly, at each turn of the drum, so the skeins are moved frequently during the dyeing. The apparatus is enclosed in a wooden case, to confine the steam and heat, and prevent too much cooling of the yarn while not submerged.

Much yarn is dyed while wound on the " cops " or spools formed on the spinning frames, the dye-liquor being forced through the perforated tubes of the spools, from the interior to the exterior of every spool. Yarn in warps is dyed by running the warp over numerous rollers submerged in the dye-liquor, in a deep vat.

The commercial dyes may be grouped, according to the method of their application to the fibre, into eight classes: —

I. Direct dyes, yielding full colors on all fibres without mordants.

II. Basic dyes, which form insoluble tannates and require mordants on vegetable fibres, but color animal fibres without mordants.

III. Acid dyes, which require no mordant on animal fibres, but are only of limited use with vegetable fibres, mordanted or not.

IV. Mordant dyes, which require metallic mordants on both animal and vegetable fibres.

V. Acid-mordant dyes, which will dye animal fibres directly, but require mordants for the development of full and fast colors.

VI. Sulphide colors which dye vegetable fibres from alkaline baths containing sodium sulphide in solution.

VII. Vat dyes, which require reduction to a soluble form in dilute alkaline solution, followed by reoxidation of the dyestuff on the fibre, to develop the color.

VIII. Ingrain colors, which are produced directly from their constituents upon the fibre.

I. The **direct dyes** are soluble colors which are adsorbed from solution by all fibres, although the adsorption from the bath is usually not very complete. These dyes, therefore, tend to " bleed " when washed, but this same property makes them easy to dye evenly, (" level ") on the goods, as they readily redissolve from a point where heavily deposited and again precipitate on less heavily colored places. They are rather fugitive to light, and are affected by acids and alkalies. By after-treatment with certain metallic salts (copper, chromium, etc.) the fastness to light and washing is much improved. Those dyes in which the auxochrome is an amino group may be diazotized and " developed " on the fibre, with phenols or amino-compounds, and thus their fastness can be increased.

The dye-baths for direct colors must be concentrated color solutions, and do not exhaust well, hence the practice of using standing baths is common, a certain amount of dye being added to the bath before the next batch of goods is entered. A so-called " **assistant** " is usually added to the dye-bath to accelerate, retard, or modify the deposition of the color; but this does not enter into combination with the color (or with the mordant when used with basic, acid, or other dyes). The assistants used for direct dyes are Glauber's salt, common salt, soda, borax, sodium phosphate, or soap; these are added in amounts varying from 5 to 50 or more per cent of the weight of the goods to be dyed. The assistant, when a neutral salt, renders the dye less soluble and causes more complete precipitation on the goods, by its " salting-out effect " *; an assistant with alkaline or acid reaction is more generally used to retard the deposition by increasing the solubility.

Wool is dyed with the direct dyes by boiling in neutral or slightly acid (acetic acid) baths, usually with the addition of Glauber's salt. As a rule the acetic acid is not added until the dye-bath is nearly exhausted. The shades produced on wool are tolerably fast to acids, washing, and milling, in most cases.

Silk is seldom dyed with direct dyes, but may be colored in weak acid (acetic, tartaric, citric, or sulphuric) baths of " boiled-off " liquor (p. 494), or soap, starting at about 40° C., and slowly raising the temperature to boiling.

* See Nernst's Theoretical Chemistry, p. 537.

Cotton is dyed with direct colors in cold, luke-warm, or boiling baths, containing 5 to 20 per cent Glauber's salt, and 3 to 5 per cent soda-ash. Sometimes 2 to 10 per cent common salt is used with, or in place of, the Glauber's salt. Caustic soda and soap may be used in the bath for cold dyeing. After dyeing the goods are worked in a solution of Turkey-red oil, or this may be added to the dye-bath.

Mixed wool and cotton goods (" unions ") are often colored with such direct dyes as have equal affinity for the two fibres, in order that the shades may match. Mixed cotton and silk goods are also dyed with direct colors; since some of them do not color silk in soap baths, it is often possible to dye two shades on such mixed goods producing varieties of " changeable " or " shot " effect. Thus, the cotton may be dyed in a soap-bath and the silk in a second bath of an azo or acid color, which has no effect on the cotton.

Diazotizing the dyed goods with sodium nitrite in acid solution, washing in cold water, and passing directly into a developing bath containing a phenol, or amino-compound (resorcinol, β-naphthol, etc.), increases the fastness greatly of many of these colors on cotton. Or the dyed goods may be worked in a diazotized solution of an amino-body (*e.g.* p-nitraniline). This process is called " *coupling*."

After-treatment with metallic salts, by working the dyed and rinsed goods in a warm acetic acid solution of copper sulphate, potassium bichromate, or chromium fluoride, is much employed with those dyes containing free OH or COOH groups, to increase the fastness. Many of the direct dyes when dyed on cotton act as mordants for basic colors, which are thus used for " topping " the dyed goods.

II. **Basic dyes** are the salts of colorless bases which contain chromophorous groups; the color does not appear until the salt is formed. These salts are not appreciably adsorbed by fibres, except those of an acid character, such as wool and silk, in which case an insoluble color salt or lake of the base with the fibre itself is probably formed; the acid of the salt in the dye-bath is largely left as free acid in the solution. The dyes of this group are the most brilliant known (such as auramine, rhodamine, malachite greens, methylene blue, and methyl violets), and are monogenetic; they vary much in constitution and fastness, but in general are rather fugitive and fade through the action of light, soap, and milling. They have great tinctorial power, one per cent usually yielding full shades.

These dyes are usually applied in neutral, or very slightly acid or alkaline baths. Calcarious water is bad for these dyes, as it precipitates the color bases as a sticky, curdy mass, which adheres to the fibre, causing spots and unevenness. The commercial dyestuffs are usually hydrochlorides, but some are acetates, oxalates, sulphates, or double salts with zinc chloride.

Wool is dyed directly in a boiling bath, by the basic dyes, for which it has great affinity, as above explained, but since with few exceptions the colors are not fast, they are little used on this fibre. The addition of a little acetic or sulphuric acid, or alum, to the bath moderates the color deposition by rendering the dye more soluble, and affords more level dyeing. Certain basic dyes (*e.g.* methyl and benzaldehyde greens) have no affinity for wool until it has been mordanted with sulphur, by treating with sodium thiosulphate and sulphuric acid, or alum. A few of the basic dyes (*e.g.* Victoria blues) are very fast to milling on wool, and thus find considerable use.

Silk is largely dyed with basic dyes, since fastness to light is less important with this material, while brilliancy of shade is much desired. The dyeing is done in neutral, or slightly acid or alkaline baths, containing "boiled-off" liquor, or neutral soap solution, and the temperature is usually kept between 70° and 100° C. Some acetic, tartaric, or citric acid, or often sulphuric acid, is used to neutralize the alkalinity of the "boiled-off liquor," and the dyed material, after washing, is generally "brightened" by passing through dilute acetic or tartaric acid,* hydroextracting, and drying without washing.

Cotton having no affinity for basic dyes requires a mordant of an acid nature. Tannin (fixed † as antimony, tin, or iron salt) or Turkey-red oil (fixed with aluminum acetate as the insoluble aluminum salt of the sulpho-acid) are the usual mordants for basic colors, the cotton being mordanted first, and then dyed in luke-warm baths, which are slowly heated to 60° C. Higher temperature may cause a loss of brilliancy in shade. The goods are hydroextracted, or evenly wrung, and dried without washing. Probably the basic dyestuff combines with the acid of the mordant to form an insoluble or at least highly adsorbed salt, leaving the free metallic hydrate in the pores of the fibre. The deposited color may, however, be of the nature of a double salt of the color-base and the metal.

Union goods are dyed in neutral or acid bath, the cotton having been previously mordanted cold, with tannin and antimony, which

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* It is probable that a part of the dye is adsorbed as the free color-base, especially from neutral or alkaline dye-baths. This acid serves to convert all to the colored salt.

† That is, rendered insoluble.

have no effect on the wool. Silk and cotton mixed goods are first dyed, so that the silk is colored, and then passed through cold tannin solution to mordant the cotton and dyed in a second bath.

III. **Acid dyes** constitute the most numerous class of artificial coloring matters. All are dyed on animal fibres in acid baths, and may be mixed in the same bath for compound shades. The commercial dyestuffs consist of alkali or lime salts of the color acid, except in the case of picric acid, which is used in the free state. The color acids of these dyes are strongly adsorbed on animal fibres, (perhaps due to interaction with the amido-groups of the fibre substance) but are not appreciably adsorbed by cellulose.

The acid dyes are grouped, according to their constitution, into

(*a*) Nitro compounds.
(*b*) Sulphonated basic dyes.
(*c*) Azo colors.
(*d*) Phthaleins.

The nitro-dyes are all yellows and owe their acid nature and coloring properties to the chromophorus nitro-groups present. They usually have auxochromous groups, such as OH, or imido (NH) also.

The sulphonated basic dyes are derived from coloring matters which are bases, by introducing the sulpho-group (SO_3H). This does not materially change the hue of the basic dye, but does reduce its tinctorial power, and destroys its affinity for tannin mordants.

The azo colors contain besides the chromophor (azo-group) $—N = N—$, certain auxochromous groups, either OH or NH_2. These are the most numerous and important of the acid dyes, and are extensively used on wool. The colors are fast on wool to light and acids, and fairly so on silk.

The phthaleins comprise certain brilliant pinks and reds (*e.g.* the eosins) much used for silk. They are dyed from very weak (acetic) acid baths.

Related to the acid dyes are the *acid-chrome colors,* which are dyed on wool from acid baths, and then fixed or developed by an after-treatment with chrome mordants.

Wool is dyed with acid colors by boiling in baths containing free sulphuric acid and 10 to 20 per cent Glauber's salt. The former sets free the color-acid and reduces its solubility by driving back its dissociation in accordance with the law of mass action, while the latter acts as a restraining assistant, and promotes level dyeing by driving back the dissociation of the sulphuric acid, thus decreasing both the amount of color-acid set free, and the lowering of its solubility. Acetic or formic acid may be used in place of the sulphuric, and being weaker, promote level shades, though their greater cost lessens their use. By adding the acid a little at a time during the boiling, the color-acid is liberated gradually and level dyeing is facilitated. The use of ammonium acetate in the dye-bath is advantageous, since it hydrolyzes slowly in the boiling liquor, the ammonia volatilizing and setting free its acid, which then decomposes the dyestuff and the color-acid is deposited on the fibre. In the case of the *alkali blues,* the color-acid is insoluble in water but its alkali salt dissolves readily, giving a colorless solution with borax or soda. The wool on boiling in this bath is impregnated with the alkaline solution but shows no color; on passing into an acid bath, the alkali salt is decomposed, and the free color-acid develops on the fibre as a deep-blue color.

Silk is dyed with acid dyes in a bath containing a large quantity of "boiled-off" liquor, which is made slightly acid by acetic or formic acid. The temperature is kept between 70° and 90° C., since boiling lessens the affinity of the silk for the dye. After dyeing and washing, the silk is "brightened" * in dilute acid and dried without washing.

Cotton and other vegetable fibres have no affinity for acid dyes, and even mordanting with alum and soda, or stannic chloride, followed by basic alum, does not produce satisfactory results. The colors are not fast to washing nor to light.

IV. The **mordant dyes** are substances not adsorbed by fibres, but strongly adsorbed on various weak, insoluble metallic hydroxides, or in some cases perhaps forming definite salts with them. In either case the product of the condensation of the dye on the hydrate is called a color-lake. They yield colors which are generally fast to washing, soaping, milling, and light. They comprise a great variety of coloring matters, both of natural and artificial origin, which in view of their nature must be dyed on all fibres by the aid of *metallic* mordants. Many of these dyes are polygenetic.

The mordanted goods are passed into a dye-bath, usually containing the color alone; but in the case of certain natural dyewoods, the mordant and dye may be applied in the same bath; in others, the goods are first impregnated with the dye, and the color fixed on the fibre by subsequent treatment in the mordant bath (*dyeing and*

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* See p. 534. In this case it is possible that the color-acid forms with the fibre a less highly colored salt; the acid treatment decomposes this, leaving all the color in the acid form.

saddening method). Mordant colors may be mixed in the same dye-bath, provided the same mordant is used for each.

The mordant oxides chiefly employed are those of aluminum, chromium, iron, and tin. The mordant colors themselves serve as mordants for fixing basic dyes, hence the latter are often used to brighten the shade of the former. Many of the artificial mordant colors are nearly insoluble in water, and if once dried are difficult to again dissolve in the dye-bath; these are often sold as "pastes," containing from 60 to 80 per cent of water.

Cotton is always mordanted in separate baths before dyeing with these colors. Cotton mordanting with chromium is difficult, but the use of basic chromium acetates, chlorides, etc., by Koechlin's method (p. 514), makes it possible. Often cotton is prepared with Turkey-red oil before mordanting with chromium. Aluminum mordants are largely used on cotton, but iron and tin less frequently. Turkey-reds, alizarin red, cœrulein, and other alizarin colors, logwood blacks, and catechu browns are the chief mordant colors on cotton.

For centuries **Turkey-reds** have been produced on cotton by the aid of madder, oil, and aluminum salts; this gives a brilliant red, very fast to light, washing, or friction, and to chemical agents. By the old process, about four weeks was required for the dyeing, but the new process reduces the time to about three days. Madder has been completely displaced by *artificial alizarin* made from anthracene (p. 524). The Turkey-red process on cotton is complicated, and requires a special mordanting of the goods. In outline the process is as follows: The bleached cotton (p. 506) is first oiled by steeping or padding in a 10 or 15 per cent solution of neutralized Turkey-red oil (p. 362) in water. The excess of oil is squeezed out and the goods "aged," or steamed, at about 5 pounds pressure, to render the oil insoluble and to fix it on the fibre. Oxidation and probable polymerizing of the oleic acid and other constituents of the oil occur, and substances are fixed on the fibre which combine with, and assist in fixing, the metallic mordants, and perhaps form a varnish coat over the color-lake, protecting it from air and chemicals, thus increasing the fastness and lustre of the dyed fabric.* The goods are mordanted by working in a tepid solution of aluminum acetate (red liquor), or basic aluminum sulphate, the oxide being fixed by aging; or in a bath of powdered chalk and water, or of sodium phosphate, which removes the excess of oil. Formerly sodium arsenate was used for

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* The oiled cotton may be steeped in a decoction of sumach, but this is not essential, and is generally omitted.

this "dung-bath," and afforded very light shades. For dyeing, the mordanted cotton is first worked in a cold bath of alizarin suspended in water, containing some lime, calcium being essential to the formation of the color-lake; hard water, free from iron, is preferred for this bath, but if not available, powdered chalk or calcium acetate is added. The bath is then very slowly heated to 70° C., where it is kept until the dye is all deposited. The cotton at this time is a dull red, and to develop the brilliant shade, the goods are steamed at about 15 pounds pressure for an hour. Sometimes they are oiled a second time before steaming. Then they are thoroughly washed with soap, two or three soapings being given; stannous chloride is often added to the soap bath to increase the brilliancy. It is very essential that neither the mordants nor the dye-bath be contaminated with the slightest trace of iron in any form. Turkey-reds are dyed by several other processes, which cannot be considered here.

Various shades of violet, lilac, and purple are dyed on cotton with alizarin, by mordanting with ferrous acetate (pyro-iron, p. 309) instead of red liquor, and usually omitting the oiling. A tannin-iron mordant affords purple blacks, while mixtures of iron and aluminum mordants give shades from claret red to chocolate. Other alizarin colors are dyed on cotton and linen with aluminum, chromium, and iron mordants. The methods vary somewhat with each dye, and must be sought for in special works on dyeing.

Linen is dyed with alizarin in the same way as cotton. The fastness of Turkey-red to washing and soap makes it especially valuable for dyeing linen yarn, which is then woven into figured wash-goods.

Logwood yields blacks and grays on cotton mordanted with tannin and iron, which were formerly very important because of their cheapness, but the new, fast, vat dyes (p. 541) and the sulphur colors (p. 540) have largely replaced them, as well as most other mordant dyes for cotton dyeing.

Wool is largely dyed with mordant colors because of their fastness to light, chemicals, milling, and washing. The fibre must be well scoured to remove oil or grease before mordanting, otherwise uneven dyeing will result. The mordants used on wool are mainly chromium salts; aluminum salts find some use with the alizarin colors. The wool is boiled with 2 to 3 per cent (of the weight of the goods) of potassium bichromate with the addition of 1 per cent of sulphuric acid; often cream of tartar is used with bichromate. Chromium fluoride (3 per cent) with oxalic acid is also used for wool. After aging for several hours in a dark place to fix the oxide, the goods are washed and at once dyed without drying.

The dye-bath usually contains only water and the dyestuff, but with some alizarins a little acetic acid is added. The goods are entered with the bath at about 40° C., and the temperature slowly raised to the boiling point in about an hour; boiling is continued for another hour or more.

Some alizarin colors are applied with the mordant (potassium bichromate or chromium fluoride) and the dye together in the same bath; the goods are entered in the cold bath, which is slowly raised to boiling. This "single bath" process wastes color (due to oxidation) and produces less fast dyeings.

Silk is rarely dyed with mordant colors, since the hues are less brilliant than those obtained with substantive dyes, and the latter are cheaper and sufficiently fast. Silk, mordanted with chromium chloride, or with basic aluminum sulphate or acetate, fixed with silicate of soda solution, may be dyed in a bath of "boiled off" liquor, neutralized or slightly acidified with acetic acid. The goods are entered in the cold bath, which is very slowly heated to boiling and held at that temperature for an hour. After washing the dyed goods are boiled in soap liquor and brightened in dilute acetic acid at 30° C.

V. **Acid-mordant dyes** (acid-chrome colors) are chiefly used on wool, and to a small extent on silk; they are not applied to cotton. These dyestuffs are usually sulphonated azo-derivatives of salicylic acid, or of orthoaminophenol bodies; some are derived from anthracene or pyrogallol. They may be used as acid dyes in the usual way, but faster and better colors are developed when they are used with mordants, chiefly chromium. These dyes include a full series of colors from reds to violets and also browns, grays, and blacks. They are especially useful for loose wool and yarn because of their fastness to milling and light.

Wool is dyed by heating to boiling in a bath containing a little free acid (1 to 4 per cent sulphuric, acetic, or formic acid) and 5 to 10 per cent of Glauber's salt. After boiling until the color is all deposited (which is aided by the gradual addition of a little more acid), the goods are lifted from the bath, and potassium bichromate or other metallic salt added, the wool reëntered, and the boiling continued another half hour. By using a mixture of neutral potassium chromate and ammonium sulphate (meta-chrome mordant) instead of the bichromate, a more gradual and even deposition of color is secured, owing to the slow liberation of the acid from the ammonium salt during the boiling. Other special modifications of the process are in use.

Silk is dyed like wool with these colors, but often chromium fluoride and acetic acid are used in the after-chroming.

VI. The **sulphide dyes** constitute a large and important group of colors, yielding fast dyeings on cotton and other vegetable fibres. They are made by fusing sulphur or sodium sulphide with various aromatic bodies containing nitro-, amino-, or imino-groups. The constitution of these colors is not fully known, but they probably contain free sulphur and mercaptans. They are insoluble in water, but dissolve in alkaline reducing solutions, especially sodium sulphide, sodium hydrosulphite, or caustic soda and glucose. These dyestuffs form insoluble products with the oxygen of the air and precipitate; this necessitates a strongly reducing bath, and also keeping the goods entirely submerged. Since the sulphide acts upon copper, forming oxygen-carrying copper salts, the dye-vats must be made of wood or iron, and no brass or copper fittings should touch the dye liquor.

The commercial dyestuffs are sold under trade names adopted by the different makers, such as Immedial, Katigene, Kryogene, Pyrogene, Sulphur, Thiogene, Thion, Thionol, and others. They are little used for wool and silk dyeing, since the alkaline bath is injurious to these fibres; but the addition of glucose to the bath protects these fibres to some extent, and thus "unions" may be dyed in the presence of glucose. The addition of glue to the bath prevents silk from taking the color, and thus mixed silk and cotton goods can be dyed in two-color effects.

Cotton and linen are dyed with sulphide colors, without previous preparation. The bath is made up with the dyestuff and an equal weight of sodium sulphide, dissolved in hot water, to which is then added about 5 per cent of soda and 10 to 50 per cent of Glauber's salt, or common salt. Turkey-red oil, or monopol soap or oil, glue, and glucose may also be added. The bath is heated to 35° to 75° C., depending on the color used. Most of these dyes work well in cold baths. The goods should be kept entirely submerged in the liquor, to prevent irregular color deposition. When removed from the bath, the goods are rapidly freed from excess liquor by squeeze-rolls or centrifugal wringing, to afford level shades. Sometimes the goods are immediately rinsed, and in other cases a short exposure to the air is desirable before rinsing.

Generally the dyed goods receive some kind of *after-treatment*, as with metallic salts, such as a mixture of copper sulphate and potassium bichromate, with a little acetic acid, for most colors; but for blacks, no copper salts should be used, as they are prone to assist oxidation of the sulphur in the dye by catalysis, thus forming sulphuric acid, which weakens the fibre after a time. A further after-treatment of the dyed material with soda, soap, sodium acetate, or formate is recommended to prevent the subsequent "tendering" of the goods. Tendering does not become obvious for several weeks or months after the goods are dyed, and has caused much deterioration of goods in storage.

Some of these colors (Immedial and Kryogene blues and others) are improved by *developing*, by steaming for half an hour, or by aging several hours in a warm, damp atmosphere.

VII. The **vat dyes** constitute an important group of dyestuffs, of which indigo (p. 521) was for long the only one known; but recently numerous others have been synthesized. The vat colors are readily reduced in alkaline solutions, and become soluble, but on oxidation, or exposure to the air, the insoluble color is reprecipitated. The solution of reduced color is called the "vat," and may be prepared in various ways. Some of them are derivatives of indigotine (the *indigoids*) and others are *anthracene* derivatives. The indigotine derivatives can be applied to both animal and vegetable fibres in the hydrosulphite vat and as they may be applied to vegetable fibres in the presence of sodium sulphide, they are often used in the same bath with sulphide colors for compound shades; but the anthracene derivatives require strong alkaline (caustic soda) vats, and are only suitable for cotton.

Dyeing with natural indigo has been practised in India, Egypt, and other eastern countries for centuries, by methods very similar to some now in use. It was not until the synthesis of artificial indigo, however, that the other dyes of this group were produced. It has recently been shown that the ancient Tyrian purple obtained from a mollusk (*Murex*) is probably identical with one of these vat colors (a dibrom-indigotine). The commercial vat dyes besides indigo are the various halogen derivatives of indigotine, methyl and tolyl indigotine, ciba colors, thioindigos, algole dyes, helindone dyes, indanthrene dyes, and others.

Wool is dyed with indigo in the old *fermentation vat,* and more largely now by the use of the *hydrosulphite vat.* Several varieties of the fermentation vat are used, the **woad vat** being most important for cloth. In this, a mixture of woad with water is incorporated with bran, madder, finely ground indigo, and some lime. A butyric fermentation sets in and hydrogen is evolved and reduces the indigo to indigo white, which dissolves in the alkaline liquor. The addition of more lime checks the fermentation, while adding bran accelerates it. The wool, wet in warm water, and wrung, is submerged in the vat and worked for some time. After wringing to remove excess indigo solution, the goods are exposed to the air to oxidize the indigo white. For dark shades the goods are returned to the vat two or three times.

The **hydrosulphite vat** is much used for rapid dyeing of large quantities of material, or where dyeing is carried on irregularly, and subject to frequent interruptions. A stock-vat is first prepared * by suspending 20 lbs. of indigo (artificial 20 per cent paste) in 2 gallons of water, and stirring in 4 lbs. of anhydrous hydrosulphite (p. 60). After 10 minutes, 4 pints of caustic soda liquor (76° Tw.) are added and the mixture heated to 50° C. Solution takes place rapidly, forming a clear greenish yellow liquid.

The dye-vat is prepared * by adding to 1000 gallons of water, warmed to 50° C., about ½ gallon of ammonia, 9 ounces hydrosulphite powder, and 3½ gallons of a solution of glue (1 : 10). The required amount of stock indigo solution is then added, stirred well, and the goods at once entered, and worked about 20 minutes. After squeezing out excess liquor, the goods are exposed to the air to oxidize the indigo, and then well washed. Often the goods are first dyed (bottomed) with a red dye, as barwood or diamine reds, before the indigo dyeing. This may be followed by " topping " with some red or violet, to add " bloom " to the color.

Cotton is dyed with indigo in several types of vat, which are, however, more strongly alkaline than for wool, and as a rule are worked cold. The **hydrosulphite vat**, similar to that for wool above, is largely used for piece-goods, with jiggers, and in dyeing machines for yarn and loose cotton.

The **zinc-lime vat**, suitable for hanks and piece-goods, is prepared by mixing the indigo (20 per cent paste) with zinc-dust and quick-lime, suspended in water, and heating to about 55° C., for 3 to 5 hours. When the liquor is a clear yellow color, it is decanted from the sediment into the dye-vat containing more water and a little lime and zinc-dust. The wet goods are then entered and worked in the liquor.

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* From Pocket Guide to the Application of the Dyestuffs of the Badische Anilin- und Soda-Fabrik. Ludwigshafen am Rhine.

The bath may be replenished with more reduced indigo liquor, and thus kept in operation for subsequent lots.

The **copperas vat**, also used for yarn and piece-goods, is prepared by mixing indigo (paste) with warm (50° C.) milk of lime, to which is added a solution of copperas (ferrous sulphate), and the whole allowed to stand 5 or 6 hours, with occasional stirring. The ferrous hydroxide, precipitated in the presence of excess calcium hydroxide and the indigo, reduces the latter. The reactions are probably as follows: —

$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4.$$
$$C_{16}H_{10}N_2O_2 + 2\ Fe(OH)_2 + 2\ H_2O = C_{16}H_{12}N_2O_2 + 2\ Fe(OH)_3.$$

The indigo white then dissolves in the excess milk of lime to form a brownish yellow solution, which after settling is ready for use. There is much sediment produced in this vat, and considerable dyestuff is lost, probably by adsorption on the ferric hydroxide; but the vat is easy to set, and keeps in good order.

Fermentation vats are also used for cotton, especially in India, Egypt, China, and other eastern countries.

VIII. The **ingrain colors** comprise a number of insoluble substances, which are produced directly on the fibres, by saturating the goods with one or more of the constituents of the color, and then causing a suitable chemical reaction to take place, by subjecting the material to treatment with the other constituents, to produce the insoluble colored precipitate within the pores of the fibre. The more important of these colors are *aniline black*, certain *azo bodies* (as para reds and browns, azo-blues, etc.), and the *mineral dyes*. Each of these colors is produced by a special process, and they are chiefly important as cotton dyes.

Aniline black consists of an insoluble black pigment produced by the oxidation of aniline in acid solution, by various agents such as chlorate, chromates, ferrocyanides, and salts of copper, vanadium, cerium, etc., acting as catalyzers to aid oxidation by air. It is used only on cotton, and much care is necessary to prevent weakening of the fibre. It is also very liable to turn greenish hue in time. Much investigation * has been carried on to determine the composition of the black, which is yet somewhat uncertain.

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* Green and Woodhead, Trans. Chem. Soc., **1910**, 223. Willstätter and Moore, Ber., **1907**, 2665; **1909**, 4118. *Ibid.*, J. Soc. Dyers and Col., **1908**, 4. Marsden, J. Soc. Dyers and Col., **1908**, 9. Nietzki, Ber., **1878**, 1094. *Ibid.*, Chemie d. Organ. Farbstoffe, 5th ed. p. 267.

The methods of producing aniline black industrially may be grouped under the headings: (*a*) *Dyed blacks;* (*b*) *Aged blacks;* (*c*) *Steam blacks.*

Dyed blacks (one-bath blacks), chiefly produced on yarn by working in a solution containing aniline hydrochloride, bichromate of soda, hydrochloric and sulphuric acids, and water, while slowly heating nearly to boiling, are not very well fixed and the color is liable to "rub." By steaming the dyed goods, the fastness is improved. This method is less injurious to the strength of the fibre than is the aging process.

Aged black is produced on both yarn and piece-goods, by padding in a solution of aniline salt an oxidizing agent (sodium chlorate) and a catalyzer (copper or vanadium salt, or a ferrocyanide). The material is dried and "aged" for six or eight hours, by passing slowly through an aging-room in which the air is moist and the temperature is kept at 45° to 50° C. The goods acquire a dark, greenish black color in the ager, and this is converted to a fast black, by chroming (without washing) for 15 minutes in a warm solution of bichromate containing a little sulphuric acid. Then the goods are soaped, rinsed, and dried. After padding and during the aging, the goods must be carefully protected from drops of water (condensed moisture, wet hands, etc.) and from alkali, or spots will be produced. The aging process is liable to weaken the fibre, and if not carefully watched may ruin the goods. In Green's process,* atmospheric air is the oxidizing agent, acting with cuprous chloride as catalyzer, and with a paradiamine in the padding liquor. Formic acid is used in place of sulphuric to reduce the risk of tendering the fibre.

Steam blacks are produced by padding in a liquor containing aniline salt, sodium chlorate, and potassium ferrocyanide, after which the goods are dried and steamed for three minutes, then chromed and soaped. These blacks are less apt to injure the fibre, but the method is expensive.

The **insoluble azo dyes** are developed on the fibre by first impregnating the goods with a phenol (β-naphthol) solution, and then passing into a cold bath of a diazo-compound, whereby the color is produced on the fibre. It is essential to keep the diazotized bath as cool as possible, and this is often done by putting ice into the bath (hence the name "ice-colors," sometimes applied to these dyes). The color

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* J. Soc. Dyers and Col., **1908**, 231; **1909**, 191.

is produced immediately as the goods enter the developing bath, and then they pass at once to the washing machines.

The most important of these colors is *paranitraniline red,* produced from β-naphthol and diazotized p-nitraniline. It is a fast and brilliant red, used as a substitute for Turkey-red (p. 537). *Azo-blues* are obtained with β-naphthol and dianisidine, with subsequent treatment with copper salts. Chloranisidine yields fast scarlets.

The **mineral dyes** are produced on the fibre by saturating it with a solution of a metallic salt, and passing into a second solution, which decomposes the first salt, forming a colored precipitate. The most important colors are the following: —

Iron buff or **Nankin yellow**, which consists of ferric hydroxide. It is dyed on cotton by steeping the goods in a solution of iron salt (basic ferric sulphate, ferric nitrate, or copperas), and the color developed by treatment with calcium hydroxide solution, or caustic soda, or soda-ash, as in mordanting (p. 515).

Chrome green can be formed on cotton by processes similar to those used for mordanting with chromium salts (p. 514). It is not very important. **Khaki** is a greenish brown produced by the simultaneous precipitation of chromium and ferric hydroxides on the fibre. The material is padded in a mixture of chromium and ferrous acetates, or chrome alum and ferric chloride, dried, and steamed. The cloth is then boiled in a solution of soda-ash containing some caustic soda to complete the precipitation.

The color is very fast to light, but leaves the goods stiff and harsh. Close imitations of this color are obtained with some of the sulphide browns, and with certain indanthrene dyes.

Chrome yellow is dyed on cotton by soaking in lime-water and after wringing, passing into a solution of basic lead acetate or nitrate. Repeat the lime-water treatment, wring, and work in a solution of sodium bichromate. Finally the goods are rinsed in dilute hydrochloric acid (1 : 300), washed, and dried. The shade can be lightened by adding zinc sulphate to the bichromate solution. The color is fast to light, soap, and weak acids, but is turned red by alkalies, and brown or black by sulphuretted hydrogen. The goods are heavily weighted by this process.

Manganese brown, or **bronze**, consists of the hydrated peroxide of manganese, and is only produced on cotton. The goods are steeped in neutralized manganese chloride, and passed through a hot, dilute solution of caustic soda, to which some sodium hypochlorite has been added. Precipitation and oxidation occur simultaneously, and a full neutral brown is developed. A mixture of potassium permanganate and soda-ash in solution can also be used as the developing bath. The color is fast to light, soap, alkalies, and weak acids.

Prussian blue is chiefly dyed on silk and cotton, especially as a base or ground color, upon which blacks or other dark colors can be dyed. On silk, Prussian blue is dyed in the process of weighting, the material being worked in a solution of basic ferric sulphate, and the iron hydroxide formed by treatment in a soap bath containing soda. The process is repeated several times, and the material then passed into an acidulated bath of potassium ferrocyanide. If the blue is to remain as the final color, the goods are softened in a bath of olive oil and a little sulphuric acid.

Cotton is first dyed an iron buff (p. 515) and then passed into a dilute sulphuric acid solution of ferrocyanide. By repeating the process deeper shades can be attained. The color may serve as a base on which logwood blacks, or other mordant dyes, may be deposited.

Wool can be dyed by steeping in the ferrocyanide solution, made acid with sulphuric or nitric acid, then slowly raising the temperature of the bath to boiling. The ferrocyanide is decomposed in part, some prussic acid escapes, and the blue pigment is deposited in the wool.

TEXTILE PRINTING

Textile printing may involve the application of a single coloring matter to one side of the fabric, or the forming of intricate designs in as many as 18 or 20 different colors, by one passage of the cloth through the printing machine. The pattern is usually produced on one side only of the cloth, but sometimes the same or a different design appears on each side. There may be a colored figure on a white or colored background, or a colorless design may be produced on a colored background.

The earliest attempts at this form of decoration, made by prehistoric races, were doubtless carried out by mixing pigments with water or with a gum solution, and painting the design on the fabric. Later, the art was developed to painting the *mordants* in the form of the design, and then dyeing the fabric in some natural dyestuffs. Stencilling was invented early, but great advances were made with the invention of block printing, which was followed by roller printing.

For **block printing** the design is made in relief on blocks of hard wood. The cloth is spread evenly on a firm table, and the printer, having daubed the *relief* with color, applies the block to the cloth and strikes it with a hammer to drive the color into the fabric. In order that the lines of the figure may not overlap, or spaces be left unprinted which should be colored, exact placing or "registering" of the block is important. This is gauged by pin points set in the corners of the block, which mark the exact spot where it is to be applied for the next impression. Much experience is necessary for this and also for judging of the amount of color taken from the daubing pad by the block. At the present time, block printing is used only for large designs; those containing many colors may be printed thus, but a separate block is necessary for each color used; and since one block usually serves only for a part of the whole design, several blocks may be needed for each color. Thus the process is slow, laborious, and expensive.

Roller or machine printing has now generally replaced all other processes. One engraved copper roll is employed for each color in the design, except in a few cases where a color is produced by printing one over another, as a yellow over a blue to make green. The design, drawn by the artist, is enlarged several times and engraved on a zinc plate. The copper roll is turned perfectly true in a lathe, and then polished. Its surface is coated with wax or a special varnish, through which the design is scratched by a stylus of a pantagraph machine, following the pattern on the zinc plate; this reproduces the design and at the same time reduces it to the required size. The roll is then etched with nitric acid, until the figures have the necessary depth. After washing off the acid, the wax is removed, and the hollow roll is slipped on a mandrel for use in the machine. The color is fed to the print roll from the color box by a revolving cylindrical brush called the "**furnisher,**" which dips into the color paste. This covers the entire surface of the roll with the color and fills the depressions of the design. A sharp steel blade, called the "**doctor,**"* rubs against the surface of the roll as the latter revolves, and scrapes off all excess of color, leaving only that contained in the *depressions* of the pattern. Beneath the cloth a similar blade rubs the roll, removing from it any bits of dirt or lint which may adhere after the cloth has been printed. The print rolls are all set around one central drum called the "**bowl,**" against which they press, and which is covered with several thicknesses of strong linen and woollen cloth called "lapping," which will withstand the repeated pressure without break-

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* In order that irregularities may not be worn in the edge of the doctor or on the print roll, the former is given a slight sidewise movement by a suitable gearing.

ing. This lapping must be evenly placed, or streaks will appear on the printed goods. The cloth to be printed passes between the rolls and the bowl, considerable pressure being brought to bear upon it, so that it is forced into the engraving on the roll and takes out all the color. Between the lapping and the cloth to be printed, an endless band or " **blanket** " of thick woollen cloth passes. This adds to the elasticity of the lapping, affording a better impression of the engraving, and protecting the lapping from color and moisture. The blanket is often 40 to 50 yards long, and goes over drying drums before it passes around the bowl. In order to keep the blanket free from color stains, a piece of unbleached cotton cloth, called " gray cloth " or " back cloth," is interposed between it and the print cloth. This gray cloth is sometimes used once or twice for this purpose and then sent to the singeing and bleaching process, after which it is itself printed, usually with a dark color. Thus three long webs of cloth pass between the rolls and the bowl at once, — the blanket, back cloth, and print cloth.

The printing colors may be soluble dyestuffs or insoluble pigments made into a paste with water, oil, or other medium; in many cases mordants alone are printed on the fabric. It is also essential that the color pastes shall contain some material by which the pigments may be fixed on the fibre so that they will not rub off in the finishing operations. In order that the printing colors may adhere to the rolls and not run when applied to the cloth, **thickening agents** are employed. The most important of these are British gum, starch, flour, gum arabic, Senegal, or tragacanth, and blood or egg albumin. It is necessary that these shall not form any chemical combination with the color or the mordants. Some thickeners are insoluble in cold water, while others are more or less soluble, and the printer must select that best adapted to his purpose and the color he wishes to use. The preparation of color pastes is called " **color mixing** " and requires much care. The ingredients are mixed in special vessels called " color pans," these being jacketed copper kettles which may be heated by steam or cooled by water, as required. If starch or flour is used, it must be very well boiled to a smooth paste before the color is stirred in. British gum and Senegal are dissolved in hot water with constant stirring, while tragacanth is boiled for several hours. Albumin is dissolved in water at less than 50° C., while stirring constantly. After mixing, the color paste must be strained to remove any lumps, dirt, or grit, and to form a smooth paste of homogeneous character. For large lots, this is sometimes done by machinery, but in most cases the straining cloth is folded over the paste like a bag, and then twisted by hand by the workmen, thus forcing the paste through the cloth. It is now ready to put into the color boxes of the machine, from which the furnisher roll feeds it to the print roll.

But the *color* is not always printed on the goods. Sometimes only the mordants, mixed in the thickener, are printed, the goods being afterwards immersed in the dye-bath, and taking the color only where mordanted. Or a substance called a "**resist**" is printed to prevent the dye from taking the fibre in the printed portions; thus white spots or figures are left on a colored background. Or "**discharges**" may be printed on dyed material, destroying or bleaching the color where they touch.

After printing, the cloth is dried by passing above a series of steam boxes, or hot pipes, but generally not close enough to touch them, lest some of the colors should be changed by the heat. With many colors, however, the drying is done more quickly by passing the print over a steam-heated roll or "drying-can." For pigments in albumin thickening, this direct drying is sufficient to fix the color on the fibre, and the goods may be finished at once.

The method of producing the colored design in calico printing is called a "**style.**" The following are the more important: pigment style, steam style, madder or dyeing style, oxidation style, discharge style, and resist style. The **pigment style** is of less importance than it formerly was. Insoluble pigments, such as ultramarine, Guignet's green, chrome yellow, vermilion, etc., are mixed with the thickening paste, printed directly, and the print dried by passing over a hot roll. If the thickening is gum, starch, or dextrine, the resulting print is not fast to washing, and is known as "loose pigment style." But if blood or egg albumin is used, and the print dried at a high temperature, or steamed to coagulate the albumin, the color is fixed on the fibre, and is fast to ordinary washing and soaping.

The **steam style**, formerly called the **extract style**, is used for those colors in which the mordant, dyestuff, and thickening can be mixed cold or at moderate temperatures without the formation of the color lake. Acetic acid is often added to retard the action between the dyestuff and mordant. Tannic acid is much used as a mordant in steam colors. The cloth is generally prepared by oiling it slightly with Turkey-red oil, or "oleine," before printing. The printed cloth is arranged on racks on a car which can be run directly into the steamer, or the goods are made to pass through a continuous steamer, consisting of a large closed vessel containing numerous rollers at the top and bottom, over which the cloth passes up and down many times. The steam is under 3 to 10 pounds pressure, whereby the acetic acid vaporizes, the reaction between the mordant and dyestuff is brought about, and the color developed on the fibre. The print is washed in a soap bath to remove the thickening. Steam style is largely used, and with many dyestuffs.

When basic dyes and tannic acid are used, the printed and steamed goods are passed through a bath of tartar emetic or other antimony salt, to fix the color on the fibre.

In the **madder** or **dyeing style**, only the mordant is printed, and fixed on the fibre by drying, steaming, or aging. The goods are usually "dunged" in a bath of phosphate or arsenate of soda (formerly cow-dung and chalk were used) to remove excess of mordant from the surface of the fibre, and thus prevent its spreading to the unprinted portions of the cloth and blending the figures. After dunging, the goods are thoroughly washed, and at once dyed in an alizarin or madder bath. With different mordants these give different shades: thus alumina yields reds and pinks; tin gives scarlet; chromium, maroon; and iron, chocolate or brown. But the number of colors obtained in this way is limited, and the process is largely given up in favor of the more convenient steam style.

The **oxidation style** is chiefly used for aniline blacks. The goods are printed with a paste containing aniline salt, sodium or potassium chlorate, and usually a trace of vanadium salt, all worked into a suitable thickening. After printing, the goods are "aged" for two days, or for a short time in a steam "ager," and are passed through a potassium bichromate solution at 70° C.; they are then washed in a hot soap solution. Manganese browns for backgrounds are sometimes printed by padding the surface of the cloth with manganous chloride or sulphate, and, after drying, padding again with caustic soda. The cloth is then washed and passed into a solution of bleaching powder, whereby a hydrated peroxide of manganese is formed on the fibre as a uniform brown color. This is then printed again by the discharge style to produce a figured pattern.

In the **discharge style**, the dyed cloth is printed with a discharge paste, leaving a white figure on a colored ground. Or it is often customary to add some color to the paste which is not affected by the discharge, and which remains on the goods where printed; *e.g.* certain pigments, such as chrome yellow, Guignet's green, and vermilion. Thus colored figures are obtained on a ground of different color.

Common discharges are stannous chloride, zinc dust, and sodium bisulphite, or sodium bichromate, the last being used in connection with a sulphuric acid bath. Tartaric, citric, and oxalic acids are used as discharges, rendering the mordants soluble in the printed portions, whence they are removed by washing, so that, in subsequent dyeing, the color does not take the fibre in these spots. Alkaline discharges, made with caustic soda and potassium ferricyanide, or potassium bichromate and caustic soda, are used with indigo.

In the **resist style**, substances are printed on the cloth which prevent the fixing of the mordant or color in the printed portions. Thus, when dyed, the printed pattern appears white on a colored ground. Resists may act mechanically or chemically. Those of the first kind are generally oils or resins with china clay, which are insoluble and prevent access of the dyestuff to the fibre. Chemical resists are generally citrate of sodium, or acetate of calcium, the former being preferred for preventing the fixing of alumina or iron mordants, and the latter to hinder the development of aniline blacks. After printing, the cloth is dunged, washed, and dyed. For resists on indigo-dyed goods, the cloth is printed with zinc sulphate or copper sulphate.

In all styles where the cloth is dyed after printing, the white parts of the figure are usually discolored by the dye, and it becomes necessary to "clear" them, generally by "chemicking" in a solution of bleaching powder so dilute as not to affect the color in the mordanted parts of the goods. This is followed by a thorough soaping and washing. The printed calico is usually finished by starching, bluing slightly to improve the appearance of the white, tentering, and finally calendering between hot rolls.

Wool is extensively printed for **delaines** and **challis**, the steam and discharge styles being most commonly employed. It is usually prepared for printing by passing through bleaching powder liquor, and then through an acid bath, the chlorine imparting to the wool a greater affinity for the acid colors. The color is prepared with thickening, much as for cotton, and after printing the cloth is usually steamed and washed. Direct and basic colors are printed without further addition to the paste; acid colors require a little oxalic or tartaric acid; for mordant colors, acetate of chromium or of aluminum is employed, while for discharge styles stannous salts are used as reducing agents in the paste.

Silk is printed in much the same way as wool. It is usually mordanted with tin, and sometimes with an acid.

REFERENCES

Dyeing and Calico Printing. F. Crace-Calvert, Manchester, 1876.
Études sur les Fibres végetales textiles. M. Vétillard, Paris, 1876.
Le Conditionnement de la Soie. Jules Persoz, Paris, 1878.
Calico Printing, Bleaching, and Dyeing. C. O'Neill, London, 1878.
Bleicherei, Färberei und Appretur. C. Romen, Berlin, 1879.
Die Gewinnung der Gespinnstfasern. H. Richard, Braunschweig, 1881.
The Wild Silks of India. Thomas Wardle, London, 1881.
Die Technologie der Gespinnstfasern. 2 Bde. H. Grothe, Berlin, 1882.
Die Wascherei, Bleicherei und Färberei von Wollengarnen. R. Sachse, Leipzig, 1882.
Dyeing and Tissue Printing. W. Crookes, London, 1882. (Bell & Sons.)
Structure of the Cotton Fibre. F. Bowman, Manchester, 1882.
Ramie, Rhea, Chinagras und Nesselfaser. Bouché u. Grothe, Berlin, 1882.
Traité pratique du Dégraissage, etc. A. Gillet, Paris, 1883.
Ueber pflanzliche Faserstoffe. F. von Höhnel, Wien, 1884.
Bleaching, Dyeing, and Calico Printing. J. Gardner, London, 1884.
The Structure of Wool Fibre. F. J. Bowman. 2d ed. Manchester, 1885.
Les Soies. N. Rondot, Paris, 1885.
Report on Indian Fibres and Fibrous Substances. C. F. Cross, E. J. Bevan, C. M. King, and E. Joynson, London, 1887.
Microscopie der Faserstoffe. F. von Hohnel, Wien, 1887.
Dyeing. A. Sansone, Manchester, 1888. (Heywood & Son.)
Das Färben und Bleichen von Baumwolle, Wolle, Seide, Jute, u.s.w. J. Herzfeld, Berlin, 1889.
Die Echtfarberei der losen Wolle in ihrem ganzen Umfange. Alfred Delmart. 3 Bde., 1887–1891. Rechenberg i. B.
Die Jute und ihre Verarbeitung. E. Pfuhl. 3 Bde. Berlin, 1888–1891.
Handbuch der Färberei. A. Ganswindt, Weimar, 1889.
L'Industrie de la Teinture. C. L. Tassart, Paris, 1890. (Bailliere.)
The Cotton Fibre, Its Structure, etc. Hugh Monie, Manchester, 1890.
Report on Flax, Hemp, Ramie, etc. U. S. Dep't of Agriculture, Washington, 1890.
La Soie. L. Vignon, Paris, 1890.
Industrie de la Soie. F. Debaitre, Paris, 1890.
Traité de Teinture sur laine et sur étoffes de laine. P. F. Levaux, Liege, 1890. (J. Godenne.)
Traité Pratique de Teinture et Impression. M. de Vinant. 2d ed. Paris, 1891.
Die chemische Technologie der Gespinnstfasern. O. N. Witt, Berlin, 1891.
Tintura della Seta. Teodoro Pascal, Milano, 1892. (U. Hoepli.)
Traité de la Teinture et de l'Impression. J. Depierre, Paris, 1891–1892. 2 Tomes. (Baudry et Cie.)
Die Praxis der Färberei von Baumwolle u.s.w. J. Herzfeld, Berlin, 1892.
Silk Dyeing, Printing, and Finishing. J. H. Hurst, London, 1892. (Bell.)
Textiles Végetaux. E. Lecompte, Paris, 1893.
La Pratique du Teinturier. Jules Jarcon, Paris, 1894. 2 Tomes.
Cellulose. Cross & Bevan, London, 1895.
Bleichen u. Färben der Seide u. Halbseide. C. H. Steinbeck, Berlin, 1895.
Bleaching and Calico Printing. Geo. Duerr and Wm. Turnbull, London, 1896.
The Cotton Plant. Bul. No. 33, U. S. Dep't of Agriculture, Washington, D.C., 1896.
Das Anthracene und seine Derivate. G. Auerbach. 2te Auf. Braunschweig, 1880.
Die Industrie der Theerfarbstoffe. C. Haussermann, Stuttgart, 1881.
Die Chemie des Steinkohlentheers. G. Schultz. 2te Auf. 2 Bde. Braunschweig, 1886.
Die künstlichen organischen Farbstoffe. P. Julius, Berlin, 1887.
The Chemistry of the Coal-Tar Colours. R. Benedikt, translated by E. Knecht. 3d ed. London, 1900. (Bell & Sons.)

Organische Farbstoffe, welche in der Textilindustrie Verwendung finden. R. Mohlau, Dresden, 1890. (Julius Bloem.)
Les Matières colorantes, etc. C. L. Tassart, Paris, 1890.
Chemistry of the Organic Dyestuffs. R. Nietzki, translated by Collin & Richardson, London, 1892.
Tabellarischen Uebersicht der künstlichen organischen Farbstoffe. A. Lehne, Berlin, 1894.
Die Chemie der Natürlichen Farbstoffe. H. Rupe, Braunschweig, 1900.
Descriptive Catalogue of the Useful Fibre Plants. Dodge. Report No. 9, U. S. Dep't of Agriculture, Washington, D. C., 1897.
Report on Flax Culture. Dodge. Report No. 10, U. S. Dep't of Agriculture, Washington, D.C., 1898.
Die Mercerisation der Baumwolle. Gardner, Berlin, 1898.
Die Künstliche Seide. Carl Süvern, Berlin, 1900. (Springer.)
Die Vegetabilischen Faserstoffe. Böttler, Leipzig, 1900.
The Printing of Cotton Fabrics. A. Sansone, Manchester, 1887. London, 1901.
The Dyeing of Textile Fabrics. J. J. Hummel, London, 1902.
Die Animalischen Faserstoffe. Böttler, Leipzig, 1902.
The Dyeing of Cotton Fabrics. Franklin Beech, London, 1901.
The Dyeing of Woollen Fabrics. Franklin Beech, London, 1902.
Researches on Cellulose. 3 vols. C. F. Cross and E. J. Bevan, London, 1901–1912.
The Chemical Technology of Textile Fibres. G. von Georgievics, trans. by Chas. Salter, London, 1902.
Taschenbuch für die Farberei und Farbenfabriken. R. Gnehm, Berlin, 1902.
Textile Fibres of Commerce. Hannan, London, 1902.
Die Rohstuffe des Pflanzenreiches. 2 vols. J. Wiesner, Leipzig, 1903.
Mercerization. Editors of Dyer and Calico Printer. London, 1903.
Tabellarische Uebersicht der künstlichen organischen Farbstoffe. Schultz & Julius. 4te Auf. Berlin, 1903.
Principles of Dyeing. G. S. Fraps, New York, 1903. (Macmillan Co.)
A Systematic Survey of the Organic Colouring Matters. Arthur G. Green. 2d ed. London, 1904. (Macmillan & Co.)
The Synthetic Dyestuffs. J. C. Cain and J. F. Thorpe, London, 1905.
Chemie der organischen Farbstoffe. R. Nietzki. 5te Auf. Berlin, 1906.
The Textile Fibres. J. Merritt Matthews. 2d ed. New York, 1907.
Laboratory Manual of Dyeing and Textile Chemistry. J. Merritt Matthews, New York, 1909.
Manual of Dyeing. E. Knecht, C. Rawson, and R. Loewenthal. 2d ed. 3 vols. London, 1910. (Griffin & Co.)
Chemical Aspects of Silk Manufacture. R. L. Fernbach, New York, 1910.
Farbenmethoden der Neuzeit. Max Bottler, Halle, a. S., 1910. (Knapp.)
Die Zellulose. C. Piest, Stuttgart, 1910. (Enke.)
Identification of the Commercial Dyestuffs. Samuel P. Mulliken, New York, 1910. (Wiley & Sons.)
Die Schwefelfarbstoffe. O. Lange, Leipzig, 1911.
Tabellarische Uebersicht der wichtigsten Kupenfarbstoffe. M. Battegay u. E. Grandmougin. Elssaachen Textil-Blatt, Gebweiler, 1911.
The Chemistry of the Coal-tar Dyes. Irving W. Fay, New York, 1911.
The Principles of Bleaching and Finishing Cotton. R. S. Trotman, London, 1911.
Bleaching and Dyeing of Vegetable Fibrous Material. J. Hübner, New York, 1912.
The Chemistry of Dyeing. J. K. Wood, 1913.
Manufacture of Organic Dyestuffs. A. Wahl, 1914.

PAPER

Paper consists of cellulose fibres matted or felted into a coherent sheet. Usually a certain amount of mineral matter, or "loading," is incorporated with the paper to increase the weight and render it smooth and less porous. The raw materials furnishing the fibre are wood pulp, cotton or linen rags, esparto, straw, hemp, flax, jute, etc. Old paper and the trimmings and waste from paper mills are also reworked. The common loading materials are clay (kaolin), ground talc or steatite, gypsum, or precipitated calcium sulphate (pearl hardening, crown filler, etc.), and barium sulphate (*blanc fixe*).

In nearly every case the cellulose fibres must be freed from incrusting matter and treated in such a way as to reduce the substance to a state of minute subdivision and to isolate more or less completely the individual fibres. It is largely in this isolation that chemical processes are involved in the industry.

Wood pulp is made from poplar (*Populus grandidentata*, Michx.), spruce (*Picea rubra*, Link.), hemlock (*Tsuga Canadensis*, Carr.), pine (*Pinus Strobus*, L.), cottonwood (*Populus monilifera*, Ait.), basswood (*Tilia Americana*, L.), white birch (*Betula papyrifera*), and maple (*Acer dasycarpum*, Ehrh.).

Wood pulp is of two kinds, mechanical and chemical. **Mechanical pulp** is made by forcing a large stick of wood against a revolving sandstone, or emery wheel, over which a jet of water plays continuously. The resulting pulp is washed away by the water and passes several screens to remove insufficiently disintegrated particles. The mixture of pulp and water then flows into a tank in which a cylinder covered with wire gauze is revolving. The water passes through and a layer of pulp adheres to the cylinder and is delivered on to an endless blanket; this carries it to a pair of squeeze-rolls where it is compacted. It is then cut into sheets of convenient size, several of which are pressed into one thick "board" for transportation. Mechanical pulp is contaminated with lignin and resinous matters, which turn brown on exposure to light. The fibres are short and do not mat together well, so the paper made from it is not strong; such pulp is only used for cheap paper (*e.g.* newspaper) and generally in conjunction with other fibres and chemical pulp. By dipping a strip of paper into a solution of phloroglucin in hydrochloric acid, the presence of ground pulp may be detected by the appearance of a magenta red color; an aqueous solution of aniline sulphate will yield a yellow color.

Chemical pulp is prepared by the soda process, the sulphite process, or by the sulphate process. The **soda process** is largely used for soft woods, especially poplar, cottonwood, and basswood. The bark is removed by hand shaves, but the knots and rotten wood are generally disregarded. The wood is put through a chipping machine which cuts it across the grain and reduces it to fragments about three-eighths of an inch thick. After the chips are dusted by blowing them against a screen, they are filled into the digesters. These consist of upright steel boilers with electrically welded joints, and heated by live steam; they hold 3 to 4 cords of chips at one charge. Sometimes rotary globular boilers holding 4 to 5 cords are used. The digester is nearly filled with chips, which are then covered with a caustic soda liquor of about 11° Bé. They are boiled for from 8 to 10 hours at a pressure of from 90 to 120 pounds. The effect of this "cooking" is to reduce the wood to a soft mass of grayish brown color, while the liquor has become dark brown and has a density of 11½° Bé. The non-cellulose matters of the wood (lignin, resins, etc.), which consist largely of organic acids, are decomposed by or combine with the soda, and consequently the alkali is nearly all neutralized during the process. The pulp and "black liquor" are blown out into a tank having a sloping bottom and covered with a closely fitting lid. Here the pulp is systematically washed and the wash-waters are saved until their average density falls below 8° or 9° Bé. The liquor is pumped into a multiple-effect evaporator and concentrated to 38° Bé., when it is sent directly to a revolving calcination furnace (p. 4) from which a dry soda-ash is recovered; this is recausticized for use in the digesters. From 85 to 90 per cent of the original soda is thus recovered.

The caustic soda has a direct action on the cellulose, especially when the pressure is high; hence some of the fibre is dissolved or destroyed, while all of it is weakened somewhat. The pulp produced is soft, and though of a dark color, is easily bleached in the case of poplar. The yield from this wood is about 40 per cent of its weight.

In the **sulphite process**, the wood (generally coniferous wood) is boiled under pressure with sulphurous acid or, more commonly, with acid sulphite of calcium and magnesium. The action of the sulphurous acid under pressure and at a high temperature upon the lignin and other incrusting matters of the wood fibre is probably a hydrolysis; by this, these complex molecules are broken down, the resulting products being largely organic acids and aldehydes, soluble in the liquor. But, owing to secondary reactions among themselves, certain acids and insoluble tar-like substances are also formed, which the reducing nature of the sulphurous acid does not appear to entirely prevent. The acid sulphites react much like sulphurous acid, but the bisulphites combine with the aldehydes formed in the first stage of the decomposition, producing stable and soluble double salts. The organic acids which are also formed decompose the bisulphites and form soluble calcium and magnesium salts, while sulphurous acid gas is set free, causing a constant increase in the pressure within the digester. The acid sulphites also tend to bleach the coloring matter of the fibres by forming colorless compounds with them, but this is a very unstable bleach and the original color soon returns when the pulp is made into paper. Hence for permanent whiteness the pulp is further bleached with chlorine. Bisulphite of calcium is unstable and decomposes readily into neutral sulphite, setting free sulphurous acid. This results in the precipitation of the neutral sulphite on the fibre, which is left harsh, even after long washing. Magnesium bisulphite is more stable, and, although less corrosive to the fibre, it dissolves the non-cellulose matter even more completely than does the lime salt; further, any sulphate or neutral sulphite which may be formed is easily washed off and the pulp is left soft and white. Sodium bisulphite gives a better product than either of the above, and strong liquors can be made from it; but it is too expensive for general use.

Bisulphite liquors are made by passing sulphur dioxide through towers packed with dolomite, over which water is trickling; or by leading sulphur dioxide into closed vessels about half full of milk of lime (prepared from dolomite). Within the vessel is a system of revolving paddles, half submerged in the liquor, and thus presenting large surfaces, wet with the liquor, to the action of the gas; they also splash the spray into the atmosphere of gas, thus securing rapid and complete absorption. Usually a series of three of these tanks is used, the strong gas entering the most concentrated liquor, which is thus brought up to a gravity of about 1.045 to 1.060 (6° to 8° Bé.), and containing $3\frac{1}{2}$ to $4\frac{1}{2}$ per cent SO_2. The sulphur dioxide is prepared by burning brimstone in an iron retort. Much care is necessary in regulating the air supply to the burner; too much air forms SO_3, which produces sulphates in the liquor; it also causes overheating of the furnace, and consequent sublimation of sulphur into the cooling pipes and absorption tanks, where polythionic acids (thiosulphates) are formed. These precipitate sulphur in the pulp in the digester, and cause trouble in the paper making. Too little air supplied to the burner also causes sublimation of sulphur. The hot gases from the burner are cooled to 10° or 15° C., by passing through water-cooled lead pipes. For the strongest liquor, the temperature in the absorption tanks must be kept as low as possible. The tanks for storing the sulphite liquors are sometimes lined with lead, though unlined tanks of hard pine are often used. Large quantities of liquor may be kept without much loss of strength, either through oxidation, or evolution of gas. Bronze rotary pumps or lead-lined acid-eggs are used for pumping the liquor.

Sulphite **digesters** are usually made of steel, lined with lead, and, inside of this, a layer of hard-burned, acid-resisting brick laid in Portland cement. Numerous half-inch holes in the steel plates allow the escape of steam or gas from behind the lining in case of a leak, thus preventing warping of the lead when the digester is blown off. Sometimes the lead lining is omitted and the brick laid in a litharge-glycerine cement, directly against the steel. The acid liquors have a very corrosive action on iron, and much experimenting has been done to find a suitable lining. Lead resists the action very well, but when used alone as a lining it soon cracks or warps, and also gives trouble through its tendency to "crawl." By filling the digester entirely full of liquor and heating, a layer of calcium sulphite may be deposited as scale on the walls, and affords much protection. Bronze digesters have been tried, but are expensive, do not resist the liquor, and are lacking in strength, several having exploded. Digesters are built upright or horizontal, and less frequently of globular form, the latter intended to rotate, the steam being admitted through the trunnions. Large digesters hold 12 to 14 cords of chips at one filling; they are provided with blow-off valves for the escape of gas during the cooking.

For making sulphite pulp, all bark, knots, and dead wood are cut out of the sticks, which are then chipped across the grain, as for soda pulp. The boiling is carried on by the "quick-cook" or the "slow-cook" method. In the **quick-cook system** the digester is completely filled with chips, and all the liquor (about 1200 gallons per cord of chips) is run in as rapidly as possible, through a large pipe. As a rule the liquor is about 10° Tw. (7° Bé.), with $3\frac{1}{2}$ per cent SO_2. The pressure is raised slowly, in order to avoid the hammer effect of the live steam coming in contact with the cold digester content, and also to avoid too high a temperature before the liquor has penetrated into the interior of the chips; otherwise the wood may be burned, and rendered brown or red. The temperature (which is the most important factor in the process) should not exceed 300° to 312°

F. (149° to 156° C.). It should be regulated by a thermometer, since no dependence can be placed on the pressure indications as a means of determining the conditions within the digester. During the 8 or 10 hours' boiling, considerable gas is evolved, and there is a steady increase in the pressure, which reaches 75 to 85 pounds.

In the **slow-cook process** a large digester (14 by 45 feet), heated by lead coils in the lower part, is used. The chips are packed evenly in the digester, and wet steam at 100° C. is introduced for 12 hours, until all the air is expelled and the charge heated to 100° C. No pressure is used, and the condensed water is allowed to flow out freely. Then the manhole and outlet cocks are closed, and the cold liquor of 1.042 sp. gr. is run in. This causes a partial vacuum, and a better penetration of the liquor into the chips is secured. When the digester is almost full of liquor, the heating is begun, and raised to 110° as rapidly as possible, though it usually requires 12 hours. The steam is so regulated that this temperature is maintained for about 12 hours, when it is slowly raised to 120° C., and a maximum pressure of about 50 pounds is secured. The total time of boiling is about 36 hours. Usually the pulp is blown out of the digester into a draining tank, where it is washed with pure water. When washed in the digester, as is sometimes done, cold water must be run in at once after the liquor is drawn off, to prevent burning the pulp by the heat radiated from the digester walls. Pulp which is to be bleached must be thoroughly washed, since any bisulphite left in the fibre acts as an "antichlor," and destroys the bleach liquor. The undecomposed shives must be removed by screening the pulp before bleaching.

Sulphite pulp has longer and stronger fibre than soda pulp, and is ligher colored, some samples being nearly as white as the bleached pulp. It is often used unbleached, but contains some dirt and has a harsh feel. If the chips have not been entirely covered by the liquor, or if the latter has been weakened by too much gas blown off during the boiling, the pulp may be burned, and black, charcoal-like specks appear in it. The waste sulphite liquors are light brown color, and contain much extractive matter from the wood; their disposal is often a serious matter, and it has been suggested * that they may furnish material for oxalic or pyroligneous acid, or alcohol.

In the **sulphate process**, the lignin and other non-cellulose matter of coniferous woods are dissolved in hot solutions of alkali sulphides, leaving a fibre of unusual strength. The sodium sulphide employed is made by the reduction of sodium sulphate (salt-cake). The sulphide

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* Griffin and Little, Chemistry of Paper Making, p. 271.

is largely recovered by evaporation and incineration of the "black liquors" from washing the pulp; the organic matter in the liquor is more than sufficient to reduce the sulphate added to make up the sulphide loss. The chipped wood (spruce, fir, pine, etc.) is cooked from four to seven hours at 100 lbs. pressure (about 160° C.) in a solution containing sodium hydroxide, sulphide, sulphate, and carbonate; of these only the first two are active in disintegrating the wood. Approximately six equivalents of hydroxide to four of sulphide are used; high sulphide with less alkali and longer cooking yields better and stronger pulp. The time of cooking is influenced by the temperature, pressure, concentration of the liquor, and amount of moisture in the wood. After cooking, the stock is blown into drainers and then washed by counter-current flow; the strongest wash-water, or black liquor, is returned to the digester room and used to dilute the solution for the next cook; the intermediate wash-water (about 10° Bé.) passes to the concentration and recovery system; the very dilute washings serve as first wash-liquor on the next batch of pulp. The concentration of the intermediate wash-liquor is done in multiple effects to 25° Bé.; then in a Porion surface heated evaporator (p. 4) to 35° Bé.; the thick liquor now passes through a 25-foot rotary furnace, where it is reduced to a pasty mass, which flows into a calcining furnace (about 10 feet diameter by 15 feet high) lined with magnesia brick and in which salt-cake, to make up the loss, is added. The charge, as a burning semi-fluid mass, lies in the bottom of the furnace, and wood is charged on top as fuel. A large excess of air is blown in at the bottom to secure rapid combustion, and the melt is drawn off into a tank of water; after solution, the carbonate is causticized with lime, and the settled liquor, containing about 5 lbs. of available Na_2O per cubic foot, is sent to the digester room and diluted with black liquor before use. The combustion gases from the calciner pass to the rotary furnace and Porion evaporator, which they heat by counter-current flow. About 400 lbs. of available Na_2O per ton of chips are required, and each digester yields about 6½ tons of finished pulp (10 per cent moisture). The pulp is difficult to bleach and finds use mainly for tough and strong wrapping paper (Kraft paper). Much sulphur dioxide is lost in the furnace gases, which lowers the sulphide content of the liquor materially.

The pulp made by any of the above processes is sent to the "**hollander,**" or "**beating engine**" (Fig. 121). This is an oval tub 15 to 20 feet long by 3½ feet deep, and having a vertical partition called the "mid-feather" extending along the middle, about two-thirds of its length. On one side of this and extending across one-half of the width of the tub is a large roll (A), carrying on its circumference a number of knives (C). The floor is curved upward *behind* the roll (A), conforming closely with its curvature, but extending only about half its height, as shown at (B). From this highest point the floor falls away to the level of the rest of the tub bottom. Under the roll is the "bed-plate" (D), fitted with knives similar to those on (A). (A) is revolved in the direction shown by the arrow, and the pulp is drawn in between the roll (A) and the curved bottom (D), and the fibres are torn apart. It then passes over the back-fall (B) and thence around through the passage on the other side of the mid-feather to the front of the roll and again passes between the knives. (A) is suspended upon adjustable bearings so that the distance between the two sets of knives may be regulated. They are not set very close for breaking and disintegrating the washed pulp, as it is not desired to break the knots and undecomposed wood, which would cause dirt and shive in the pulp.

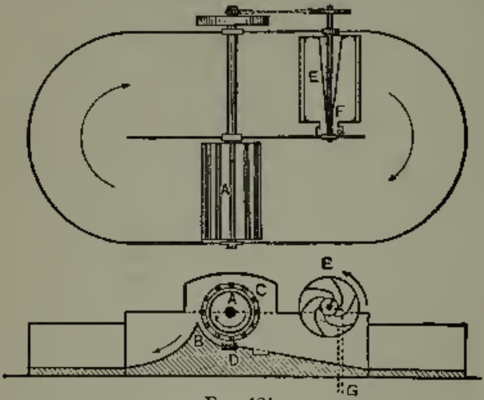

FIG. 121.

In order to complete the washing of the pulp during its disintegration one or two **drum-washers** (E) are usually placed in each hollander. These are rotating cylinders covered with fine wire gauze and divided into compartments by curved partitions. A conical tube passes through the centre of the drum, the narrow end being towards the mid-feather. The partitions radiate from this cone to the wire gauze periphery of the drum. The outer end of the drum is solid, but that next the mid-feather has a central opening (F), through which each compartment discharges its content of water into the trough attached to the mid-feather. The drum, supported in adjustable bearings, is partly submerged, and the water, passing through the gauze, is caught in the compartments as the drum rotates and discharged through (F). It flows into the trough and out through the pipe (G). The gauze holds back the pulp, which again passes around the mid-feather to the roll (A).

* a splinter or cluster of splinters of raw

A form of hollander, requiring less floor space, is shown in Fig. 122. In this the pulp passes *below* the floor and back-fall on its return to the front of the roll. The machine is but little wider than the length of the roll (A), the washing drum (E) being directly behind the roll.

After breaking, the pulp is carried by a strong stream of water on to a sluice or inclined way having a number of transverse slats across the bottom. The knots and lumps lodge against these obstructions, while the fine pulp flows on with the water to the bleaching tanks.

Rags, both cotton and linen, are largely used in paper making. These are collected in all countries, and arrive at the mill in various conditions of filth. They are sorted by hand, the seams cut open, and all buttons, metallic hooks, etc., removed. The dust is beaten out in machines having rapidly revolving arms, and then the rags are cut into small pieces and boiled for 12 hours or longer, under the pressure of 60 or 70 pounds, in rotary horizontal cylinders, or in horizontal kiers (p. 504), with 5 to 18 per cent of milk of lime. Sometimes a little soda-ash is added to the liquor for colored rags. After boiling, they are dumped in heaps to drain and soften for a day or two. After washing with hot water, they are sent to the pulping machine.

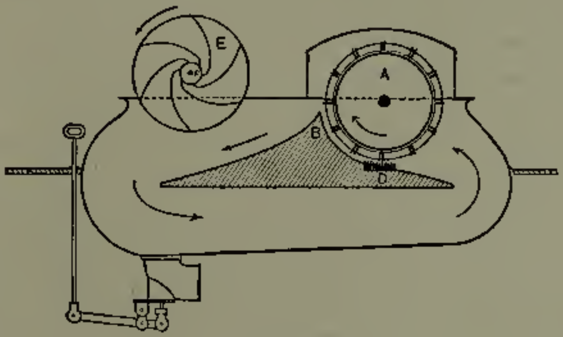

FIG. 122.

Esparto, or Spanish grass, is derived from *Lygeum Spartum*, Loefl, and *Stipa tenacissima*, L. The bast fibres are similar to those of straw, but give a stronger paper. It is chiefly used in Europe, being too expensive to compete with wood pulp in this country. Esparto and straw are boiled with caustic soda in upright digesters. In rotary boilers the fibre forms little balls (" fish eggs "), which cause little spots or lumps in the paper. The pressure and time of boiling vary. The waste liquor is evaporated, and the alkali recovered (p. 555). After washing, the pulp bleaches well with bleaching liquor. In this country, straw is generally boiled with lime to prepare a pulp for strawboard.

Jute has very short fibre, so the fibre bundles are not separated, and only the lime-boil is employed.

The bleaching of paper pulp is done by agitation with a weak calcium hypochlorite solution. If the liquor is heated to 90° or 100° F., or a little acid added, the process is hastened. Alum forms aluminum hypochlorite with bleaching powder solutions, which is very effective; a slightly acid alum or "bleaching" alum is commonly used. The bleaching is carried on in special vessels ("chests"), or in the beating engines or hollanders, the latter giving the best results. Only a clear solution of bleaching powder should be used, so that no dirt be introduced, as it would cause spots in the paper. Rags require the least bleaching (2 to 5 pounds bleaching powder to 100 pounds of stock), and spruce pulp the most (about 18 to 25 pounds per 100 pounds for sulphite spruce pulp). As soon as bleached, the process should be stopped, especially if the liquor has been heated; otherwise the fibre is liable to be chlorinated, and color again taken up. The excess of hypochlorite in the pulp is washed out with water, or is destroyed by adding an antichlor, such as sodium thiosulphate (p. 61), in the beating engine. Neutral calcium sulphite is also recommended, but its action is slow: —

$$Ca(ClO)_2 + 2\ CaSO_3 = 2\ CaSO_4 + 2\ CaCl_2.$$

The pulp must be thoroughly washed after bleaching, even when antichlors are used, since injurious substances may be left in the pulp. The action of the antichlor is as follows: —

$$2\ Ca(ClO)_2 + Na_2S_2O_3 + H_2O = 2\ NaCl + 2\ CaSO_4 + 2\ HCl;$$

or, in dilute solutions: —

$$Ca(ClO)_2 + 4\,Na_2S_2O_3 + H_2O = 2\,Na_2S_4O_6 + 2\,NaOH + CaO + 2\,NaCl.$$

Materials such as ozone, hydrogen peroxide, sulphurous acid, or liquid chlorine, have been suggested for bleaching, but these are of much less importance than the hypochlorites.

The **paper-making process** is chiefly mechanical. It is essential that the water used be clear and colorless, since color or suspended matter will be taken up by the pulp. The first operation is "**furnishing**" or charging the hollander with the stock; the kinds and quantity of material employed depend on the quality of the paper to be produced. Rag stock is only used for the best grades, especially writing papers. New linen rags and waste are used for bond paper, but the softer writing papers are made from old rags. The quality of paper depends largely on the thorough separation of the fibres and mixing of the ingredients in the hollander. In order to give the paper body, weight, and smoothness, mineral filler or "loading" material is employed. This must be exceedingly fine, and not have too high a specific gravity or solubility in water, as its retention in the mat of the fibre would be thus reduced. It must be free from dirt, grit, and mica, since these cause scratches on the polishing rolls or spots on the paper. The loading is done in the hollander after the fibre has been well beaten with water. The filler is mixed with the pulp, and then, for engine-sized paper, the sizing materials are added, and the whole beaten until a perfect mixture of the materials is obtained.

Papers intended for printing or writing must be **sized** or coated on the surface with some substance which will prevent the absorption and consequent spreading of the ink. For liquid writing inks, the sizing must be more perfect than for the viscid printing inks. Almost the only sizing materials now used are gelatine, "animal size" (used on the better grades of paper), rosin, and casein. These are applied in several ways. Animal size is applied to hand-made papers by dipping each sheet separately into a tub of the glue solution, and allowing it to dry slowly. The operation is called "tub sizing." Machine-made writing paper is passed in continuous web through a trough filled with the glue solution. It is then cut into sheets, and dried very slowly by hanging it in a loft kept at an even temperature; or, in cheaper grades, after leaving the size trough, the web passes over a series of skeleton driers, within which fans keep up a rapid circulation of air. Slow drying is essential to animal size, in order to bring it to the surface. Printing papers (except some kinds of newspaper) are "engine-sized"; *i.e.* a rosin soap (prepared by boiling rosin with soda-ash) is added in the hollander, and, after beating, a solution of aluminum sulphate is introduced. The alum decomposes the rosin soap, forming a precipitate of free rosin, and perhaps some alumina, which become entangled between the fibres. When the paper passes between the hot calender rolls in finishing, this rosin fuses and forms a varnish-like layer on the surface. The aluminum sulphate should be neutral or basic, since free acid decomposes the size and injures the color and strength of the paper. An excess of alum over the amount needed to decompose the rosin soap must be used; and the precipitated alumina helps to hold the finer parts of the fibre and filler in the pulp while forming the sheet.

Paper is usually colored by adding pigments or dyes to the pulp in the hollander. For white paper, the slight yellow tinge of bleached fibre is neutralized with a trace of blue or pink, ultramarine or coal-tar dyes being used. Some pigments are precipitated on the fibre by adding solutions in the hollander; *e.g.* potassium bichromate and lead acetate.

The sheet is formed in three different ways: by the hand frame, by the cylinder machine, and by the Fourdrinier machine. The **hand frame**, used for hand-made paper, is simply a rectangular frame, covered with wire gauze, and having a slight, removable ledge around the sides. This frame is submerged in the pulp, mixed to a thin cream with water; when raised, the ledge retains some of the pulp on the gauze, while the water drains through; at the same time the workman shakes the frame slightly from side to side, causing the fibres to "felt," and forming a mat of pulp on the gauze. The frame is then inverted over a woollen felt blanket, on which the sheet of pulp drops. A number of these pieces of felt, each carrying a sheet of pulp, are piled one above the other, and heavily pressed until the water is expelled. The sheets are then "tub-sized," as above described. The final finish is given by calendering between hot rolls.

The **cylinder machine** is essentially the same as that described for mechanical pulp, on p. 554. The web of paper pulp is carried on an endless blanket over a large drying cylinder, and then lifted and passed between heated rolls. The paper thus made is weak, since the fibres are not well felted. They are used for tissue and blotting papers, and are not sized.

The **Fourdrinier machine** is very complicated. Essentially, it is as follows: An endless web of wire gauze is supported horizontally on a number of rollers, and travels continually in one direction. The paper pulp flows on to this from a storage tank called the "stuff chest," the thickness of the sheet being regulated by the supply of pulp. The wire gauze is given a continuous sidewise shaking motion which felts the pulp, while the water drains away. The water is drawn away by the action of "suction boxes" from which the air can be partially exhausted, and over which the gauze travels. The web is next transferred to an endless blanket which carries it between squeeze-rolls, and then on to a second felt, where it is again passed between rolls. It finally passes a series of "couch rolls," "press rolls," drying cylinders, and calender rolls to compact, dry, and polish the paper.

By fixing a slightly raised design on the wire gauze of the hand frame the paper is made slightly thinner along the lines of the pattern, and so-called "**water marks**" are made. The same effect is obtained on paper made on the Fourdrinier machine by placing a light roller ("dandy roll") carrying the design in relief, between the first and second suction boxes, so that an impression is made on the soft pulp. If the roll is covered with wire gauze, the impression of the weave of the gauze is obtained, producing the "wove" papers. A smooth roll carrying ridges forms the parallel lines on "laid" paper. By using a roll with a depressed or engraved design the paper is made thicker in the lines of the pattern. Imitation water marks are often made by pressing the finished paper with plates carrying the design in relief, or by slightly parchmentizing the surface by printing with certain chemicals, such as zinc chloride or sulphuric acid.

The finishing of smooth and highly sized paper is done by calendering, or passing the web between polished rolls of chilled iron, under heavy pressure. A higher gloss is obtained by using calenders with rolls made of heavily pressed paper, alternating with polished iron rolls. Friction calendering consists in passing the paper between a pressed paper roll running at high speed, and an iron roll running slowly. For very high gloss the paper is "plated"; *i.e.* passed through heavy rolls while the sheets lie between polished zinc plates.

Printing papers are usually white, and often contain a large amount of loading material. In this country they are chiefly made from wood pulp. Some kinds are heavily calendered to secure a smooth surface. Cheap newspaper is largely made of mechanical pulp.

Wrapping papers are made from straw, jute, manila hemp, old rope, and colored rags. The stock is seldom bleached, and hence is very often deeply colored. Wrapping papers are frequently calendered and always sized.

Writing papers are made from the best materials, and are highly sized and carefully calendered.

Blotting and **tissue papers** are unsized and unfilled, the former being loosely felted and thick; the latter is made from long fibres, especially hemp and cotton, and is the thinnest paper made.

Parchment paper is made by dipping unsized paper into sulphuric acid, diluted with one-fourth its volume of water, to which a little glycerine is added. It is quickly removed and washed with water, then with dilute ammonia, and again with water. The acid converts the exterior cellulose of the fibres into amyloid, which coats the fibres and cements them together, forming a translucent parchment-like material of great toughness. The action of strong zinc chloride solution (sp. gr. 1.82) is also to parchmentize the paper. After washing, the paper is pressed between rolls, dried, and calendered.

By long-continued beating of pulp or rags, in the hollander, until all fibre structure is broken down, a gelatinous mass is produced, which, when run upon a paper machine, gives a thin, transparent film, resembling ordinary parchment paper. This is much used for wrapping confectionery, butter, and for other purposes when imperviousness is desirable.

Willesden paper is made by passing the web through a strong solution of Schweitzer's reagent (copper hydroxide dissolved in strong ammonia), and pressing together several sheets so prepared without washing. The surface of the cellulose is softened and the sticky sheets are compacted into a single thick one. The evaporation of the ammonia leaves the cupro-cellulose in the fibres, which are thus coated with a green varnish-like substance, and rendered water-proof.

Vulcanized fibre * was invented by an English chemist named Taylor about the year 1869. Although the original patents included the use of sulphuric and nitric acids, with or without the addition of various metallic salts, the process as commercially practised to-day is confined to the action of zinc chloride on pure cotton cellulose paper.† The paper is passed over heated cylinders through a bath of zinc chloride maintained at about 70° Bé. and 40° C., depending upon the quality of the paper and the atmospheric conditions. It is then rolled up over large heated drums to the desired thickness, the zinc chloride hydrolyzing the cellulose and gelatinizing the surface to such an extent that the paper unites together and forms an almost homogeneous mass. Fibre tubes may be made in a similar manner by substituting for the large drums mandrels of the proper size to give the desired inside diameter. The " green fibre " is now washed in baths of zinc chloride of progressively diminishing concentration until it is entirely pure, when it is dried at 40° to 60° C., pressed, and calendered. The finished product, which has shrunk to one-half its original thickness, is a homogeneous, tough, hornlike material, which can be readily machined, threaded, embossed, etc., and which can be given a high polish. It may be rendered flexible by soaking

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* J. Soc. Chem. Ind., **1897**, 552.

† U. S. Pat., 114880.

in calcium chloride or glycerine solutions. Some of its more important properties are: Specific gravity, 1.2–1.5; dielectric strength, 100–175 kilo volts per cm.; tensile strength, 10,000–12,000 lbs. per sq. in.; compressive strength, 35,000–40,000 lbs. per sq. in.

Vulcanized fibre is used for all kinds of electrical insulation; for trunks, roving cans, waste baskets, and similar receptacles; and for a great variety of mechanical purposes, such as, gears, valves, washers, bushings, etc.

The testing of paper should be both microscopical and chemical; considerable attention is given to this on the continent of Europe, but in this country it is seldom employed. The methods and details may be found fully described in Griffin and Little's Chemistry of Paper-Making, Chap. IX., and in the works of Wiesner and of Herzberg.

REFERENCES

Die Fabrikation des Papiers. L. Müller, Berlin, 1877.
The Manufacture of Paper. C. T. Davis, Philadelphia, 1882.
Guide pratique de la Fabrication du Papier. A. Proteaux, Paris, 1884.
Handbuch der Papierfabrikation. S. Mierzinski, Wien, 1886.
Die Microscopische Untersuchung des Papiers. J. Wiesner, Leipzig, 1887.
Die Fabrikation des Papiers. E. Hoyer, Braunschweig, 1887. (Vieweg.)
Die Bestimmung des Holzschliffes im Papier. A. Müller, Berlin, 1887.
The Practical Paper Maker. J. Dunbar. 3d ed. London, 1887. (Spon.)
Papier Prüfung. W. Herzberg, Berlin, 1888. (J. Springer.)
Le Papier. P. Charpentier, Paris, 1890. (Tome X., Encyclope die Chimique, par M. Frémy.)
The Art of Paper Making. A. Watt, London, 1890.
Technologie der Papier Fabrikation. Würtemberg, 1893.
The Chemistry of Paper-Making. R. B. Griffin and A. D. Little, New York, 1894. (Lockwood & Co.)
United States Consular Reports, **1894**. Parchment Paper.
A Treatise on Paper-Making. Carl Hoffman, New York, 1895.
A Textbook of Paper Making. C. F. Cross and E. J. Bevan. 2d ed. London, 1900. (E. and F. N. Spon.)
Paper Trade Journal, New York, **1893**, June 24, et seq.: —
Evolution of the Sulphite Digester. H. A. Rademacher.
Journal of the Society of Chemical Industry: —
1890, Chemistry of Hypochlorite Bleaching. C. F. Cross and E. J. Bevan.
1890, 9, 241, Paper Testing. H. Schlichter.

GLUE

Glue is the first product of the hydrolysis of animal connective and elastic tissues. When heated with water, these tissues lose their peculiar structure, swell, and finally dissolve; on cooling, this solution jellies and dries into a horny, translucent mass, which is the glue. When redissolved in hot water, this forms a thick solution having strong adhesive properties. **Gelatine** is made more carefully, from better stock, but chemically there is no difference between it and glue. Both swell with cold water, but do not dissolve until the water is heated.

Glue is a colloid, a water "solution" of which has as the dispersing medium a dilute solution of glue (the more completely hydrolized part) in water, in which is suspended as the disperse phase, a liquid, or more probably a semi-solid, consisting of a solution of water in glue. The more water present, the greater the fraction of the gelatine dissolved in the dispersing medium, and the less in the disperse phase. At high temperatures (above 40° to 50° C.) the solubility of gelatine in water is so great that the amount present as disperse phase is small, but as the temperature decreases, this phase increases at the expense of the dispersing medium, till a point is reached at which the components interchange functions, the semi-solid becoming the dispersing medium, and the residual liquid (largely water) the disperse phase, existing as drops throughout the solid. The system is now called a jelly or *gel*, and the temperature of transition of the given solution, its jellying point.

Commercial glue from any source contains two essential constituents, — **glutin**, an amorphous, odorless, tasteless, protein substance, soluble in hot water, having great adhesive strength, and precipitated from solution by tannin or alcohol; and **chondrin**, similar to glutin, but mainly derived from the cartilaginous and young bone tissues, and having less adhesive strength. There are three general classes, hide glue, bone glue, and fish glue. **Hide glue** is made from glue stock, *i.e.* waste bits of hide trimmings, skivings, fleshings, and other *untanned* refuse from the beam house; slaughter-house waste, such as the ear-laps and heads (petes), sinews, feet, and tails of cattle and sheep; and the skins of rabbits, hares, and dogs, and scraps of alum-tawed leather. The external horny parts of hoofs and horns are of no value as glue stock.

The stock, wet, or dried and salted, is washed, and then limed for from six weeks to several months, during which time it is thoroughly and frequently stirred. It swells, and the fats are converted into lime soap, while blood, flesh, and coriin are partly dissolved. The stock is then thoroughly washed in tubs, with mechanical stirrers, or rollers, to remove the lime, lime soap, and dirt; the last trace of lime is removed by treating with dilute hydrochloric acid, or, better, with sulphurous acid, which both plumps and bleaches the stock. The excess acid is washed away, and the stock is ready for "cooking" or "boiling," to convert the collagen into glue. The temperature of heating is from 65° to 100° C., although actual boiling of the liquor is avoided. The kettles are open wooden vats,* heated by closed steam coils, above which is a perforated false bottom covered with a layer of excelsior or straw, and finally an iron grating, upon which the glue stock rests. Water is added, and the kettle is heated until the stock dissolves, forming a solution thick enough to jelly on cooling. Long cooking of the solution must be avoided, or considerable decomposition occurs and the strength of the product is decreased. The grease and lime soaps rise, and are skimmed off; the solid matter, consisting of hair, etc., sinks, and, together with the excelsior, forms a filter through which the liquor is drawn off from under the false bottom, and a clear solution is obtained; or the liquor may be filtered on felt or in bag filters.

The stock is not all dissolved in the first liquor, and usually from three to five boilings with fresh water are necessary to extract all the glue; these later solutions are thicker and stronger, so all the liquors are usually mixed, except the first, which yields the finest product. Sometimes the stock is treated in closed kettles with direct steam under pressure, thus causing rapid melting.

If the liquor is too thin to jelly, it is concentrated in a vacuum pan. The solution is run into coolers, which differ in size and shape. A good form is a galvanized iron or aluminum pan 13 inches long by 11 inches wide by 9 inches deep, and having slightly flaring sides. This is cooled by standing in cold water, or by the use of refrigerating machines.

In from 12 to 24 hours the solution jellies, forming a mass containing about 85 per cent water. This is turned out on a table and cut into plates from one-eighth to one-fourth of an inch thick, by means of wires stretched tightly across a frame. These slices must be carefully dried at once; they are put in single layers on wire frames and passed into the dry-room, a long, narrow room from which sunlight is excluded, and which is heated by hot air, blown

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* Tinned metal kettles are sometimes used instead of wooden vats.

in at the end farthest from where the glue enters. The jelly is very apt to develop mould or to liquefy through the action of bacteria, while if the temperature rises over 35° to 40° C., it is liable to melt, forming a "daub." But in clear, cold weather, the temperature of the dry-room may rise to 43° C. In summer it is nearly impossible to dry the films properly and no glue is made. If the wet film is frozen and then dried, the glue is spongy and porous. The glue should dry in about 24 hours, when the trays are removed from the hot end of the drying-room, and the films broken or ground in a disintegrator and packed for shipment. The dry glue contains about 15 per cent water.

Bone glue is not essentially different from hide glue, and is made from green bones which, for the better qualities, must be quite fresh. They are boiled with water, and the oily matter skimmed off as it rises; or better, the bones are extracted with benzine or other solvent, in a "rendering tank," p. 354. The extracted bones are crushed and treated with dilute hydrochloric acid (sp. gr. 1.05) until the calcium phosphate and other salts dissolve. The cartilaginous residue is treated with lime-water to remove any acid. After washing, the mass is boiled with water or steamed in a digester until dissolved. Any grease is skimmed or filtered off and the gelatine is chilled and dried as already described. Benzine-extracted bones are often crushed and boiled directly or steamed for glue. The glue solution is then strained through a cloth, bleached by treatment with sulphurous acid, and evaporated at about 60° C. *in vacuo*, or in open troughs with a rotary steam-coil half submerged in the liquid. The thick solution is chilled, jellied, and dried as above.

Fish glue is made by boiling the heads, fins, and tails of fish at 110° C. It has very weak jellying properties and is generally made into liquid glue, the disagreeable odor being destroyed by adding creosote, oil of sassafras, or other strong-smelling substance.

Liquid glue is made by treating fish or common glue with acetic, nitric, or hydrochloric acid, whereby the property of gelatinizing when cold is lost. But the adhesiveness is not materially changed; and since such glues do not require to be heated or applied to hot surfaces, they are extensively used.

Gelatine is prepared from calf or sheep skin and from sturgeon and other fish skin. The first liquors formed in the boiling or steaming yield a colorless gelatine which is used for food and in the preparation of photographic emulsions. The solution is often filtered on bone-black or bleached with sulphur dioxide before jellying. Much is used in clarifying liquors containing tannins, especially wines, etc.

Isinglass is a pure white, odorless, tasteless gelatine, prepared by drying the inner skins of the swimming bladders of fish. The degree of molecular association is not sufficient to require a preliminary hydrolysis, as in the case of ordinary glue stock. It is almost entirely soluble in water at about 50° C., and forms a transparent jelly on cooling. Owing to its high price and slight adhesive strength, it is used only for food and in clarifying liquors, such as wine, beer, coffee, etc.

A vegetable gelatine derived from a species of algæ or seaweed forms the **agar-agar**, p. 400, or **Bengal isinglass** of commerce.

Satisfactory methods for glue testing have not yet been devised. The usual tests are determinations of the viscosity of the solution and the firmness of the jelly formed, but the adhesiveness does not depend upon the quality of the jelly. Glue is usually sold according to its color and physical properties, and should be free from grease.

REFERENCES

Die Fabrikation chemischen Producte aus thierischen Abfällen. H. Fleck, Braunschweig, 1878.
Die Leim und Gelatin Fabrikation. 2te Auf. F. Dawidowsky, Wien, 1879.
Glue and Gelatine. Dawidowsky-Brannt, Philadelphia, 1884. (Baird.)
Cements, Pastes, Glues, and Gums. H. C. Standage, London, 1893.

LEATHER

The skin, when removed from the animal, very soon becomes putrid if kept moist, and is hard and horny when dried; in either case, boiling water converts it into soluble glue. **Leather** is skin so treated that it remains more or less soft and pliable, does not putrefy, and is not readily changed into glue. Animal skins are made up of three layers, — the epidermis, the fatty tissues, and between them the corium, cutis, or skin proper. The **epidermis** is thin and the roots of the hair are attached to it. It consists of individual cells, which become dead and dry on the outer surface, and are easily detached by friction or abrasion. These cells are largely composed of **keratin**, a substance rich in sulphur, and very little affected by cold water; even hot water does not produce gelatine from it. But the young, interior cells are somewhat attacked by lime-water. The hair and keratin substances are dissolved by concentrated alkali and especially alkaline sulphide solutions. The **fatty tissues** form the innermost layer of the skin, and consist of a loose network of connective tissue, containing fat cells, blood vessels, sudorific glands, and muscular fibres. The ducts of the sweat glands pass through the corium and epidermis.

The **corium** or **dermis** is the only part of the skin of value for leather; it consists of connective tissue composed of bundles of fibres which interlace somewhat loosely on the under side of the skin, but are closely matted on the epidermal side. This fibrous substance consists chiefly of **collagen**, which appears to be altered by the action of boiling water and converted into soluble gelatine or glue. Some authorities hold that an intercellular substance, **coriin**, comparable to sericine or silk glue, p. 492, fills the spaces between the bundles of fibres, and cements them together when the skin dries, making the skin hard and stiff. Other writers regard the coriin as merely an alteration or decomposition product of collagen. Both collagen and coriin are albuminoids, complex condensation products of amino-acids, capable of progressive hydrolysis, the ultimate product being the simple acids. This hydrolysis takes place even in cold water, though slowly, but is greatly accelerated by heat, by electrolytes (especially acids in proportion to their strength, *i.e.* H^+ ion concentration), and by various enzymes. The first effect of the hydrolysis is a mechanical weakening of the fibre, rapidly followed by solution (conversion to glue), and ultimately resulting in the production of the component amino-acids. Coriin is the more readily hydrolyzed, and is perhaps the first product of the hydrolysis of collagen.

The tannage of leather consists in the separation of the cutis from the accompanying tissues, the conversion of it into an insoluble form, and the subsequent treatment or finishing of the leather to secure the necessary body and appearance.

Hide substance is an organized gel (pp. 30; 568), the solid dispersing medium being the fibre bundles of the skin, the liquid dispersed phase being perhaps the contents of the individual cells; the latter contain in true solution hydrolysis products of the collagen, the less complex condensation products of amino-acids which are amphoteric (since they contain both free amino and carboxyl groups), and therefore react with both acids and bases, the basic character being somewhat the stronger. The collagen of the dispersing medium is, in its normal state, highly hydrated, elastic, and semi-permeable (allowing almost perfect diffusion of strong inorganic electrolytes), but is entirely impervious to the amphoteric contents of the cells, whether ionized or not. Like all albumins and the so-called emulsoids or emulsion colloids, it is readily dehydrated, either by drying, by the action of strong solutions of electrolytes, or by coprecipitation with other emulsoids. When thus dehydrated, it shrinks and loses its elasticity. It is also readily hydrolyzed to less and less complex products, the reaction being hastened especially by hydrogen ion and by heat, but also by hydroxyl and various enzymes. Any acidic or basic groups in the collagen are exceedingly weak, as is to be expected from its complex structure. The conversion of hide into leather consists in the dehydration of the collagen by coprecipitation with other emulsoids. To secure penetration and uniformity of action the precipitating colloid must be in solution and the collagen itself must be completely and uniformly hydrated.

Pelts are divided by the tanner, according to their size, into three classes: (*a*) **hides**, comprising the skins from large and fully grown animals, such as the cow, ox, horse, buffalo, walrus, etc.; these form thick, heavy leather, used for shoe soles, machinery belting, trunks, and other purposes where stiffness and strength, combined with great wearing properties, are essential; (*b*) **kips**, the skins from undersized animals or yearlings of the above species; (*c*) **skins** obtained from small animals, such as calves, sheep, goats, dogs, etc. These yield lighter leather suitable for a great variety of purposes. The thickest and heaviest hides come from rough, sparsely settled countries. The same hide varies in thickness and texture in different parts, being thicker on the neck and butt than on the flank and belly. They frequently show injury, such as cuts, brand marks, and holes or thin places caused by the bot-fly or warble. Diseased pelts are often sold, which, besides yielding a poor leather, are a source of danger to the workmen, owing to the contagious nature of some of the diseases (especially anthrax); hence disinfectants should be freely used in the tannery.

Pelts come to the tanner "green" (fresh from the animal), salted (where the salt has been thickly rubbed on the flesh side), or dried. **Green pelts** are washed in clear water to free them from blood and dirt; **salted pelts**, if not dried, are merely washed in several changes of water. It is essential to remove all the salt before beginning the unhairing process, as it retards the action of the lime and interferes with the "plumping" of the skin. It is also liable to cause an efflorescence ("spueing") on the finished leather. **Dried hides** must be thoroughly rehydrated by soaking in water, using care to secure uniformity. Luke-warm water, or the liquor from the soaking of a previous lot, may be used to promote fermentation, resulting in the production of ammonia and amines, but the use of this "putrid soak" must be carefully watched to prevent putrefactive injury to the skin; more often in modern practice, soda-ash, borax, or sodium sulphide are added * in small amounts to the soak. Acids cannot be used for softening, on account of the destruction of the fibre by hydrolysis in the presence of hydrogen ion. After hydration is sufficient so that the hide may be bent double without breaking, it is furthered by mechanical working, by tumbling (submerged in water) in drums, or by mauling in "stocks" or mills with wooden mauls or rollers.

The character of the water used in the tannery is important. Soft water makes the skins thin and slim, which is desirable in light leather. Water containing calcium or magnesium sulphate "plumps" or swells the hide, thus exposing a larger surface to the action of the

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* The probable action of these alkalies in assisting hydration is as follows: As soon as hydration begins, there is within the cell, as the disperse phase, a solution of a body which may be represented by a general formula, $NH_2 \cdot B \cdot COOH$, where B indicates an organic complex. With alkalies this reacts:

$$NH_2 \cdot B \cdot COOH + Na^+ + OH^- \rightarrow NH_2 \cdot B \cdot COO^- + Na^+ + H_2O.$$

The dilute solution of the sodium salt of this acid is, like all such salts, almost completely dissociated, and since the anion cannot diffuse through the dispersing medium, its corresponding sodium ion is held in the cell by electrostatic attraction. Fresh alkali will enter the cell by diffusion to replace that consumed by the reaction. This reaction in consequence of the production of a highly dissociated salt in place of an undissociated acid (two mols derived from one), has therefore doubled the molecular concentration of non-diffusible material, and hence doubled the net osmotic pressure in the cell, which results in its distention. This distention opens up the fibres of the hide and draws through them the water necessary for the increase in size of the cell, which greatly promotes the hydration of the collagen.

tan liquors, which is desirable for heavy hides. Chlorides cause the hides to "**fall**," *i.e.* to become thin and flabby. This is due to the dehydrating action of the electrolyte. If used for washing after the liming, water having temporary hardness tends to fix the lime among the fibres in an insoluble form, thus causing the leather to be harsh on the grain and producing colored spots because of unequal deposits of tannin and coloring matters in the tan pits. Hard water also causes waste of tannin matters through the formation of insoluble compounds with lime and magnesia. Water carrying organic impurities may have an acid nature and cause the hides to "fall" after liming, or it may engender putrefactive changes in the skin.

When thoroughly cleaned and softened, the hides undergo the **depilation** or **unhairing process.** This removes the hair and epidermis, and also the fatty tissues from the under side of the skin. It is done by treatment with an alkaline solution, which attacks and softens the inner layers of epidermal cells, loosening the outer layer and hair, so that they may be scraped away; or by "sweating," in which the young epidermal cells are softened by bacterial action until the outer layers are loosened. Lime is the most common unhairing material, sometimes aided by the addition of sodium sulphide, arsenic compounds, or calcium hydrosulphide. Skins are sometimes unhaired by dilute solution of sodium sulphide, which dissolves the hair completely; this cannot be used if the hair is to be saved as by-product, and care is needed to prevent injury to the skins.

Liming. — The skins are laid in a vat or pit with milk of lime, which loosens the epidermis and forms a soap with the fatty matter. It also dissolves the coriin, loosening the fibres, which swell and "plump" the hides. It is used in excess in amounts varying from one-half pound for a small light skin to 4 pounds for a heavy one. The vats or pits when prepared to receive the skins are called "limes." The skins are frequently turned over and worked about ("handled"); for heavy hides which are to form stiff, hard leather, the liming only lasts a few days; but for a soft, elastic, pliable product, the process continues for 15 or 20 days, or longer. Warming the limes to 85° or 90° F. hastens the action, but causes the skins to "fall." The addition of sodium sulphide to a thick cream of lime yields a paste which may be spread on the hair side of the skin, and, after being folded together for a few hours, the hair is easily detached. Arsenic sulphides, realgar and orpiment (about 10 per cent of the weight of the lime), are frequently added to the limes, forming calcium sulph-arsenite ($HCaAsS_3$), which is a rapid depilatory.

"**Sweating**" is used for hides which are to be made into sole or other stiff leather. The hides are hung in a room kept at a constant temperature of 18° to 21° C., the atmosphere being saturated with moisture. Bacterial decomposition of the inner layer of the epidermis sets in and after a few days the hair is loosened. The bacteria which are effective in sweating are aërobic; the putrefactive bacteria are anaërobic, hence decomposition of the fibre can be controlled by providing an adequate air supply. Before treating with tannin, sweated hides must be "plumped" by immersion in dilute acid.

After the hair has been loosened, the skin is laid across a sloping "beam" of wood, and the hair and epidermis are scraped away with a blunt knife. The fatty tissues are removed in the same way. These operations, known as "**beaming**," are carried on in the "beam house" of the tannery. After trimming off the waste parts of the skin, it is thoroughly washed, and is usually again scraped on the "beam" (scudded) to remove as much of the lime as possible.

If soft, pliable leather is to be made, the skins are next subjected to the "**bating**," or "**puering**," process to destroy the "plumping" produced by the lime, and also to cause other changes, the nature of which is rather obscure. Some authorities claim that the bate merely removes the lime from the pores of the hide, while others assert that it also takes away some of the coriin, thus leaving the fibres looser, and allowing more perfect action of the tan liquors. The latter view seems probable, and there is little doubt that the bacteria in the bate do feed upon the hide substance. Further, the ferments, tripepsin, pancreatin, etc., present, undoubtedly exercise some function, for when used alone they will cause a "plumped" skin to fall. The ammonium salts formed doubtless also assist in the solution of the lime in the skin. Bating consists in soaking the hides in a mixture of dog or bird dung in warm water. This quickly becomes putrid, and evolves hydrogen sulphide, while the liquor acquires an alkaline reaction. The process lasts from 2 to 4 days, according to the thickness of the skin and the temperature. It is largely dependent upon the atmospheric conditions; in the warm, sultry weather, such as usually precedes a thunder-storm in this climate, the action becomes extremely rapid, and a few hours is often sufficient to injure the skin. Great care must be exercised at all times, and the skins stirred about frequently to prevent too great local action, resulting in thin places or in holes in the leather.

Many proposals have been made to replace the offensive bate with pure solutions of weak mineral and organic acids; but these have not generally found favor with tanners, the common objection being that the leather is made harsh, and has a bad grain.

After bating, the fibres have become soft and pliable, and the whole skin has a smooth, slippery feel. As these qualities are not desirable in sole leather, *heavy hides are not bated.*

In order to complete the removal of the lime, it is customary to next pass the skins into the "**bran drench,**" consisting of an infusion of bran and water at a temperature of about 32° C. On standing, this soon develops a fermentation, in which lactic with some butyric and acetic acids are formed, dissolving the lime.

The skins are now ready for actual conversion into leather, or the **tanning process.** This is done in three ways: —

(1) With tannin in any form (vegetable tannage).

(2) With metallic salts (mineral tannage).

(3) With oils or fats (oil tannage).

1. The sources of vegetable tannins have been considered on p. 518. For leather, it has been found essential that the tannin material shall yield other extractive matters than tannic acid when treated with water. These non-tannins are mainly sugars, gums, resins, and coloring matters.* They assist in the tanning in several ways, — some of them are directly absorbed by the skin, increasing its weight and solidity; others set up fermentations in the tan pit, producing organic acids which assist in the formation of a leather of a good body and weight. The tan liquors are prepared by systematic lixiviation of the ground tan-stuffs, the strongest liquors coming in contact with the freshly ground material. The temperature is important, warm water being generally best for complete extraction, although gambier requires cold water. The spent tan is usually burned for fuel. Extracts, alone or in conjunction with tan liquors, are becoming more generally used. They are simply dissolved in water, and may be added as needed; but they are often adulterated with glucose or molasses, consequently tests with the barkometer † are of no value unless the material is known to be pure.

Vegetable tanning is used for sole leather, upper leathers, and colored leathers (morocco). Sole leather is heavy, solid, and stiff, but may be bent without cracking. For this, tanning materials such as oak or hemlock bark, mimosa, chestnut wood, quebracho, valonia,

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* The tannins derived from gallic acid cause a white efflorescence (ellagic acid) on the leather, while those of the protocatechuic acid group deposit red coloring matters (phlobaphenes) in it.

† A special form of hydrometer for determining the strength of tan liquors.

and myrabolans are used. The hides ("butts") are first hung from frames in pits (**suspenders**), containing *weak* or nearly spent tan liquors from a previous lot. Here they are mechanically agitated, by rocking the frames so that the hides take up the tannin evenly. Every few days they are transferred ("handled") into pits containing stronger liquor, until, after two weeks, the hides are brought into full strength solutions. If treated with too strong liquor at first, the surface would be so hardened that thorough penetration into the interior of the hides could not take place. The partially spent liquors are transferred, according to the counter-current principle, from each pit into the next succeeding containing hides which have taken up less tannin. The hides are then put into the "**layers**," *i.e.* pits in which the hides are spread flat, sprinkled with ground tanstuff (bark, valonia, etc.), and strong liquor (ooze) at 25° barkometer is run in until the pack is submerged. After 7 or 8 days, the hides are taken out, brushed clean, and again "laid away" in fresh tan and stronger liquor, to remain 12 to 14 days; the process is repeated with about 20 days' submergence, and finally about 4 weeks' "laying away" in full strength liquor at 40° barkometer and fresh ground tan completes the process. Frequently the temperature of the liquor in the "layers" is progressively raised from about 70° F. in the first to 90° or 100° F. in the last. Thus the whole tanning treatment requires about 3 months or more, for heavy sole leathers; it may be hastened by keeping the liquors in constant circulation, or by continual movement of the hides and using strong extracts.

Various electrical tannage processes have been devised, but these have generally proved failures in use.

Sole leather is usually finished by brushing and washing, followed by slow drying; the drying is retarded by oiling the leather several times on the grain. When partly dry, it is "**sammied**" by piling in a heap and covering until heating is induced. It is then "**struck out**," *i.e.* stretched by working with a triangular tool having blunt edges, or by rolling with a heavy roller under pressure in a machine. The weight of the leather is sometimes increased by impregnating it with glucose, or with barytes or other mineral salts. Dry hides yield about 180 per cent of their weight in leather, while green hides make only about 55 per cent.

Upper or **dressed leather** is made from kips and large calf skins. After bating, the skin is usually shaved on the flesh side to make it of uniform thickness. It is then tanned and the grain hardened by handling or tumbling in revolving boxes or drums, in a rather strong solution of tan liquor, usually prepared from gambier. The tannage is completed with mimosa, myrabolans, valonia, or bark, the liquors sometimes being heated to 50° or 60° C. and a final tumbling in sumach liquor.

Leather is finished by a process called **currying.** That is, it is first scoured with brushes and then rubbed with a "sleeker," a smooth stone or piece of glass which removes the creases and wrinkles and stretches the leather. It is then "stuffed" with a mixture of oil, soap, and tallow, which is worked into it by rolling or tumbling in a drum. Olive, neat's-foot, sperm, and fish oils are much used for this, as is also degras (p. 581). Upper leathers are usually blacked by rubbing with a mixture of lampblack and oil or tallow; or they may be painted with a solution of copperas and logwood.

Colored leather is made chiefly from goat, sheep, and calf skins. These are limed, unhaired, bated, and drenched as above described, and are tanned with gambier or sumach liquors, in tumblers or drums, or in tubs, or handlers where they are kept in motion.

Colored leathers are usually dyed with basic dyestuffs or with natural dyewood extracts, particularly logwood. After tanning, they are passed into a bath of tartar emetic to fix the tannin before dyeing. The dyeing is done in slightly warm baths, as hot liquors are injurious. The skin is folded down the middle with the grain side out, and is then laid in a slightly warm solution of the dye in a shallow tray; or the skin may be sponged with the dye on the grain side while spread on a table. If it is to be dyed through, it is worked with the dye solution in a tumbler or paddle-wheel.

After bating or when partially tanned, the skins are usually split into two or three layers, by a sharp knife driven by machinery. The grain side is finished to form "**skivers,**" while the flesh side is made into **patent leather, wash leather** (chamois), or into cheap leather with an artificial grain. The very thin grain splits from sheep and calf leather are used for book bindings. The flesh splits are often given an artificial grain ("pebbled"), by rolling with an engraved roll, or with a die under heavy pressure. This imitation may be carried so far as to make small punctures in the leather with fine pin points to resemble the pores and hair sheaths of the natural grain. Or an electrotype may be made from a piece of natural leather, and this copy fixed on the die.

2. Tanning with metallic salts, or **tawing,** is employed for small skins and light leathers, and is very important in this country; the salts used are aluminum and chromium compounds, especially

sulphates, chlorides, and bichromates. Alum (or aluminum sulphate) is employed (in conjunction with common salt) for white and kid leathers. After liming, usually with the addition of arsenic, for three or four weeks, and unhairing and fleshing, the skins are thoroughly bated, drenched, and scudded. For white leather, the split skins are tumbled in a drum with a solution of alum and salt, and after lying folded several hours are dried without washing. The hard skin is then softened by pounding, rolling, and stretching. Kid leather for gloves, and calf kid are made by tumbling or treading the split skins in a mixture of alum, salt, flour, egg-yolk, and olive oil, until they are thoroughly impregnated, and then drying. The leather is colored with natural or coal-tar dyes, and is usually again tumbled in the salt and egg-yolk emulsion. It is softened by "**staking**," *i.e.* pulling across the edge of a blunt knife fixed in a vertical position in a post. The flesh side is shaved, and the grain glazed or polished by rubbing with a sleeker, or in a glazing machine.

Excellent leather is produced by combining the alum tanning process with tannage in gambier liquor, the method being known as the **combination tannage, or dongola process.** This is much used for making leather resembling kid, but stronger and cheaper, which is largely used for ladies' shoes. The prepared skins are tawed in alum and salt and then laid in gambier liquor for several days or a week.

Chrome tannage, or tawing with chromium salts, has been chiefly developed in this country and is in general use here. The principle of the process consists in precipitating an insoluble chromium hydroxide or oxide on the fibres of a skin which has been impregnated with a soluble chromium salt, usually potassium bichromate; basic chromium chloride, chromium chromate, and chrome alum are also used. The skins, having been limed, unhaired, fleshed, bated, drenched, and scudded, are worked in a solution of potassium bichromate to which some common salt has been added, together with one-fourth to three-fourths of the theoretical amount of hydrochloric or sulphuric acid necessary to liberate all the chromic acid (CrO_3). After several hours, when the skin shows a uniform yellow color when cut through the thickest part, it is removed, the excess of water pressed out or drained away, and the skin worked in a bath of sodium bisulphite ($NaHSO_3$), or thiosulphate, to which has been added some mineral acid to liberate the sulphur dioxide: —

1) $K_2Cr_2O_7 + 2\ HCl = 2\ KCl + H_2O + 2\ CrO_3.$
2) $Na_2S_2O_3 + 2\ HCl = 2\ NaCl + H_2O + S + SO_2.$
3) $2\ CrO_3 + 3\ SO_2 + 3\ H_2O = 3\ H_2SO_4 + Cr_2O_3.$

The chromic acid is absorbed by the fibre and is later reduced *in situ* by the sulphurous acid. It is necessary to use a strong solution of the reducing agent, so that the reduction may be fully accomplished before the chromic acid has time to " bleed " from the skin. The strength of solutions varies somewhat in the various processes, but is usually made from 10 to 30 grams per litre for the bichromate, and 30 to 50 grams for sodium thiosulphate. Calculated on the weight of the skin, from 4 to 9 per cent of bichromate and about 15 per cent thiosulphate are usually employed. The amount of chromic acid fixed on the fibre is about 4 to 6 per cent, calculated as $K_2Cr_2O_7$.

Chrome leather is tough and resists moisture very thoroughly. On this latter account, skins which are to be dyed should be introduced into the dye at once after reducing and washing, for if allowed to dry, the dyeing is incomplete. The leather may be heated to 80° C. or more without injury, and hence can be dyed with some of the alizarin colors. It is a rapid process, the time of steeping in the chrome bath being only a few hours and even less in the reducing bath. It is a light tannage, and on thick skins has considerable tendency to contract the fibre, and so is not much used for sole leather. It is chiefly employed for glazed kid, calf kid, and glove leathers. The tanned or colored skins are oiled and stuffed before drying.

Tawing with iron salts has been the subject of several patents, but these processes are not used.

3. **Tanning with oils** consists in saturating the flesh side of split skins with oils (whale or cod liver), and allowing them to lie in heaps until an oxidation or fermentation of the oil ensues. The mass heats, and a soft, spongy leather, such as **chamois** and buff leather, is formed. The skin being limed, bated, and drenched, excess of water is removed by pressing, and the skin is worked in the stocks with oil. After partial drying, it is again stocked with oil; this is continued until all the moisture in the skin has been replaced by oil. After partial oxidation, the excess grease is removed by pressing, or in the centrifugal machine. The thick, greasy mass expressed, called "**moellen degras,**" consists of semi-oxidized oil, and is a valuable currying agent. The skins are now washed in a bath of soda or potash to remove the rest of the grease. These alkaline wash-waters are treated with mineral acid, decomposing the soaps, and setting free the fatty acids which rise, and are skimmed off as "**sod-oil,**" also used in currying. These oils have undergone an oxidation, probably with formation of aldehyde-like bodies, which unite with the hide fibre, similarly to the

combination of tannic acid, and washing with soap or alkali is not sufficient to remove the combined fat; but the uncombined fat is washed away completely.

The oil-tanned skins are finally stretched, scraped, and bleached in the sun, or in sulphur dioxide. Chamois leather is often further softened by freezing while wet.

Dilute alkaline solutions of formaldehyde will also tan skins; the product is white, strong and soft, and is used for gloves.

Morocco leather is made from goat skins tanned with sumach, which gives a light-colored product. The prepared skins are tanned by paddling in sumach liquor; or they are sewed up to form bags which are filled with the liquor, and then piled in a tank where the pressure of one bag upon the other forces the liquor through the skins. The so-called French morocco is made from sheep skins, either whole ("roans") or split ("skivers"). These leathers are usually dyed in colors, two skins being placed with their flesh sides together, and brushed over with the color, or immersed in a tray or drum filled with the dye liquor. To imitate the grain of goat skin, the skin is usually "**grained**" by rolling under a cork-surfaced board.

Russia leather was formerly tanned with willow bark, but oak bark is now much used, especially for imitations. The peculiar odor is due to an oil obtained by distilling birch bark, and used for currying the leather. The dull red color is produced by dyeing with red wood (Brazil or saunders-wood).

Patent leather is made by coating a tightly stretched split skin, or "skiver," with a varnish of linseed oil, containing lampblack, Prussian blue, or other pigment. While the leather is still stretched the varnish is dried at 70° C., and the surface is smoothed with fine pumice, and other coats of varnish laid on and dried. The final coat is polished with tripoli, or rotten stone and exposed to sunlight to develop a high gloss, possibly due to the action of ultraviolet rays on the linseed oil.

Parchment and **vellum** are made from untanned split skins. The former is made by stretching wet sheep skin, after liming and fleshing, on a frame, and drawing it smooth and free from wrinkles. Powdered chalk is dusted over it, or mixed with water and painted on the skin to absorb the grease, and the surface is then smoothed by rubbing with pumice. After scraping with a steel blade and a final smoothing, the skin is slowly dried in a shady place. Vellum is made from calfskin, only those of uniform color being used. The liming lasts for three or four weeks, and the washing is very thorough. The skin is then split and stretched on a frame, and dried with scraping and pumicing, as in the case of parchment.

Artificial leather is made from various kinds of fibrous materials, usually cellulose, coated with gelatine and heavily compressed. Sometimes leather scraps are ground to shreds, soaked in gum or gelatine, and formed into boards by heavy pressure. These leatherettes are chiefly used for embossed trimmings in book binding, and in places where pliability is not essential.

Degras (moellen) is now so important as a currying agent that it is manufactured on an extensive scale. The wash leather produced is again saturated with oil, and the oxidized oil pressed out; the process is repeated any number of times, as long as the skin holds together.

The exact nature of tanning was for long not understood, two theories being maintained. The **physical theory** held that the hide fibre is merely coated with a layer of the tan-stuff, which prevents adhesion of the fibres on drying; the **chemical theory** assumed a true chemical combination between tan-stuff and hide substance. At the present time it is generally thought that the tanning agent is adsorbed on the surface of the fibre. Only substances of high molecular weight, colloidal in their nature, are capable of such adsorption; these are the vegetable tannins, chromium and aluminum hydrates produced by hydrolysis of their salts, and aldehydic condensation products in the case of oil and formaldehyde tannages.

REFERENCES

Grundzüge der Lederbereitung. C. Heinzerling, Braunschweig, 1882.
Text-book of Tanning. H. R. Procter, London, 1885.
Traité pratique de la Fabrication des Cuirs, etc. A. M. Villon, Paris, 1889.
Die Lohgerberei. F. Wiener. 2te Auf. Leipzig, 1890.
Leather Manufacture. J. W. Stevens, London, 1891.
Praktisches Lehrbuch der Lohgerberei. S. Kas, Weimar, 1891. (Voigt.)
Industrie des Cuirs et des Peaux. T. Jean, Paris, 1892.
Cuirs et Peaux. H. Voinesson de Lavelines, Paris, 1894. (Bailliere.)
Die Herstellung der lohgaren Leder. L. Hoffmanns, Weimar, 1893.
The Manufacture of Leather. C. T. Davis. 2d ed. Philadelphia, 1897.
The Art of Leather Manufacture. A. Watt. 4th ed. London, 1897.
Die Chromgerbung. S. Hegel, Berlin. (Springer.)
Leather Industries Laboratory Book. H. R. Procter, London, 1898.
Leather-Worker's Manual. H. C. Standage, London, 1900.
The Principles of Leather Manufacture. H. R. Procter, London, 1903.

PLASTICS

Plastics include those solid materials capable of being bent, modelled or molded into various shapes, and the fresh surfaces of which coalesce under pressure. These properties constitute plasticity, and in many substances this may be destroyed by suitable treatment (p. 31). The plastic condition may be considered as to a degree intermediate between the solid and liquid states. Industrially only those substances are important in which plasticity can be decreased or destroyed by specific treatment: glass, clays, resins, etc., may properly be classed under this head also.

CELLULOID

Celluloid is an artificial plastic material prepared from collodion-cotton (p. 479), camphor, and a suitable solvent material, usually alcohol. It has become an important substitute for ivory, tortoise-shell, horn, bone, hard-rubber, and other natural products; also it has made possible the production of thin, flexible, transparent, or translucent films and sheets used to a large extent in place of glass. It can be readily cut, bored, machined, and polished, and when warm can be pressed and bent into shapes which are retained after cooling. It is not attacked by water, oil, dilute acids, or alkali, and is a non-conductor of electricity. Either natural or artificial camphor (p. 389) may be used, but must be pure and free from acid or chlorine. The collodion-cotton must be free from acid, and must dissolve completely; the presence of acid or oxidized cellulose causes turbidity in the finished product.

The collodion, camphor, and alcohol are worked together in a machine (having a steam-jacketed pan) at a temperature of 80° to 90° C. for two to four hours, until a tough, pasty mass is produced. The pan of the machine is covered and a pipe leads to a condenser for recovery of the alcohol evaporated during the mixing. The hot mass is then forced under heavy pressure through fine sieves to remove dirt, undissolved fibre, or hard lumps. The soft material is then worked from two to four hours between steam-heated rolls to evaporate the remainder of the solvent and remove air bubbles from the mass. A draught hood over the rolls leads the vapors to a condenser for recovery. Any coloring matter, such as zinc oxide, ultramarine, lampblack, etc., or various coal-tar colors, to be added is often introduced during this final rolling process. By use of calender rolls, very thin, evenly colored films are produced, which are then arranged in piles and heavily compressed to form blocks, from which sheets or slabs of any desired thickness can be cut across the ends of the layers, thus giving the fine striated appearance of ivory; or with thicker films of various colors, close imitation of stripe prints can be obtained. Imitation horn and tortoise-shell are made by rolling or pressing together transparent yellow-colored blocks, with brown or black pieces, until well amalgamated, but not worked to a uniform color.

Owing to the inflammability of celluloid, its manufacture and storage are subject to legislative control in most countries, the restrictions imposed being similar to those prescribed for explosives.

Substitutes for celluloid which are less inflammable have been much desired, especially for photographic and theatrical use; of these **cellulose acetate** has been much employed. Purified cotton is treated with acetic anhydride, diluted with glacial acetic acid, until it dissolves, and the solution then poured into water, whereby the cellulose triacetate is precipitated. This is soluble in chloroform, acetone, and acetylene tetrachloride, is not inflammable, and is an excellent insulator for electrical use. Besides its use for films, excellent insulating and protecting varnish is made from it dissolved in chloroform, or in a mixture of alcohol and benzine.

Another substitute for cellulose is the viscose described on p. 490.

BAKELITE *

Bakelite is a plastic produced by the condensation of phenol and formaldehyde in the presence of an alkaline condensation agent. Three forms of the material are prepared as Bakelite A, B, and C. The first product of the condensation is the A-form, soluble in alcohol, acetone, glycerine, caustic soda, and other solvents; it is also fusible at about 170° C., without decomposition.

By heating, the A-form passes into the B-form, which is solid when cold, but plastic when hot, but swells in acetone and other solvents without dissolving. By further heating this passes into the C-form, which is not fusible without decomposition, does not become plastic by heating, and is insoluble in the various solvents. By heating the material under pressure, the C-form is obtained without formation of gas bubbles, as a hard, colorless, or light yellow material. It is a non-conductor of electricity and heat, and is claimed to be a

* See Journ. Ind. & Eng. Chem, Vol. 8, No 2, Feb. 1916, p17

useful insulator; it is not affected by moisture, dilute acids, chlorine, or alkalies. It can be cut, turned, and machined, and is an excellent substitute for ivory, horn, amber, and similar articles. Bakelite A in solution forms an insoluble and brilliant varnish, when applied to wood or metal surfaces; when mixed with sawdust, wood-pulp, asbestos, graphite, powdered mica, or other filler, and the mass pressed in moulds and heated, the plastic becomes solid, and cements the particles of filler together; thus disks, handles, buttons, and various other articles can be produced.

Galalith is a plastic material produced by the condensation of formaldehyde with casein, similarly to the formaldehyde tannage of skins, p. 582. Casein is separated from skimmed milk by coagulation with rennet, and the curd, freed from the whey, is carefully dried in warm air, ground, and sifted. The fine powder is moistened with acetic acid and worked in a mixing machine to form a dough, which by gentle warming is made plastic and is then given the desired shape by pressing in moulds and drying. The articles are then cured by long steeping in formaldehyde solution followed by drying in warm air.

CAOUTCHOUC OR INDIA RUBBER

Caoutchouc or **India rubber** is suspended in minute globules in the juice or latex of certain plants belonging to the orders *Euphorbiaceæ, Apocynaceæ,* and *Artocarpaceæ,* native in nearly all tropical countries. There are some 60 species grouped in the 5 genera, *Havea, Manihot, Vahea, Landolphia,* and *Castilloa.* The finest grades come from South America (Para) and Madagascar. In Brazil the trees are from 12 to 15 years old when tapped, and yield about 10 pounds of milky juice, or over 3 pounds of gum daily. Medium and low grades are obtained from Central America, East India, Java, Borneo, and the west coast of Africa. The plants in Africa are generally vines; the bark is partly stripped off, and the juice coagulates on the vine by the evaporation of its volatile constituents.

Jelutong (or **Pontianak**) from the species *Dyera,* indigenous to Malacca and Borneo, and **guayule** from *Parthenium,* a shrub indigenous to the Chihuahuan Desert of Mexico, have furnished much low-grade rubber of recent years. But as the plants are destroyed by the methods of collecting the latex, these materials will probably soon cease to be very important. Guayule yields about 9 per cent of the weight of the plant as crude rubber.

Rubber plants (chiefly *Havea*) are now extensively cultivated in

Ceylon, Malacca, Borneo, and other tropical countries, and the excellent product (*plantation rubber*) has become a large factor in the crude rubber market.

The milky white juice, which seems to be distinct from the sap of the plant, is collected during July to November, and coagulated by heating and exposing in thin layers to wood smoke, or that of burning palm nuts (as in Brazil); or the latex is heated to boiling; or the juice of certain other plants is added*; or dilute acetic or formic acid, salt solutions, alum, phenol, or formalin may be used. The rubber may also be separated from the diluted juice in a cream separator or centrifugal.

Caoutchouc $(C_{10}H_{16})_n$ is a polymer of polyprene $(C_{10}H_{16})$, which is derived from isoprene (C_5H_8). *Synthetic rubber* † can be prepared by polymerizing isoprene (C_5H_8), or by heating isoprene with dimethylbutadiene in the presence of alkali. The lower cost of natural rubber would seem to prevent further development in this field at present.

Rubber is a highly plastic colloid and probably contains aggregates in varying degrees of polymerization; the smaller molecular aggregates are soluble in carbon disulphide, benzene, and other solvents, but the larger, which may combine with the solvent similarly to the hydration of a plastic clay, are not truly soluble. These swell in the solvent to form membraneous cells, which in sufficient solvent are distended and ruptured by the osmotic pressure of the soluble part, thus decreasing the average size of the aggregates. This decrease in polymerization increases plasticity but decreases strength.

Commercial crude rubber, when freshly collected, is often nearly white, but darkens on exposure to the air or to smoke, and may become almost black. Well-prepared plantation rubber is often very light in color. Lower grades of crude rubber often have a foul odor due to fermentation of albumins in the juice. Raw rubber has a specific gravity of 0.915, is sticky, and freshly cut surfaces unite firmly; it is soft and elastic at ordinary temperatures, but if heated to about 120° C., loses its elasticity and melts at 150° C. It dissolves in carbon disulphide and chloroform, and softens in ether, oil of turpentine, benzene, and naphtha. Dilute acids and alkalies have no action on it, but concentrated acids or free bromine or chlorine destroy it. Oils and grease also cause it to become hard and brittle. The content of free resin (soluble in acetone) may range from 1 or 2 per cent in fine Para to 12 or 15 per cent in low grades of rubber.

The crude gum contains much dirt, sand, gravel, bark, etc.,

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* J. Soc. Chem. Ind., **1902**, 1461.

† J. Am. Chem. Soc., **1914**, 165.

which is removed by a washing process. It is boiled in water until softened, and ground between corrugated rolls, which flatten the lumps into thin sheets while a stream of water plays over the mass, washing away the impurities. Good Para rubber loses about 15 per cent of its weight during this washing, while low grades shrink from 30 to 40 per cent. The rubber is then thoroughly dried, hanging for several weeks in well-ventilated lofts heated to 90° F. But for most manufacturing purposes, a pure gum is neither necessary nor desirable, and to impart to it certain properties, it is mixed or "compounded" with various materials in a "mixing mill," which consists of a pair of heavy, smooth, hollow, iron rollers, one of which is heated by steam to about 80° C. The materials added are vulcanizing agents, such as sulphur, and some metallic sulphides; certain sulphides and oxides as catalytic agents; coloring pigments, fillers, or inert "make weights," such as whiting, barytes, lithopone, etc.; rubber substitutes; or coal-tar pitch. These are thoroughly ground with the rubber to a homogeneous mass, which can then be fashioned into any desired form and finally vulcanized.

Unvulcanized rubber is plastic, is readily moulded, and clean surfaces unite if brought in contact with each other. It is on this property that the manufacture of soft-rubber goods chiefly depends. To prevent accidental adhesion, fresh surfaces are dusted with talc, starch, or flour, or pieces of plain cotton sheeting are interposed.

Vulcanization or **curing** is due to a combination of sulphur with the rubber. Rubber unites with sulphur by chemical addition to the double bonds of the polyprene molecule, in any proportion up to 30 per cent; but above 10 to 12 per cent, the product is hard and brittle (*ebonite*). The end product of the vulcanization is probably $(C_{10}H_{16}S_2)_n$, and the result of this addition is an increase in size of the aggregates, due to increase in the units, from the polymerization of which the aggregate is formed. This increase results in greatly lessened plasticity and increased inertness, hardness, and strength. Controlling the amount of sulphur determines the extent of these changes; in industrial practice the combined sulphur varies from about 1 to 2 per cent in soft-rubber articles to 20 per cent, or more, in ebonite. Excess of sulphur over what it is desired to combine is always added and remains as amorphous sulphur in the product. The process is facilitated by the presence of metallic oxides or sulphides, and is carried on by dry heat at 125° to 140° C., if litharge, zinc oxide, or other metallic oxides are present in the compound. The goods (placed in a closed chamber) are heated by steam, which by this method does not come into contact with the rubber. For soft-rubber goods some 8 to 10 per cent of sulphur is added in the compounding mill, but only a part of it combines in the curing, the rest being merely disseminated through the mass.

A cold process of vulcanizing, discovered by Alexander Parkes, consists in immersing the rubber in a solution of sulphur chloride in carbon disulphide. It is used only for small articles having thin layers of rubber, since the solution does not penetrate deeply.

Vulcanizing destroys the adhesive property of rubber, renders it more elastic,* less soluble, and less susceptible to temperature changes, — it neither becomes sticky when moderately heated, nor brittle when cold. If antimony sulphide, Sb_2S_5, is used when vulcanizing, the color of the product is red, owing to the formation of the trisulphide, Sb_2S_3, the remainder of the sulphur combining with the rubber.

Rubber substitutes are extensively used in the so-called mechanical goods, such as bicycle pedals, door-mats, solid cushions, and springs. The best of these is **balata**, obtained from the juice of *Mimusops Kauki*, L., a tree native in Guiana. This is an intermediate substance between gutta-percha and caoutchouc.

By mixing powdered sulphur with raw linseed oil † and heating in a vulcanizer, a substance somewhat resembling rubber is obtained. Or by treating the oil with sulphur chloride, a gummy mass of light color is produced. These "sulphurized oils" are largely mixed with low-grade rubber and with coal-tar or resins, for cheap goods. Sometimes they are used without the addition of any rubber whatever.

Vulcanized rubber can have its plasticity restored by the action of heat, in the presence of oils. Stock so treated is called **reclaimed**, **recovered**, or **devulcanized** (p. 590) rubber and its use for low-grade articles, usually with the addition of some new rubber, is extensive. In reclaimed rubber, the uncombined sulphur of the vulcanized stock is essentially all combined under the action of the heat during the recovery process; this increases the size of the polyprene unit and thus tends to decrease plasticity. The principal change during recovery must then be a decrease in polymerization sufficient to offset the increase in combined sulphur. According to Weber, recovered rubber always contains free oil, and the solvent

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* When unvulcanized rubber is stretched, it regains its original form only very slowly.

† Rape seed and castor oils are much used abroad and corn oil in this country for these rubber substitutes.

and consequent depolymerizing action of this oil at high temperatures is the essential factor in the process. Rubber goods seldom contain over 15 per cent of total sulphur, while polyprene can combine with over 30 per cent, so recovered rubber still has capacity to absorb sulphur; this decreases its plasticity because of the greater complexity of the aggregate, *i.e.* recovered rubber is capable of revulcanization. But the product thus obtained will not be identical with ordinary vulcanized rubber; in the complex $(C_{10}H_{16}S_x)_n$, the value of x will be greater and of n less. Recovered rubber, when revulcanized, gives a weaker and less distensible product.

The recovery process consists in grinding old rubber stock and scrap to powder, removing the cloth or other fibre present, by sifting or blowing with an air-blast, or by carbonization (p. 501) with dilute sulphuric acid; or the acid-carbonized old rubber may be boiled in an 8 per cent caustic soda solution for removal of the free sulphur; and after washing and drying, the product is sheeted in the usual mixing-mill. The stock so treated may be used directly as filler in a batch containing sufficient new rubber to secure plasticity; or plasticity may be restored after the treatment with acid or caustic, or both, by heating in the presence of oils of various sorts, *e.g.* rosin oil. In both cases the stock is called reclaimed or recovered rubber; the term "devulcanized" should be reserved for stock the plasticity of which has been restored by the oil treatment.

The soda treatment is especially useful preceding devulcanization; otherwise during the oil treatment, the free sulphur in the stock combines with the rubber and the use of more softening agents is necessary, giving a poorer product. Furthermore, after free sulphur is removed, corn oil and other similar oils can be used in devulcanization, which will themselves "vulcanize" on revulcanization of the batch. This leaves no free oil in the final product, to cause deterioration.

Vulcanized rubber deteriorates by keeping, and ultimately becomes hard and brittle. This apparently occurs through oxidation, and is influenced by the nature of the compound, oxidizing substances such as lampblack being especially liable to spoil the rubber. Oils, even at ordinary temperatures, slowly attack rubber, restoring plasticity by their solvent action, thus destroying strength and promoting oxidation.

The uses of rubber are exceedingly numerous, but the largest quantities are used for overshoes, boots, rubber clothing, automobile and bicycle tires, and hose. It may be moulded, as for boot heels, solid-rubber hose, etc., or made into rubber fabric. This latter is done by spreading a thin layer of the unvulcanized rubber compound on a backing of cotton or woollen cloth. The rubber may be calendered in such a way that it penetrates between the fibres ("friction coating"), or it may be simply applied to the surface of the cloth ("even-motion coating"). Rubber shoes and clothing, and other fabric articles are entirely put together before vulcanizing, the seams being joined by rolling the edges into contact, when they adhere. Such goods are usually vulcanized by heating at 260° F. for about six hours.

Rubber cement is made by dissolving a pure rubber in cold naphtha. A little powdered chalk is usually added.

Hard rubber, vulcanite, or **ebonite** is usually made from the cheaper grades of rubber, especially that from Borneo and Java, and contains a large amount of filling material. From 25 to 50 per cent of sulphur is added, and the mass heated to 140° to 150° C., in vulcanizing. It is often shaped in the form desired *after* it has been vulcanized.

GUTTA-PERCHA

Gutta-percha* is obtained from the juice of *Dichopsis Gutta,* Benth. & Hook, a tree native in the East Indies. The tree is tapped in much the same way as for caoutchouc. The crude material is purified by grinding in hot water, by which the chips, bark, sand, etc., are removed. The plastic mass is then rolled into sheets or formed into threads and rolled into balls and pressed. In composition it is a terpene $(C_{10}H_{16})_n$, but it also contains some oxygenated resinous bodies. Its texture is fibrous, its color varies from white to brown, and when free from air its specific gravity is slightly greater than 1.000. It is tough and inelastic when cold, but becomes plastic at 50° C., and melts at 120° C. It is soluble in carbon disulphide, chloroform, and warm benzene. Alkalies and dilute acids have no action on it, but strong nitric and sulphuric acids destroy it. By vulcanizing with sulphur, it is rendered harder and less plastic when heated. It is easily oxidized in the air and becomes brittle. It is a poor conductor of electricity and is better than rubber for insulating purposes, for which it finds its chief use.

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* J. Soc. Chem. Ind., **1897**, 815.

REFERENCES

Manufacture of India Rubber and Gutta-percha. Cantor Lectures Soc. of Arts. Thos. Bolas, London, 1880.
Practical Treatise on Caoutchouc and Gutta-percha. R. Hoffer. Translated by Wm. Brannt, Philadelphia, 1883. (Baird & Co.)
Die Fabrikation der Kautschuk- und Gutta-perchawaaren. C. Heinzerling, Braunschweig, 1883. (Vieweg.)
Practical Treatise on the Raw Material and Manufacture of Rubber. G. N. Nesienson, New York, 1890.
India Rubber. Special Consular Reports, Washington, 1892. (Government Printing Office.)
Le Caoutchouc et la Gutta Percha. E. Chapel, Paris, 1892.
Le Caoutchouc et la Gutta-percha à L'Exposition Universelle de 1889. René Bobet, Paris, 1893.
Journal of the Society of Chemical Industry. **1894**. C. O. Weber.
Die Gutta-percha. E. Obach, Dresden, 1899.
Crude Rubber and Compounding Ingredients. H. C. Pearson, New York, 1899.
Chemistry of India-Rubber. C. O. Weber, Philadelphia, 1902.

PART III

METALLURGY

METALLURGY is the art of extracting metals from their ores, refining them, and separating them from one another; it also includes the preparation of alloys; sometimes a careful mechanical and heat treatment of the metals is necessary in order to impart desired qualities. A few metals, notably gold, platinum, silver, copper, and bismuth, are found "native," *i.e.* in the metallic state or as alloys; but generally the ores consist of oxides, sulphides, carbonates, or other salts, more or less impure, mixed with each other, with gangue rock and earthy matter.

Metallurgical processes form two general classes, *wet* and *dry;* the former are carried on in aqueous solution, and the latter involve changes and reactions at high temperatures.

Before attempting the separation of the metal from its ore, certain preliminary operations (" *ore-dressing* ") are generally necessary to remove at least a part of the gangue mechanically, and to bring the valuable portion into proper condition for further treatment. **Sizing** and **concentration** are accomplished by hand picking (" *cobbing*") to separate large lumps, and by pulverizing and levigating the fine material. The gangue, being lighter specifically than the ore, is carried off by the water. The residue left from this process is called the " **concentrates.**" If magnetic substances are present, the ore is often concentrated by allowing the pulverized material to fall between the poles of a magnet, so that the magnetic particles are deflected and separated from the non-magnetic.

In the wet metallurgical processes, the metal is extracted by some form of leaching, generally after preliminary treatment, to get the metal into the form of a soluble salt. This preliminary treatment varies much, and will be considered in connection with each special case.

In the dry processes, the ore is usually calcined or roasted and then reduced in another furnace. This **reduction** generally consists in exposing the ore to the action of carbon and carbon monoxide at high temperatures, or sulphur may be relied upon to take oxygen from the oxides in the prepared ore. The gangue substances are rendered fluid by adding fluxes which fuse to liquid slag with them. Commonly the flux is silica (SiO_2) where acid conditions are desired; for basic, lime is used.

The crude metal obtained by any reduction process generally requires "**refining,**" to remove the impurities left in it. The methods for this refining will be considered in connection with the individual metals.

ROASTING

Roasting consists in producing chemical changes at a temperature which, though quite high, is not sufficient to cause fusion. No metallurgical operation is more important, for the results of various processes depend on converting the ore into a suitable chemical condition by roasting. For example, in the chlorination of gold ores, sulphur and arsenic must first be completely removed; or, to reduce zinc from sulphide, the latter must first be converted into oxide.

An **oxidizing roast** serves to remove sulphur, arsenic, etc., by conversion to SO_2, As_2O_3, etc., which are carried away by the draft.

$$PbS + 3\ O = PbO + SO_2.$$

A **sulphatizing roast** converts sulphides to sulphates, usually with the object of leaving some metal in a soluble condition. This is accomplished by keeping the temperature somewhat lower, and the depth of the ore bed greater, than for an oxidizing roast, and reducing the draft. These conditions favor the maximum production of SO_3 from the sulphur in the ore, and prevent it being carried into the stack before it can combine with the metallic oxides.

When it is necessary to remove all of the sulphur, arsenic, etc., from an ore, any sulphates, arsenates, etc., that have formed are reduced by stirring in fine coal with the ore and excluding the air as much as possible. The resulting sulphides are then given a further oxidizing roast. When the sulphur, arsenic, etc., are practically all removed, the ore is said to be **dead roasted,** or **sweet roasted.**

A **chloridizing roast** converts metals into chlorides by means of the interaction of atmospheric oxygen and common salt with the sulphides, arsenides, etc. In the most important case of chloridizing, that of silver, the sulphide is first oxidized to sulphate, and then the following reaction takes place: —

$$Ag_2SO_4 + 2\ NaCl = 2\ AgCl + Na_2SO_4.$$

Roasting of fine ores is more common than of lump. Fines are heated in beds only a few inches deep, so that they do not pack and prevent their proper exposure to the air. They are turned over and over to expose new surfaces. Coarse ores worked in this way can receive only a superficial roast in any reasonable time, and are therefore roasted in large heaps 5 or 6 feet deep.

Figure 123 shows a reverberatory furnace that has been used to prepare ores for the lead blast-furnace. (C) is the fire-box. The ore is charged through the hole (D) in lots of about two tons, and is gradually turned over and worked along the hearth (A) by means of hand rabbles inserted through the side doors. The purpose of the stepped hearth is to bring the ore nearer the roof at the flue end, and thus get more benefit of what heat remains in the gases. A rather better construction omits the steps and gives the hearth a gentle uniform slope from the flue toward the fire. When the ore reaches the lower end of the hearth (A), the sulphur is mostly burned off. The charge is then dropped to the hearth (B), where it is slagged or partially fused. This is possible because the heat comes directly from the fire-box and is confined in a narrower space than in the long hearth. The purpose of this fusing is to prevent the fine ore being carried away by the strong draft when put into the blast-furnace later. It also removes more sulphur by the reaction, —

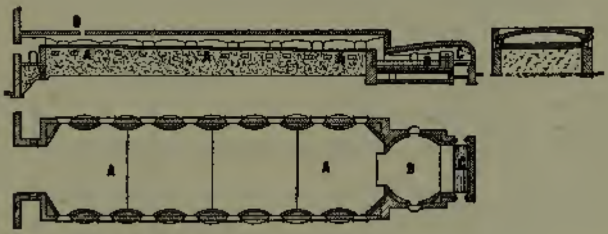

Fig. 123.

$$2\ PbSO_4 + SiO_2 = Pb_2SiO_4 + 2\ SO_2 + O_2.$$

The slag hearth is now seldom used because the high temperature increases the metal losses in the fume. Instead, the ore is moderately sintered at the bridge end of the roasting hearth.

This same style of furnace with no slagging hearth is used to roast gold-bearing pyrite (FeS_2) previous to chlorination; also blende (ZnS). There are usually doors on both sides of the furnace, and the hearth is not over 15 feet wide. To lessen the labor in moving the ore, the hearth for blende roasting is not over 7 or 8 feet wide with doors on only one side, to prevent excessive admission of cold air; blende is specially difficult to roast if the proper temperature is not maintained. For galena or blende, the length of hearth is about 40 feet; but it may be 65 feet for pyrite, which generates a good deal of heat in roasting, and hence is less dependent on the heat from the fireplace.

In recent years mechanical furnaces have, to a considerable extent, though by no means wholly, supplanted hand-operated furnaces. These are cheaper and permit better regulation of the air supply and uniformity of operation. They are not well adapted to roasting galena ores, because the latter become so sticky at a moderate temperature that they cannot be efficiently handled by mechanical means. The Ropp furnace (Fig. 124) may be taken as typical of a class that has been used with much success for roasting pyrite and blende. Ore is supplied regularly by the automatic feeders (M), is moved along the hearth (A) by the rakes (R), and is discharged at the farther end. The rakes are carried by trucks (E) running on a narrow track. The trucks are propelled by a wire rope which passes around the sheaves (I) and (I′), power being applied through the latter. When the rakes enter the furnace, cold air is kept out by means of the doors (L) and (L′), which are hinged at the top and form a sort of air lock, (L) closing before the rake pushes (L′) open. The device is used at the discharge end of the hearth, as shown by (K) and (K′). Heat is supplied from the fireplaces (N), and the gases pass to the flue (O). The rakes are exposed to the air outside the

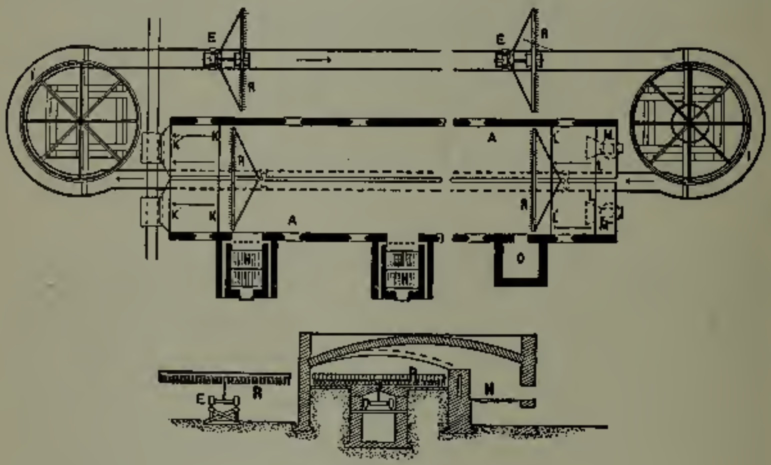

Fig. 124.

furnace longer than to the heat and fumes of the furnace. This prolongs their life.

The McDougal furnace (Fig. 125 *) is circular in horizontal section and so has less wall surface in proportion to the hearth area than any other shape; thus there is less radiation of heat. Further, the large amount of brick in the several hearths absorbs much heat from one hearth and transmits it to the ore lying on the next above. The furnace is largely used for roasting copper ores that contain a good deal of pyrite, and for ordinary pyrite in the manufacture of sulphuric acid. This mineral generates so much heat in roasting that no other fuel is required. The furnace is also coming into use for ores that are not self-roasting, one or more auxiliary fireplaces being attached in this case. It has a considerably greater diameter (14 ft. 6 in.) than most designs of the McDougal type, and this large size presented a special difficulty owing to the distortion of the stirring arms and the vertical shaft when heated. The trouble was avoided by water cooling. Water is delivered from the pipe (B) extending to the bottom of the hollow vertical shaft, and, in passing upward, is directed to the end of each rabble arm and back to the shaft by means of a baffle, and finally discharges through the pipe (C) into a stationary annular cup, from which it runs away. The principal wear is on the stirring blades, and these are easily detached from the horizontal arms.

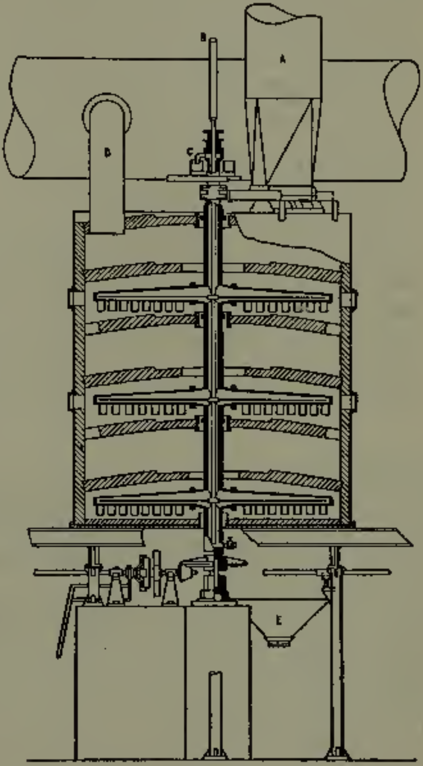

FIG. 125.

In starting, a wood fire is kept on the bottom hearth till enough heat is stored in the brickwork to ignite the ore; the fire is drawn,

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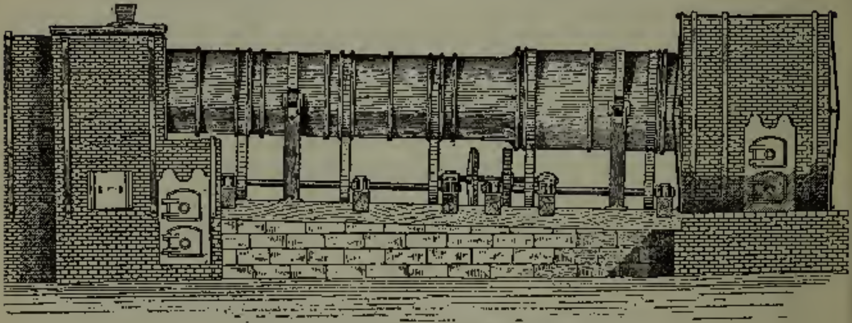
* Eng. and Min. Journal, **76**, 123.

the shaft and stirring arms set in motion by the gearing beneath the furnace, and the ore is delivered to the top hearth by an automatic feeder in the hopper (A). The stirring blades on one hearth turn the ore over and gradually move it to the centre, where it drops to the next lower hearth. On this the ore travels to the circumference, in which there are two discharge holes. A receiving hopper (E) is placed beneath the lowest hearth. The air for oxidation admitted through doors on the bottom hearth passes upward by the same openings through which the ore falls, discharging by the pipe (D) to the main flue. The strong draft at the holes connecting the different hearths carries considerable fine ore into the flue; to prevent this, the ore may be discharged from one hearth to another through a tube independently of the air passage.*

The diameter of the old McDougal-type furnace was limited by the allowable length of the arms. Even when water-cooled, they sag at the ends because they are supported only at the centre of the furnace. By using a large central driving shaft (4 feet in diameter) and the same length of arms, the area of the annular hearth is greatly increased. Furnaces 22 feet in diameter are now constructed. The weight of the central shaft and rabble arms is carried on roller bearers at the bottom.



WHITE-HOWELL ROASTING FURNACE

Fig. 126.

The Howell-White furnace (Fig. 126), resembling the Oxland calciner, considerably used to roast gold and silver ores, is a brick-lined iron cylinder, set on friction rollers at a gentle angle to the horizontal. It is about 25 feet long and 4 or 5 feet in diameter. Heat comes from a stationary furnace at the lower end, and ore is automatically fed at the upper end. The revolution of the cylinder turns the ore over and over and makes it travel to the discharge end, where

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* U. S. Patents, 729170, May 26, 1903, and 740589, Oct. 6, 1903.

t falls into a hopper. The oxidizing action is increased by blades long the sides, which lift the ore and let it fall in a shower. The draft arries out a good deal of fine dust as it falls from the feed hopper into he furnace, and also as it drops from the blades, making a dust cham- er necessary. The dust can be much lessened by feeding the ore hrough a Rumsey diaphragm, in which the opening for the discharge f gases is contracted and the ore is fed through a bent pipe on to the ottom of the cylinder out of the draft.

Figure 127 * shows a shaft furnace that is used to calcine coarse inc ores for the expulsion of CO_2 and H_2O. The ore, charged at A), passes downward and is drawn off at (B), eing heated, in its descent, by the gases from ie fire grates (C).

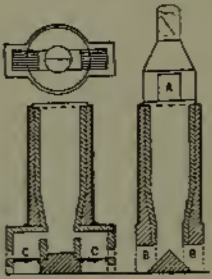

Fig. 127.

To roast lump ore in a heap, the ground made smooth and firm, with a little slope to rain water off to the sides in case of rain. wo layers of cord wood, or more if necessary, e placed regularly on this ground to cover slightly greater area than is planned for the ap (say 25 feet wide and 40 feet long, or more). the bottom layer of wood are left several aces 6 inches wide, extending from the sides to the centre, serving flues to start the ignition of the heap. These flues are loosely lled with small sticks, and connect with wooden chimneys along the ntre line of the pile. Ore from 1 to 3 inches in diameter is piled the wood to a depth of about 5 feet; the top and sides are covered everal inches deep with pieces as small as ¼ inch, and a last layer fines is placed over this, to prevent rapid combustion that would se the ore and thus stop the roasting. The fire started in the small les gradually spreads and ignites the ore, which may burn for two three months, the air entering at the base of the heap and escap- ig through small cracks in the surface. Care is used that these cks do not become so large as to cause excessive draft. Part of e ore is not properly roasted, and goes into a subsequent heap. the ore does not contain enough sulphur to maintain the roast, a tain amount of coal or small wood is mixed in the pile when first de.

The heaps emit the disagreeable sulphur fumes near the ground, ad require a long time to do the work. These disadvantages are ercome by the use of cubical stalls (300 or 400 cubic feet) placed

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* After Ingalls, Metallurgy of Zinc and Cadmium. New York, 1903.

side by side; they are enclosed by substantial brick walls, and connected to a high chimney by a common flue. The operation of stalls is similar to that of heaps.

Dwight-Lloyd Sintering Machine. — This machine (Fig. 128) is extensively used for sintering (agglomerating or partially slagging) or rough roasting ores and for removing volatile matter. Its essential feature is a series of pallets that are pushed into contact like the pans of a pan conveyor, but which are not attached to each other. Each pallet is 30 inches wide and 18 inches long, and has a perforated bottom, planed to make a tight joint when pushed over the suction-box. At other points in its circuit, it is supported by four wheels that roll on guides. Each pallet is successively pushed under the feed hopper, receives a layer (usually 4 inches) of charge, then goes under the ignition box in which a coal, gas, or oil flame playing down on the top ignites the charge. Continuing over the suction-box, combustion, induced by the down draft, progresses downward through the material so that roasting and agglomeration are completed when the pallet discharges its cake into a car or hopper at the end. It is evident that unless there is sufficient sulphur in the charge to furnish heat, coal or other combustible material must be added. The tonnage treated will vary from 30 to 75 tons in 24 hours according to the charge and the completeness of the roasting.

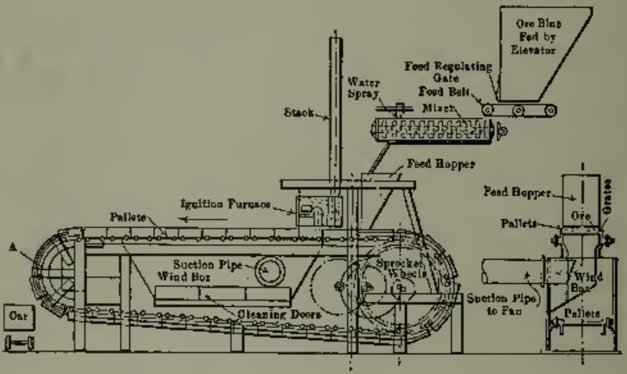

Fig. 128.

IRON AND STEEL

The ores of iron are red hematite (Fe_2O_3), brown hematite — the limonite of the mineralogist — ($2\ Fe_2O_3 \cdot 3\ H_2O$), magnetite (Fe_3O_4), and siderite ($FeCO_3$), these minerals being mixed with more or less silica, clay, etc., besides containing small percentages of manganese, phosphorus, and sulphur.

The crude iron is made in large **blast furnaces** (Fig. 129 *), which are circular in horizontal section, and are lined with refractory fire-brick. The ore, together with coke and limestone, is raised to the top of the furnace by a hoist (A) and discharged into the hopper (B). By lowering the bell (C) the materials fall into the hopper (D), from which they are dropped into the furnace by lowering the bell (E). The object of the two bells and hoppers is to prevent the escape of large volumes of gas from the top of the furnace.

Immense volumes of air, heated to 600 or 800° C., are blown through a set of **tuyeres** (F), near the bottom of the furnace, at a pressure of 12 to 15 pounds per square inch.

In a blast furnace, there are two currents passing in opposite directions. A rapid gas current, heated to nearly 1600° C., just above the tuyeres, rises through the slowly descending solid charge to the throat (top), and escapes into a large pipe (J), the "*downcomer.*" In ascending, it cools to 200–300° C., and acts chemically on the charge.

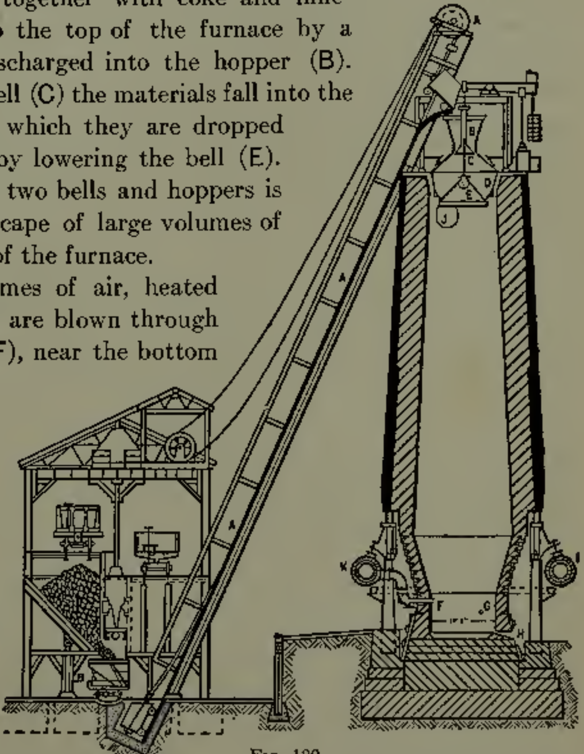

Fig. 129.

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* After Campbell, The Manufacture of Iron and Steel. New York, 1903.

tuē yấn

Following the descending column of ore, flux, and coke, four zones of reactions can be distinguished: —

(1) *Zone of Preparatory Heating* (100–300° C.), at the top of the furnace, in which all the moisture and much of the combined water are given up to the gas current and heat is absorbed from it.

(2) *Upper Zone of Reduction* (300–900° C.). (*a*). CO present in the gas acts on the ore according to the exothermic reactions: —

$3\ Fe_2O_3 + CO = 2\ Fe_3O_4 + CO_2$ (begins at 200° C.).
$Fe_3O_4 + CO = 3\ FeO + CO_2$ (begins above 450° C.).
$FeO + CO = Fe + CO_2$ (begins at about 700° C.).

The CO_2 resulting from these reactions joins the gas current and heats it, while the spongy iron continues its descent. These reactions are reversible unless the CO_2 is diluted with CO, and they are never complete in the furnace.

(*b*) The CO_2 content of the gas is also increased by a partial decomposition of CO in the presence of the heated charge which acts as a catalyzer between 250 and 600° C. in the reversible reaction: —

$$2\ CO = CO_2 + C.$$

(*c*) A third source of CO_2 in this zone, lower down at about 800° C., is the lime-rock flux (and siderite, if present). Much of this is, however, reduced to CO by the coke.

(3) *Lower Zone of Reduction* (900–1200° C). Here, the characteristic reaction is: —

$$FeO + C = Fe + CO.$$

Small amounts of Mn, Si, and P are also reduced from their oxides by the solid carbon which continues its action into the lower part of the furnace.

(4) *Zone of Fusion* (1200–1600° C.). This zone is filled with glowing coke, through which the melting charge trickles down. The molten iron becomes saturated with carbon, and dissolves all the metals reduced from the ore together with any free S or P. The silica and alumina (clay) of the gangue, combining with the lime of the flux, fuse to a slag (waste product), which collects above the molten iron in the space below the tuyeres, called the **crucible**.

The slag, being specifically lighter than the metal, rises to the top, and is tapped out through the cinder notch (G) at intervals of about 2 hours. Every 4 to 6 hours, the iron is drawn off through the metal tap (H). The slag notch is stopped with a metal plate that chills the slag and closes the opening. The metal tap is closed by ramming in a clay plug. The slag may be either run into ladles (holding several tons) and hauled to a dump, or granulated by pouring into water and sluiced away. Granulated slag is often dried, ground, and made into slag cement. Typical slags run 30–35 per cent SiO_2, 10–15 per cent Al_2O_3, and 50–55 per cent CaO.

The iron is run into " sows " (moulds) and cast into pigs before shipping, or, if the iron is made into steel near by, it is tapped into ladles and sent molten to the steel plant.

Up to about 90 feet, increasing the height of an iron blast furnace saves fuel, since the deep charge absorbs more of the heat of the gas. Higher furnaces have been built, but have not proved so efficient, and it is doubtful if a height of 90 or 100 feet will again be exceeded. A furnace 12 to 14 feet in diameter and 90 feet high commonly produces 500 to 600 tons of pig iron in 24 hours. This involves the charging of 1500 to 2000 tons of ore, fuel, and flux.

The shape of the furnace walls has a marked effect on the capacity. A gentle increase in diameter from the throat down to the fusion zone allows for expansion of the charge as it heats up and prevents " hanging " of the charge followed by " slips " (falls) that interfere with the working of the furnace and cause explosions. The fusion zone narrows down rapidly to the tuyere level to provide for the contraction of the charge when melted. This section is called the **bosh**. The walls are cooled with water-blocks to protect them from the effects of heat and chemical action.

The gas from the top of the furnace usually contains over 20 per cent CO by volume, and has about one-half the heating value of the coke. A part of it is used for pre-heating the blast and the remainder is available for generating power either by burning it directly under boilers or, more recently, directly in internal combustion engines. When the latter are used, careful washing is necessary to remove dust that would clog the ports of the engines. One large American plant develops 40,000 H.P. from its gas engines. Thirty per cent of the calorific power of the gas may be utilized in gas engines as against a maximum of about 15 per cent in steam engines.

The air-blast is heated by passing it through " **stoves**," which are large cylindrical structures filled with checkerwork of fire-brick, and thoroughly pre-heated by burning in them some of the gas from the top of the furnace. There are usually three or four stoves for one blast-furnace, the blast passing through one while the others are heating.

Moisture in the air greatly reduces the capacity, and its variations interfere with the smoothness of operation of a blast furnace. This is owing to the heat absorbed in the fusion zone by the reaction, $C + H_2O \rightarrow CO + H_2$ (see p. 40). The gases produced are effective reducing agents in the upper zones, but are not needed, as the reduction capacity of the furnace is much greater than the fusion capacity. The latter alone limits the output. The moisture is removed from the air before going to the stoves, in the Gayley dry-blast by artificial refrigeration. Trays of calcium chloride have also been used, the calcium chloride being regenerated by evaporation of the absorbed moisture by a blast of hot gas.

Pig iron is the metal produced in the blast furnace. Its composition varies according to the character of the ore and the operation of the furnace. The composition of the slag, percentage of the fuel, and regulation of the blast determine the quantities of Si, C, S, and Mn in the iron. The iron may take up 3 or 4 per cent of C, somewhat less than 3 per cent each of Mn and Si, and the greater part of the P and S in the original ore. Carbon and silicon are the most important elements taken up by the iron, as the hardness, strength, and other properties vary with their percentages. Phosphorus makes the metal brittle when cold, but a small amount is desirable in making intricate castings, as it increases the fluidity and causes the metal to fill all parts of the mould. Sulphur makes the iron (or steel) " red short " or brittle at high temperatures.

In chemical composition **cast iron** is identical with pig iron; it usually contains over 2.2 per cent of carbon, and is either gray or white, depending on whether the carbon is separated out as flakes of graphite (slow cooling) or is in the form of carbide (chilled). Mottled iron is a mixture of the two. Cast iron is not malleable at any temperature.

Steel is iron that is malleable at some temperature and, in addition, is (1) either cast into an initially malleable mass (mild steel) or (2) may be hardened by sudden cooling. The carbon content varies from practically zero in soft steels (that cannot be hardened) up to 2.2 per cent. Ordinary steels contain from 0.75 to 1.5 per cent carbon, the hardness increasing with the carbon content. Mild steels with less than 0.2 per cent carbon cannot be hardened, and are distinguished from wrought iron of similar composition only by the manner of manufacture.

Wrought-iron is usually made from pig (though considerable scrap-iron is utilized) by burning out the carbon, silicon, manganese, phosphorus, and sulphur as far as possible, in reverberatory furnaces lined with hematite or magnetite. The oxidation of these elements is effected partly by atmospheric oxygen, but also by the iron oxide of the furnace lining. The pig-iron may contain 6 per cent or more of these elements, but they amount to less than 1 per cent in the finished product. The metal becomes less fusible as they are removed, and finally it is in a pasty state, so that the slag cannot be completely separated. The iron is gathered into large balls and the slag partly removed by working in a mechanical squeezer or under a steam hammer. It still may contain as much as 2 per cent of slag, which gives the metal its special quality of welding readily, and largely prevents the tendency to crystallize, due to the small quantity of phosphorus and sulphur present. However, the slag decreases the tenacity by preventing the complete union of the particles of the iron.

While soft steel has largely displaced wrought-iron, the latter is still demanded by blacksmiths and machinists for certain purposes.

Steel is made from iron by four different methods: the Bessemer process is the cheapest and produces the largest quantity; the open hearth is next and its product is generally considered more reliable for structural work that is subject to frequent shocks; the crucible and the cementation processes produce only small quantities, supplying the demand for fine tools, watch-springs, needles, etc.

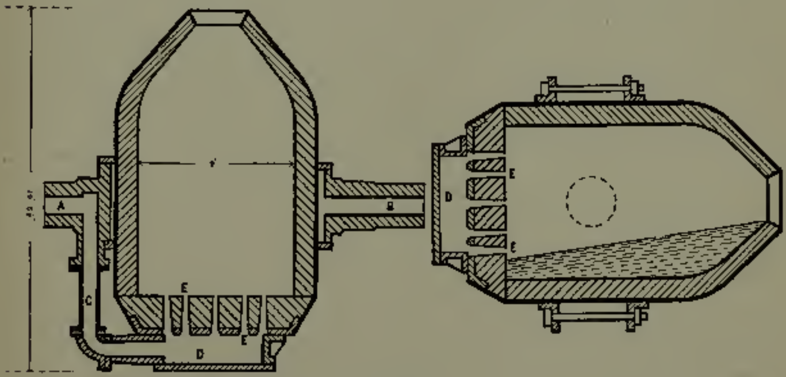

Fig. 130.

The Bessemer process is conducted in a "converter," shown unmounted in Fig. 130.* It is supported by and revolves on the trunnions (A), (B), being turned by a pinion fastened on (B), which

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* After Campbell, The Manufacture of Iron and Steel. New York, 1903.

meshes with a rack moved by a hydraulic piston. The converter is lined with refractory material, and as the bottom lining wears away much faster than the side the entire bottom is made removable, being held in position by clamps, so that it may be quickly replaced by a new one, which has been previously prepared and heated.

In operation the converter is turned to a horizontal position, and molten pig-iron poured in. An air-blast, with a pressure of 20 to 30 pounds per square inch, is turned on, entering through the trunnion (A), pipe (C), wind-box (D), and tuyeres (E), and the converter is turned to a vertical position. The air passing through the metal in many fine jets first oxidizes the manganese and silicon, thus generating enough heat to greatly increase the temperature of the charge. When the silicon has been largely removed the carbon begins to burn; and even with a charge of 18 tons, in less than 15 minutes after the blast is turned on, almost the whole of the manganese, silicon, and carbon have been oxidized, the last passing off as CO, which burns at the mouth of the vessel to CO_2, while the others combine with a certain amount of oxidized iron to form slag. Above a certain temperature, carbon has a greater affinity than silicon for oxygen, and will burn first; but in American practice it is customary to add some cold scrap-iron to the charge to keep the temperature below this critical point. Another method of lowering the temperature is to introduce steam with the air-blast; the decomposition of this steam absorbs a large amount of heat. After the carbon has practically all burned out (shown by the dropping of the flame at the converter mouth), the converter is turned down and hot lumps of ferromanganese or melted spiegeleisen added to supply the proper percentages of manganese and carbon; then the metal is poured into a ladle from which the ingot moulds are filled. The manganese makes the metal work well in the subsequent rolling, and also combines with the dissolved oxygen, lessening the blow-holes in the solid ingot; while the carbon imparts the proper degree of hardness, strength, etc.

Spiegeleisen is pig-iron containing 4 or 5 per cent of carbon and 5 to 20 per cent manganese; **ferromanganese** is pig with 6 or 7 per cent carbon and 25 to 85 per cent manganese. A considerable weight of the former is used to produce hard (high carbon) steel, while a small amount of the latter yields soft (low carbon) steel.

In the United States the **acid process** is employed in making Bessemer steel, and as neither phosphorus nor sulphur is removed, only iron low in these substances is used. The converter is lined with silicious sandstone, and as there is not enough base to combine with any P_2O_5 which may form, this is at once reduced by the iron, the phosphorus passing into the steel.

In the **basic process** the converter lining is calcined dolomite or limestone (cemented by tar), and the slag is so basic that the P_2O_5 is strongly held by the CaO. To lessen corrosion of the lining, lumps of quicklime are added with the charge. The silicon in the pig-iron charged is kept lower than in the acid process to make the slag as basic as possible by keeping out silica. In the basic process much of the heat is due to the oxidation of phosphorus (of which the pig must contain nearly 2 per cent in order to supply enough heat), while in the acid process it is mainly due to burning the silicon. Sulphur is removed with the phosphorus; but if the sulphur is high, the blow may have to be continued after the phosphorus is sufficiently removed. There is almost no flame during the burning of the phosphorus and sulphur. Therefore, small sample ingots are cast from a hand ladle, and the condition of the charge is determined by the appearance of the fracture of the chilled ingot. The process is completed by the addition of spiegeleisen as in the acid process. The slags are so rich in phosphorus that they are valuable for fertilizer (p. 171).

The basic process is more expensive than the acid and is not used in the United States because we have an abundance of ores low in phosphorus. In this country, phosphorus is never allowed to be over 0.1 per cent in the steel, and must often be less. Germany is the chief user of the basic process.

In some plants, the iron for the converter is remelted in cupolas, which in a general way resemble a blast-furnace, though much smaller; but at large plants producing their own iron near at hand the metal comes direct from the blast-furnace still molten. It is stored in large covered "**mixers**," or reservoirs, in which oil or gas is burned, if necessary, to prevent the surface chilling. These "mixers" equalize the composition of the different charges of iron, thus permitting the uniform operation of the converters.

In the **open-hearth process**, pig-iron, scrap steel, and iron ore are melted in a regenerative, reverberatory furnace. Without the regenerative principle (p. 43) a sufficient temperature cannot be maintained to keep the charge properly fused after the impurities are oxidized. In this country the usual practice, when using a silicious hearth, is to first charge the scrap and put the pig-iron on this, so that, in melting, the silicon, manganese, and carbon of the pig having, greater affinity for oxygen, oxidize first, protecting the iron of the pig and scrap from oxidation. Any oxidized iron will form slag on coming into contact with silica. Silicon and manganese are largely burned by the air entering from the regenerative chambers, and the carbon is oxidized by reaction with iron ore, still assisted by the air. The process is sometimes conducted with the omission of either the scrap or the iron ore.

With an acid (silicious) hearth, phosphorus and sulphur are not removed, because they are retained by the iron instead of entering an acid slag. With a basic lining (usually burned dolomite), and the addition of burned lime with the iron ore, the basic slag formed has so strong an affinity for phosphoric acid that the iron does not reduce the latter. Consequently, the phosphorus is largely removed, as is also the sulphur. The proper amounts of carbon and manganese are restored to the metal by the use of ferromanganese.

Figure 131 * shows, on the left, a half-longitudinal section through a Campbell furnace, and on the right a half-longitudinal elevation with a section through the two regenerative chambers on that side; two similar regenerators on the other side connect the air and gas tunnels (a) and (b). To avoid excessive oxidation of the metal, the air enters the furnace at (a′), *above* the gas which goes in at (b′); proper mixture is obtained by having the two streams enter at slightly different angles.

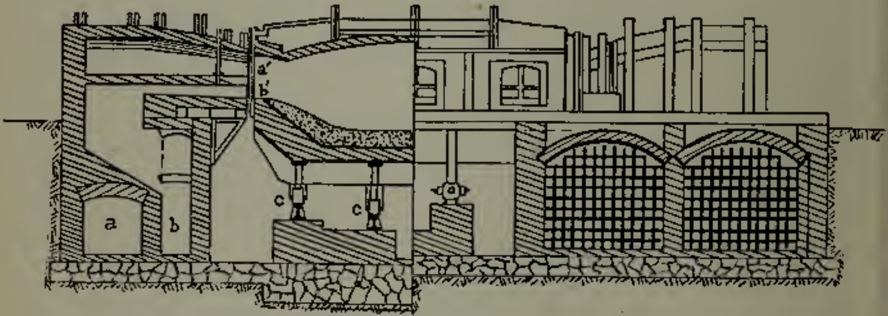

FIG. 131.

The Campbell furnace has loose connection with gas and air ports, and rests on several sets of heavy steel rollers (c), so that it can be tilted about its longitudinal axis for quickly pouring the product when it has reached the proper composition. This saves considerable time; and in cases where the composition must be kept within narrow limits the quick pouring is of special advantage.

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* After Campbell, The Manufacture of Iron and Steel. New York, 1903.

An important difference between the basic open hearth and the basic Bessemer process is that, in the former, iron with any percentage of phosphorus can be used, while in the latter the phosphorus content must be nearly 2 per cent, and is often about 3 per cent. The reason for this difference is that the basic Bessemer converter depends chiefly on the rapid oxidation of phosphorus to maintain the proper temperature, while in the open-hearth process the temperature is maintained by carbonaceous fuel. A basic Bessemer blow is completed in 20 minutes or less; but in the open-hearth process it takes 6 to 12 hours to finish a charge, depending on the size and style of furnace, the composition of the stock used, etc. Several modifications of the ordinary procedure have been devised to save time, one of which, the **Monell process**, is being considerably adopted in this country. In this, iron ore and burned lime are first heated in the furnace, and iron, still molten from the blast-furnace, but moderately cool, is then poured in. Most of the phosphorus and some of the carbon are quite rapidly oxidized; the former combining with the lime, the latter escaping as gas, which puffs up the phosphoric slag and causes most of it to run out of the furnace; but this raising of the slag is much less violent than if the ore and lime were not first heated. An advantage of this process is that the phosphorus is chiefly removed at an early stage (while at a high temperature it would go off less rapidly than the carbon); and therefore the steel can be poured as soon as the carbon is reduced to the right point.

The crucible process, as commonly practised in the United States, consists in melting the best grade of wrought-iron with charcoal in either graphite or clay crucibles, the molten iron absorbing the proper amount of carbon from the charcoal. The usual weight of the charge is 80 pounds or less, and the melt lasts 3 or 4 hours. Sometimes a little manganese oxide is added, as the manganese reduced by the charcoal renders the steel more forgeable. In Sweden, pig-iron is melted with iron ore, the latter oxidizing the excess of carbon. When the melting is thoroughly under way, a certain amount of silicon is reduced from the SiO_2 in the crucible. Part of this silicon combines with the iron, and part unites with any dissolved oxygen, and thus decreases the blow-holes that would remain in the metal after casting.

In the **cementation process**, bars of wrought-iron are embedded in charcoal, in long covered chests of fire-brick, and kept at a yellow heat for a week or more. Carbon is slowly absorbed by the iron, the slag in the latter remaining in the steel. This slag may be removed from the steel by melting in crucibles, thus improving the quality, but increasing the cost. Since the process lasts two or three weeks, including the time necessary to heat the furnace and cool it afterward, the method is too expensive, and has been largely superseded by the ordinary crucible process.

Special Steels. — Manganese, chromium, nickel, tungsten, molybdenum, etc., are used to produce special steels noted for their hardness, toughness, resistance to shock, strength, etc. Small quantities of manganese are added to ordinary steel to lessen blow-holes and make the metal work well when rolled or forged. Increase of manganese above 1.5 per cent and up to 6 or 8 per cent makes the steel brittle, but at the latter point the character entirely changes, and the product combines extreme hardness with unusual toughness. Chromium also imparts great hardness. Tungsten and molybdenum are used to make **self-hardening steel**, so-called because tools made from it do not need to be heated and quenched to make a hard cutting edge. This edge is retained much longer than with ordinary steel.

Manganese, chrome, and nickel steels are frequently used for such purposes as burglar-proof safes, armor plate, and machine parts subject to excessive wear and shock. Nickel steel has been used for several of the largest engine shafts ever made.

Electrical methods of making iron and steel have advanced so far that they are producing in commercial quantities, but do not yet really compete with the common methods. The products are claimed, however, to be of exceptional quality. In most of the furnaces the charge is heated by the electric arc, coke being used for reduction and carburization as in the ordinary blast-furnace. In some cases the heat is produced by an induction current, the material in the furnace taking the place of the secondary coil of a transformer.

COPPER

The chief sources of copper are sulphide ores, the most important being chalcocite (Cu_2S), bornite (Cu_3FeS_3), and chalcopyrite ($CuFeS_2$). These minerals are almost invariably associated with large quantities of pyrite (FeS_2); and in some cases, notably the Spanish copper mines, the yield is principally cupriferous pyrite. Oxides and carbonates are common in the upper zones of copper deposits, but are of much less importance than the sulphides. Native copper (*i.e.* copper occurring in the metallic state in nature) is found in a number of places, but not in commercial quantities except in the famous Lake Superior mines in Michigan.

The common method of copper extraction is to smelt the ore to produce a slag, which is thrown away, and a *matte, i.e.* a mixture of copper and other heavy metals as sulphides, which is further treated to remove iron and sulphur, and leave the copper in the metallic state. Fine ore is treated in reverberatory furnaces, and coarse in blast-furnaces.

Reverberatory smelting of copper ores is done in furnaces which somewhat resemble a simple, hand-roasting furnace; but with a horizontal instead of sloping hearth, to prevent the molten charge running to one end (see Fig. 14). The roof slopes downward from the fire-bridge toward the flue, to bring the gases closer to the material on the hearth as they become cooler, and thereby get more benefit of their heat. The width also gradually decreases toward the flue end, so that the material there is kept hot enough in the corners of the furnace.

The heat required for smelting is usually generated by burning bituminous coal in a fire-box and using an induced draught. With long flame coals the hearth may be between 80 and 100 feet long. By using oil, gas, or powdered coal in specially designed burners, the length of hearth may be increased up to 120 feet. The width is seldom greater than 20 feet, as this is about the maximum distance allowable for working a charge from the side doors. Charges of 400 tons may be smelted in 24 hours in the largest furnaces.

The charge is dropped through holes in the roof near the fire-bridge where the heat is greatest. Silicious ore is also occasionally fed along the sides of the furnace near the walls, to cool and protect them from chemical action (ore-fettling).

The material commonly treated in a reverberatory furnace is the finer portion (seldom as coarse as half-inch particles) resulting from the mechanical concentration of the ore. As this is very likely to contain over 30 per cent sulphur and 25 per cent iron, with only 5 to 10 per cent copper, its direct fusion would produce a matte too low in copper. It is, therefore, roasted till the sulphur is reduced to 8 or 10 per cent, and then should go directly to the smelting furnace with as little cooling as possible, to save fuel.

Any Fe_2O_3 produced in roasting is reduced by reaction with some of the remaining sulphide —

$$3\ Fe_2O_3 + FeS = 7\ FeO + SO_2.$$

The FeO and any CaO, Al_2O_3, etc., combine with the SiO_2 to form slag, while the remaining iron and sulphur unite with the copper to form matte, which also takes up whatever gold and silver there is in the charge. The copper in the matte varies from 35 to 50 per cent, depending on the ore. The slag rises while the matte sinks, their respective specific gravities being about 3.5 and 5. As the separation is not perfect, the slag contains approximately $\frac{1}{2}$ per cent copper.

The composition of the slag varies considerably with the ore. Uncombined silica is often present and is apt to contain copper, thus increasing the loss. It is better to add enough limestone to slag this silica, and form a more fluid slag that retains less matte. The best practice is to add the limestone before the ore goes to the roasting furnace, because it gets thoroughly mixed in the latter and therefore causes quicker smelting.

The slag is skimmed through a door at the end of the furnace opposite the fire-box, and the matte is tapped through a hole in the furnace side which is closed by a clay plug, and is opened by driving in a pointed steel bar. Usually, the slag from several charges is skimmed before any matte is tapped; and, except for special reasons, the matte and slag are never completely removed. By keeping a large body of molten material on the hearth, an extra reservoir of heat is provided to quickly melt a new charge, and the latter is prevented from seriously sticking to the bottom.

The matte is carried in large ladles, holding several tons, directly to the converters (p. 615), or is cast in moulds and cooled if the plant is not arranged for direct conversion. If the contour of the ground permits, the best way to get rid of the slag is to run it into a large stream of water when available. This suddenly chills and granulates it, and carries it away to the dump. Before falling into the water the slag runs through a large cast-iron pot, so that any matte, accidentally run out of the furnace with it, may have a chance to settle. When skimming is finished, the upper part of the liquid slag in this pot is either poured or tapped out, but the rest is resmelted. If granulation cannot be used, the slag is carried to the dump in large cast-iron pots or cars.

As the temperature of the gases escaping from the furnace will average from 1200° to 1400° C., it is well to utilize them in a steam boiler, which may easily reduce them to 350° C. Care must be used, however, that the boiler is so arranged as not to injure the draught of the furnace, for this would reduce the smelting capacity, which is the first consideration.

Blast-furnace Smelting. — A blast-furnace for copper must be much lower than for iron, to avoid the strongly reducing conditions that would precipitate metallic iron. The depth of charge is only 8 to 12 feet above the tuyeres, and the width must be much less than in an iron furnace, for the strong blast needed to penetrate the charge in a wide furnace would blow too much material out of the top. Widths at the tuyere level vary from 35 to 56 inches; but with the circular form these would give too little capacity, so the furnaces are made rectangular. In most plants, the furnaces are between 15 and 21 feet long and treat 400 to 600 tons in 24 hours. One furnace in Montana is 87 feet long and treats 2500 tons of charge every 24 hours. By shutting off the blast from a section of this furnace, it is possible to make repairs without seriously interfering with the operation of the main portion, so there seems to be no limit to the length, provided the conditions of ore supply warrant such large capacities. The walls are of steel or iron, water-jacketed to prevent their fusion. Brick walls, formerly in common use, still survive in some places, but are liable to be partially eaten away by the slag, and the half-fused ore forms accretions on them. When these are barred off, the walls are apt to be more or less broken. Neither of these troubles can occur in the case of a water-jacket.

The fuel is coke, introduced alternately with the ore and flux through charging doors on both sides. Air is blown in through the tuyeres, under a pressure of about 2 pounds per square inch. A few ores are self-fluxing, but usually it is necessary to add either limestone or quartz to form an easily fusible slag. Considerable variation is allowable in the composition of the slag, but if it gets much over 40 per cent SiO_2, it will not flow well nor allow a good separation of matte without the use of excessive fuel. The quantity of coke used in common practice varies from 8 to 14 per cent of the total weight of ore and flux, depending on the ease with which the charge fuses, the quality of the coke, volume and pressure of the air-blast, the detail shape of the furnace, and the depth of the charge above the tuyeres. Considerable of the sulphur in the ore may be burned, and the heat thus generated, with that of the oxidation of the iron of the pyrite, decreases the quantity of coke required. Some sulphur is also volatilized without burning, since one atom of sulphur is quite readily distilled from pyrite, FeS_2, leaving FeS. Frequently two-thirds of the sulphur in the ore is either burned or volatilized. The vigorous oxidizing conditions produced in the blast-furnace make it commonly unnecessary to give the ore the preliminary roast that is usual in reverberatory practice. However, when there is a large per cent of sulphur and very little copper, preliminary roasting may be advisable, lest the resulting matte be of too low grade to handle economically. A number of large scale experiments have been made with a view to smelting without a preliminary roast, or the use of coke, and the process has been perfected in one or two places where the right kind of ores are at hand. A large percentage of iron pyrite is necessary to supply sufficient heat (but such ores are generally low in copper), and unusually large quantities of air must be blown in. At Mt. Lyell, Tasmania, as much as 80 or 90 per cent of the sulphur is thus removed, yielding a high-grade matte from low-grade ore in one operation. Usually the first operation under this method yields matte too low in copper for the converters, and this is smelted again to raise the grade. At Mt. Lyell only $\frac{1}{2}$ per cent of coke is used, this being fed along the sides to lessen the chilling of slag by the air-blast and consequent stopping of tuyeres.

If there is any Fe_2O_3 in the material charged to the furnace, it is reduced to FeO either by reaction with sulphide according to the equation given on p. 612, or by means of CO from the combustion of the coke.

$$Fe_2O_3 + CO = 2\,FeO + CO_2.$$

The various elements unite to form the slag and matte the same as in the reverberatory, but it is not possible to "float" uncombined silica in the blast furnace, as may be done in the reverberatory, since a pasty slag cannot be made.

There is but little space below the tuyeres to collect the molten products, so these run out together into a large forehearth, or settler. The spout from the furnace is arranged with an inverted dam that dips below the surface of the slag, and thus prevents any air from the tuyeres escaping at this point. For large furnaces, the settler just mentioned is a circular basin, 15 feet in diameter and 4 feet deep inside, made of fire-brick. While this is filling up when the furnace is first put in blast, the matte and slag separate according to their specific gravities, and the surface of the slag chills, thus making an effective cover. The slag flows out continuously from the full settler, through a spout at the top and on the side opposite the furnace. The matte is tapped periodically from a hole in the side, near the bottom. Both products are disposed of in the same way as in reverberatory smelting.

Comparison of Reverberatory and Blast-furnaces. — The chief difference between these two is that the former is best suited for fine, and the latter for coarse, ore. Coarse ore in the reverberatory would smelt very slowly, because the total surface for a unit weight is comparatively so small that the bases (iron, lime, etc.) cannot come in intimate contact with the acid (silica). This difficulty is compensated in the blast-furnace because the very high temperature right at the point of combustion is applied immediately to the ore. Consequently, where the silica and bases do come in contact, there is a rapid reaction and fusion, and fresh surfaces are quickly exposed. On the other hand, any large proportion of fine ore is not permissible in the blast-furnace because some of it would be carried out by the blast, and the rest would so choke the furnace as to cause reducing conditions sufficient to precipitate metallic iron, which, however, would not be really melted and would therefore form "sows," and these would gradually fill up the furnace and put it out of commission. Reverberatory smelting is now on the increase, largely because recent improvements in ore-dressing and mining methods have made available large bodies of low-grade copper ore which yield fine concentrates.

Copper-converting. — The matte, either directly from one of the processes just described, or (occasionally) after remelting in a special blast-furnace, is blown in a converter resembling that used in the Bessemer steel process. The chief difference is that the tuyeres are in the side several inches above the bottom, yet below the surface of the charge. The object of this is to keep the air from passing through and chilling the metallic copper that results from the operation. A modern design resembles a barrel resting on its side upon rollers, with a row of tuyeres along one side and an opening above for charging and discharging and for the escape of the gases. The advantage of this shape is that, for a given capacity, the charge is not so deep as in the upright form, and a lower blast pressure can be used, with less cost for blowing and less loss of solid material blown out of the converter. The converter lining is ground quartz or silicious ore, with just enough plastic clay to hold it together.

The chemistry of the process is very different from that of a steel converter. The elements to be removed from the matte, aside from small amounts of zinc, arsenic, etc., are nearly 25 per cent of sulphur and 25 to 40 per cent of iron, instead of say 6 per cent of carbon, silicon, etc., as in the conversion of iron into steel. The sulphur passes off as SO_2, while the iron oxide combines with silica from the lining to form slag, which, when all the iron is thus removed, is poured off, and the blow continued till the last of the sulphur is oxidized, leaving the metallic copper. The finishing reaction after all the iron is removed is:

$$Cu_2S + 2\ Cu_2O = 6\ Cu + SO_2.$$

A lining must be repaired on the average after 3 to 6 charges, instead of lasting for thousands of charges, as in acid steel converters. The time required to finish a 10-ton charge is about 2 hours, while a steel converter of the same capacity will be ready for a second charge in about 15 minutes after receiving the first. Converter slag carries 1½ to 2½ per cent copper, and is returned to the blast-furnace or reverberatory.

The necessity of frequent relining of the converters with silica, and the heavy cost, have led to the adoption of inert basic linings. These are usually made of magnesite brick, and may be further protected by a coating of fused magnetite. Greater economies in labor, power, air, and repairs are possible; and larger charges can be handled in the same sized shell, since the acid lining must be very thick. The chief advantage of the basic converter is that 2500 tons or more of copper can be converted without relining, as compared with 10 tons when an acid lining is used. The chemical reactions in both converters are the same, the difference being that silica is derived, in one case from the lining, and in the other from silicious ore or quartz charged at intervals into the mouth. Basic converters are rapidly displacing acid converters in all the large smelters.

Copper-leaching Processes. — Large quantities of Spanish pyrite, containing 3 per cent or less copper, are piled in immense heaps as much as 30 feet high, wet down with water and allowed to slowly oxidize. $CuSO_4$, together with a good deal of $FeSO_4$ and $Fe_2(SO_4)_3$, and H_2SO_4 form and are leached out by percolating water through the heaps. The solution is run on to fresh heaps of ore, where considerable of the $Fe_2(SO_4)_3$ is reduced to $FeSO_4$ by reaction with FeS_2 and Cu_2S. This reduces the consumption of iron in the next operation, in which the liquors run over pig-iron in a series of troughs to precipitate the copper. The material cleaned from these troughs is screened to remove scraps of iron, and the copper is refined.

These heaps are treated for years before the last of the available copper is removed, but the process may be hastened by heap roasting the pyrite, and leaching in tanks, though this adds much to the expense.

In the **Longmaid process**, copper-bearing residues from pyrite-burning in sulphuric acid works are mixed with common salt, a small amount of raw pyrite being added if the sulphur does not exceed $1\frac{1}{2}$ times the copper. The whole is ground moderately fine and roasted at a low temperature to avoid volatilizing the copper chlorides. The following is probably the main reaction: —

$$CuO + SO_2 + O + 2\,NaCl = CuCl_2 + Na_2SO_4.$$

Some HCl is also formed and may react with CuO, but most of it escapes into the stack, where it is recovered by a water spray. The roasted ore is leached twice with water, and then with this dilute acid. The second wash-water is used as first wash on another lot of ore. Copper is precipitated from the solution by pig- or scrap-iron.

Copper-refining. — If the copper contains no appreciable amounts of gold or silver, it is refined by oxidation in a furnace similar to a reverberatory smelting furnace, but smaller, to remove small amounts of iron, sulphur, arsenic, etc. The old way of getting complete oxidation was by a tedious *flapping* of the molten copper with rabbles. An easier and more effective method is to blow in compressed air from an iron pipe, the end of which dips into the metal. Iron and other metallic oxides, including more or less copper, are slagged, while sulphur, arsenic, etc., volatilize. During this refining, considerable Cu_2O dissolves in the metal and must be reduced again, which is done by forcing wooden poles beneath the surface. The hydrocarbons evolved thoroughly stir the bath, and act jointly with the charcoal as reducing agents. The copper is then cast in moulds, preferably by mechanical means, as in the case of pig-iron.

Most copper contains enough silver and gold to pay for refining by electrolysis, in which process the precious metals, with some other impurities, fall to the bottom of the lead-lined or tarred-wood tank in the form of slime, while the copper is deposited as a refined cathode. In the common method of arrangement, a number of anodes and cathodes, having an area of 6 square feet on each side, are placed "in parallel," 1 to 2 inches apart. The anodes are plates of cast copper about 1 inch thick; the cathodes are thin sheets of electrolytic copper, which become thicker as the refining progresses. The electrolyte is a 12 to 20 per cent solution of bluestone with 4 to 15 per cent of free sulphuric acid. A little hydrochloric acid or common salt is added to precipitate into the slimes any silver that may possibly go into solution and which would otherwise deposit on the cathode. The solution is circulated to maintain a uniform composition, and is kept at a uniform temperature of 40° to 60° C. Impurities accumulate in the solution, portions of which are periodically removed for purification. The current is commonly 8 to 18 ampères per square foot of total cathode surface.

The silver slimes are taken from the tanks at intervals, screened to remove scrap copper, and refined in either of two ways: they may be treated with hot, aërated sulphuric acid to dissolve copper, washed, dried, and melted in a small reverberatory furnace with a little sand, soda-ash, and occasionally nitre, to slag the remaining impurities. The bullion is then parted to separate silver and gold (see p. 634). The other method is to add the dried slimes to lead on a cupelling hearth, the silver and gold being absorbed by the lead, and recovered, as described on p. 622.

Because of its properties, copper finds extensive use in the arts, both in its pure state and in its many alloys. Its strength, ductility, and considerable resistance to attack by ordinary atmospheric and chemical agents, together with its high conductivity for heat, make it suitable for vessels and apparatus in various chemical works. It is readily rolled, pressed, or hammered into thin sheets or other forms, but is too ductile for working in the lathe. It alloys readily with zinc, tin, aluminum, manganese, and phosphorus, forming brass and bronzes which are harder and stiffer than the pure metal, and may be cast in moulds or worked in the lathe. Copper is the best industrially available conductor of electricity; in general the conductivity of metals is greatly diminished by the presence of impurities in solid solution; cuprous oxide and practically all metals dissolve in solid copper; thus cast copper, whether deoxidized or not, is unsuited for electrical work. Since neither metallic boron nor its oxides dissolves in copper, boron and boron sub-oxide have been introduced for casting copper for electrical work.

LEAD

The chief lead ore is galena, PbS; the carbonate and sulphate are of some importance. The principal method of reduction is in blast-furnaces similar to those used in copper-matte smelting. As the intense heat does not extend so high as in a copper furnace, the walls for some distance below the charging floor are of brick, the lower part only being water-jacketed. The ore is charged into the furnace, either raw or after a rough roast. Formerly, lead ores were roasted sweet if they did not contain much silver that would volatilize. Usually 2 or 3 per cent of sulphur is now left in the ore, and often with raw ore this percentage is largely exceeded. This procedure yields more matte, to be roasted and resmelted, yet it affords an increased saving.

Lead smelters treat considerable quantities of gold and silver ores that contain no lead, as this is a convenient way of recovering the precious metals.

In recent years considerable progress has been made in the blast roasting (often termed "lime-roasting") of lead ores previous to sending them to the blast furnace, and this method has been widely adopted. The sulphide ore, sometimes after a partial preliminary roast, is roasted and sintered in pots with a blast of air. Usually lime rock or gypsum is added as a diluent and to aid in slagging. These pots are so built that a blast of air can be blown up through a grating on the bottom on which a coal or wood fire has been made. The ore and lime rock charge is put on top and a light blast is turned on. The sulphur in the ore ignites and, when the blast is increased, most of the charge is sintered together into a large cake. After breaking up, the caked material is ready for the blast furnace. The capacity of the blast furnace may be increased one-third by using the blast-roasted charge instead of raw ore. The flue-dust made and the fuel required are greatly reduced. In place of the pots, the Dwight-Lloyd machine (p. 600) is often used.

The ore, sinter, by-products, and the necessary fluxes (usually lime rock and iron ore), together with 13 to 16 per cent of coke, go to the blast furnace, where the lead is largely reduced to metal by the coke and carbon monoxide and settles into the crucible, from the bottom of which it runs out through the Arents siphon tap (a sloping channel that leads up from the bottom of the crucible to a basin outside), and is removed to moulds. The matte and slag run out together, through an opening above the lead, into a small forehearth much the same as in a copper furnace. The slag runs away continuously from the top of the forehearth, while the matte is periodically tapped from the bottom. The cold matte is crushed moderately fine, and roasted. If low in copper, it is then returned to the regular blast-furnaces, for which its iron provides an excellent flux; but if it contains over 10 per cent copper, it goes to a special furnace, yielding a matte high in copper. The slag is removed in large pots, in the bottom of which some extra matte may settle. This, together with the slag skulls from the pot, is re-smelted, the waste slag going to the dump. The composition of the slag is more important than in copper-smelting; if too silicious, it takes up considerable lead oxide; if too refractory, it requires a high temperature for fusion, and the top of the charge becomes too hot, increasing the loss of lead by volatilizing both sulphide and oxide. Much of the silver will be lost in the same way. Common slags contain 33–35 per cent SiO_2, about 55 per cent $FeO + CaO$, the rest being Al_2O_3, etc.

Zinc compounds are objectionable, forming troublesome accretions on the furnace walls. They make both slag and matte less fusible and decrease the difference in their specific gravities, hindering good separation.

Reverberatory smelting of lead ores was formerly much used, but has now been largely superseded. The ores need to be rich in galena, and should not contain over 5 per cent of silica, as the amount of slag must be very small, for it coats the ore particles and hinders the reactions. The furnaces are comparatively small and of various designs. The charge is first roasted, with frequent rabbling, at a moderate heat; and when a certain amount of lead oxide has been formed, the heat is increased to produce reaction between this oxide and the remaining lead sulphide, yielding metal. The main reaction is

$$PbS + 2\ PbO = 3\ Pb + SO_2,$$

though others occur. As the metallic lead separates, it runs down the sloping hearth into an external basin. The charge is allowed only to soften, quicklime being commonly stirred in to prevent fusion which would interfere with the next roasting operation. The roasting and reaction stages are alternately repeated several times; and toward the end fine coal is added to reduce the last of the oxide. For a good extraction the temperatures must increase in each succeeding reduction stage; but in some cases, to reduce the volatilization losses, a high temperature is avoided, leaving more value in the residue, which is smelted in a blast-furnace. This residue is sometimes treated in the reverberatory, at a moderately high temperature, being intimately mixed with fine coal.

The "**ore hearth**" is a small furnace easily and inexpensively started and stopped, used where the ore supply is small and perhaps intermittent; but it is not suited to argentiferous ores, because too much value would be lost in the fumes. The American water-back variety (Fig. 132 *) is a moderate-sized basin made of brick and lined with cast-iron. Surmounting it on three sides is a cast-iron water-jacket (J), through which pass three tuyeres (D) from the wind-box (B). A wood fire is made in the basin, or hearth, some coal added, and the blast turned on through the tuyeres. When well heated, ash and clinker are removed, ore is placed on the hot fuel, gradually oxidizing and yielding lead by the same reactions as in the reverberatory furnace. The ore is covered with a thin layer of coal, and there is the extra reaction $2\,PbO + C = 2\,Pb + CO_2$. When the hearth is filled with lead, the latter runs out over a grooved iron plate (G) into a kettle (H) kept hot by a small fire, to permit ladling into moulds. The ore must be low in silica, and is mixed with a small amount of burned lime to prevent actual fusion. The charge is loosened and stirred by the workmen, and the residue removed before adding a fresh charge.

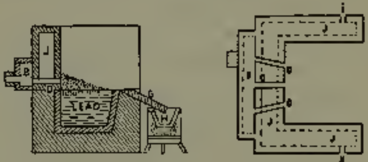

FIG. 132.

Unless the ores are exceptionally pure, the lead obtained by the above methods contains impurities, which are removed by slowly melting down and stirring with a jet of dry steam. Arsenic, antimony, tin, iron, etc., with some of the lead, are oxidized, and are skimmed off.

If the lead contains valuable quantities of silver and gold, they are recovered generally by the **Parkes process**. After the refining or "softening" process, just described, the lead is run into a large kettle, holding 30 tons or more, pure zinc is stirred in, the metal allowed to cool, and a zinc crust (rich in gold, copper, and silver) forms on the surface. By using only a small amount of zinc at first the gold and copper can all be removed without much silver; and a second zincing then takes out most of the remaining silver, though a third zincing is usually needed, the crust from this third treatment being used for the second treatment of another lot. If the preliminary softening is omitted, several additions of zinc might be necessary to remove the

* After Broadhead, Geological Survey of Missouri, 1873–74, 492.

impurities before much of the silver would be taken up by the zinc. The gold and the silver crusts are treated separately. They are slowly heated to " sweat out " lead, after which they still contain 50 per cent or more of lead alloyed with the zinc and precious metals. A better way is to lower the cylinder of a **Howard press** into the desilverizing kettle. When this reaches the temperature of the lead, the crust is skimmed into the cylinder, which is then raised, pressure is applied from above, and the excess lead runs back into the kettle through the perforated bottom.

The zinc is removed from the crusts by distillation in a graphite retort, a large part being condensed and saved in the metallic state, while a portion is oxidized. The silver and gold remain in the retort with about 5 per cent of the original lead, and are recovered by **cupellation.** This consists in melting the metal on a small hearth (of crushed limestone and clay, or of Portland cement either alone or mixed with ground fire-brick) and oxidizing the lead by means of an air jet, which blows the lead oxide toward the front of the hearth, where it is skimmed off. The remaining bullion is either refined on the hearth with nitre or by treatment in graphite crucibles. Silver and gold are parted as described on p. 634.

Pattinson's process is sometimes used for this desilverization of lead. It is based upon the crystallization of purer lead from the argentiferous lead bath. The plant consists of large cast-iron pots in which a temperature slightly above the melting-point of lead (335° C.) is maintained. In a pot near the middle of the series the crude lead is kept in fusion for a time and then cooled slightly while thoroughly stirred; when a considerable part of the lead has solidified, the crystals are fished out with a perforated ladle and put into the next pot to one side, while the liquid is ladled into the next pot on the other side. More crude lead is run into the first pot, and the process repeated. The crystals and liquid portion are each fused and cooled again while stirring, a new crop of purer crystals and a more concentrated argentiferous lead being obtained. This fractional crystallization is repeated a number of times, until a desilverized market lead, on the one hand, and a highly argentiferous metal, on the other, is obtained, which latter is then cupelled. The process can be worked in only one large pot by tapping off the melted lead from the crystals, and again refining each. Steam is generally introduced for agitation purposes.

Lead shows a brilliant bluish white metallic lustre on freshly cut surfaces, but tarnishes rapidly by oxidation in the air. It is very soft when pure, but impurities increase its hardness. It is very malleable and ductile, but its tenacity or strength is low, hence it is usually worked by pressing or rolling. It melts at 330° C., and shrinks upon solidifying from fusion. Its specific gravity is 11.35. Owing to the slight action of sulphuric and hydrochloric acids and salts on the metal in the cold, lead is extensively used for chemical vessels and apparatus, for pipes, drains, roofs, etc. Much of it goes into compositions and alloys, *e.g.* solder, pewter, fusible metals, type-metal, etc.

ZINC

Zinc is obtained chiefly from blende (ZnS), smithsonite ($ZnCO_3$), and calamine ($Zn_2SiO_4 + H_2O$). In New Jersey, willemite (Zn_2SiO_4), zincite (ZnO), and franklinite (a complex oxide of zinc, iron, and manganese) are important, the last not being used for the metal, but to manufacture zinc white, and its residue utilized to make ferromanganese. Blende must be roasted to remove practically all the sulphur. Smithsonite and calamine are often calcined (see p. 599 and Fig. 127) to get rid of CO_2 and H_2O, though they are sometimes used without calcining.

The pulverized ore is intimately mixed with either anthracite coal or with about one-third of the total weight of the mixture of coke and soft coal, and is charged into retorts made of clay (see Fig. 133, A). The more intimate the mixture of the charge the better; consequently large plants use mechanical mixers which are more effective than handwork. In the United States cylindrical retorts, 4 or 5 feet long and 8 to 10 inches in diameter, are usual. Several hundred are set in a large combustion chamber, in a nearly horizontal position, but sloping gently toward the front. This slope is convenient for charging and discharging; and, if any fusible slag forms, permits it to run to the coolest part, where it is least likely to corrode the retort, which may have a refractory lining of chromite or magnesia to prevent such corrosion. In mixing the charges, care is used to have them as infusible as may be, adding quicklime, etc., if necessary. Of the common slag-forming materials, iron minerals have most frequently to be contended with. Iron pyrite is a common associate of blende, and great care is used to remove it before shipping to smelters. Abroad, the retorts are larger and of somewhat different shape, and there are fewer of them to one furnace. The retorts are made by machine, which yields a stronger and

Fig. 133.

denser product than if made by hand. These qualities are important on account of the very considerable absorption of metal by the retort, the danger of losing metal through cracks, and the entrance of harmful fire-gases. Heating is by producer or natural gas, which gives better control than the old method of direct firing with solid fuel. The air for burning the gas is pre-heated by the waste products of combustion, either by the regenerative or the recuperative system.

After withdrawing the residue from one charge and filling with a new batch, the temperature in the retorts is gradually brought from 800° C. to 1200° or 1300° C. The zinc oxide (and, less readily, the silicate) is reduced to metal, which volatilizes (boiling point = 920° C.) and passes out of the retort into a condenser (Fig. 133, B). This is a small, tubular, clay receptacle, open at each end, inserted in the open end of the retort, and exposed all round to the air. Since metal conducts heat better than clay, a sheet-iron " prolong " is sometimes attached to the outer end of the condenser to catch additional zinc fume and to prevent air from entering the condensers and oxidizing the metal.

At first the hydrocarbons are distilled from the coal, and some CO_2 is produced; but later the gas in the retort is almost wholly CO, from the reduction of metallic oxides by the excess of carbon. The zinc fume is oxidized to ZnO by CO_2, as well as by free oxygen, this taking place chiefly at the beginning of the distillation. The ZnO mixes with and coats fine particles of metallic zinc, forming **zinc dust** or " **blue powder**," which makes up 5 to 10 per cent of the total product, and contains 10 per cent of ZnO. The quantity will be increased if the furnace temperature is allowed to get too low; the metal cannot be separated from it by simple melting, so it is returned to the retorts with the fresh charge. Both CO and the uncondensed zinc burn with a bluish flame, but of distinct tints; the character of this flame guides the furnace men in regulating the distillation. The complete treatment of a charge requires about 24 hours, and the zinc is drawn from the condensers into a kettle every 8 hours. The blue powder is skimmed from the surface of the metal in the kettle.

The most common impurities left in the zinc are lead and iron, the latter being taken up to some extent from the working tools. When refining is necessary, it is done in a small reverberatory furnace of special design. At a temperature not much above the melting point of zinc (415° C.) the lead settles to the bottom with very little zinc; while a zinc-iron alloy deposits on top of the lead.

As galena is a common associate of blende, a number of methods have been devised to separate them; but the most successful is to treat for zinc in much the ordinary way, distilling at a lower temperature than usual and treating the residue as lead ore. Distilling at higher temperatures vaporizes too much lead with the zinc. The recovery of zinc is less than at the temperatures permissible with ores fairly free from lead; but the residue is moderately low in zinc, which is so troublesome in lead smelting, and the process thus makes many ores valuable which would otherwise be useless.

Zinc has a specific gravity of 7; it melts at 419° C. It is brittle when cold, but becomes softer and malleable at about 120° C., so that thin sheets can be rolled from it, but at 200° C. it becomes so brittle that it can be pulverized. It is much used for battery plates and poles; in the preparation of brass and other alloys with copper, tin, and lead. Since it is only slowly attacked by atmospheric agents, sheet zinc is largely used for cornices, roofs, gutters, pipes, etc.; also to furnish a protective coating on iron, by the process of "**galvanizing**," in which the clean iron is dipped into a bath of fused zinc. The zinc-iron alloy formed on the surface is hard and brittle and lessens the strength of the iron, but prevents rusting.

CADMIUM

Cadmium is found associated with zinc to the extent of 4 or 5 per cent in some ores. Commercially it is obtained as a by-product in zinc smelting. In the reduction of the zinc (p. 623), the cadmium, being more volatile, passes over first with zinc dust as a brownish powder. This is collected and distilled again at low red heat, with reducing material. The product contains some zinc, and further purification is possible by repeating the process.

Cadmium is a silver-white, lustrous metal of 8.55 sp. gr. (cast), harder than tin, and of fibrous texture. It may be drawn into wire or rolled into plate. It melts at 321° C. and vaporizes at 778° C. It is readily attacked by mineral acids. Its chief use is in the preparation of fusible alloys with bismuth, tin, and lead, and for amalgam for dental use. The iodide and bromide are used somewhat for photographic purposes.

TIN

The only commercial source of tin is cassiterite or tinstone (SnO_2). In the United States this is not found in large quantities, and none of the metal is produced here from ore. A certain amount is recovered from tin scrap by chemical solution and electrical precipitation.

Sometimes the cassiterite after mechanical concentration from the ore is still accompanied by considerable arsenopyrite ($FeAsS$) and pyrite (FeS_2), which are injurious to the smelting. To remove these, the ore is roasted, leaving a light, porous oxide of iron, the tin remaining unchanged; the iron oxide is removed by washing.

Smelting is done both in blast-furnaces (employed only with extremely pure, lump ores) and in reverberatories. The blast-furnaces are built of stone or brick and clay, and the ore is charged alternately with charcoal, which is used because of its low percentage of ash. To avoid the strong reducing conditions that would precipitate metallic iron, the furnaces are shallow (the charge often being only 3 or 4 feet deep above the tuyeres), and only a moderate blast pressure is used. Despite these precautions a certain amount of iron is always contained in the metal. The tin and slag run out together into a small forehearth.

In the reverberatory method the ore is mixed with 15 to 20 per cent of anthracite or semibituminous coal and charged into the furnace, which is then closed, and a good fire is maintained for 3 or 4 hours. The charge is then stirred, and firing repeated till the reduction is satisfactory. A small amount of lime may be used in the charge to slag the ash from the intermixed coal. When the smelting is completed the tin may first be tapped into an external basin, and then the slag tapped separately, or the slag may be skimmed out through a door before tapping the metal. In the latter case the first portion of slag may be sufficiently free from tin to throw away at once.

Some of the tin contained in the slag is present as metallic particles, which are occasionally recovered by crushing and mechanical separation; but a large part of the slag must be re-smelted (often several times), using either the blast or the reverberatory furnace. This is done at a higher temperature than in ore-smelting in order to get the stronger reducing action needed, and scrap-iron or iron ore may be added to assist the recovery of the slagged tin. Under these conditions more iron is reduced than in ore-smelting, making a poorer grade of tin.

A good deal of the iron contained in the tin is removed by **liquation.** The cast slabs are slowly melted on the sloping hearth of a reverberatory furnace, the tin running into the external basin, while the iron remains as "hardhead." This iron, however, still retains some tin, and is sometimes added to the slag-smelting charge. Sometimes liquation is performed by pouring the molten tin over red-hot charcoal on an inclined iron plate, the charcoal acting as a filter to hold back the "hardhead." After liquation the metal is further refined by "boiling" or "tossing." **Boiling** consists in a vigorous agitation produced by forcing pieces of green wood into the metal bath, which is kept molten by a fire beneath the kettle. The gases evolved from the wood throw the metal into the air in small quantities at a time, thus oxidizing the impurities, together with some of the tin. The oxides collect on the surface as a dross, which is skimmed off and added to the ore charge. **Tossing** produces the same result as boiling, and consists in taking out ladlefuls of the metal and pouring it back in a small stream. It is a very laborious method, and the impurities might be oxidized by blowing in air, as in the case of copper refining.

Tin has a specific gravity of 7.285, and melts at 232° C. It is a soft metal of no great tensile strength, is rather brittle when cold, and when bent emits a peculiar crackling sound. At about 100° C. it is malleable, and may be rolled into sheets (tin-foil) or drawn into pipes. Not being corroded by water or by most organic acids, it is extensively used for lining copper and iron tanks, cooking vessels, etc. It forms valuable alloys, as solder, bell- and speculum-metals, bronze and Britannia metal. On sheet-iron it is extensively used as *tinned plate.*

SILVER

Much silver is obtained in copper and lead smelting (p. 618). The important silver ores are native silver, argentite or silver glance (Ag_2S), stephanite or brittle silver (Ag_5SbS_4), pyrargyrite or "dark ruby silver" (Ag_3SbS_3), proustite or "light ruby silver" (Ag_3AsS_3), cerargyrite or "horn silver" ($AgCl$), and polybasite [$(AgCu)_9SbS_6$]. These are associated with many other minerals. For the direct extraction of silver the Patio, Washoe, and Reese River processes are now seldom used. In modern practice, the ore is generally leached with cyanide solution as for gold ores (p. 631). The dissolving rate of silver is only two-thirds that of gold and stronger solutions (often one per cent) are required. **Amalgamation** is occasionally employed as with gold ores. In Cobalt, Ontario, high-grade ores and concentrates are treated in tube-mills with both mercury and strong cyanide solution. The latter keeps the mercury bright and hastens amalgamation in addition to its dissolving action.

In the **Patio process** the reactions are similar to those of the Washoe, but the apparatus is crude. It is used only in warm climates (Mexico and South America). No heat is used except from the sun and that generated by the chemical reactions. The fine grinding is done in an *arrastra*, a pan-shaped stone structure 6 to 20 feet in diameter. If the ore contains gold, mercury is put into the arrastra, and the gold amalgam accumulates in the bottom during a number of charges. After grinding, the water is drained off and the pulp removed to the patio, a large, stone-paved area on which the pulp is spread about a foot deep, and salt scattered on it. Mixing is done by driving mules through the pulp and spading it over. Copper sulphate and mercury are in turn mixed in in the same manner, and the silver chloride is decomposed by the mercury. The process often requires weeks, the recovery is not as good as in the Washoe process, and the mercury loss is higher.

In the **Washoe process** the ore is pulverized by gravity stamps to pass a 24 to 80 mesh screen, water being run in continuously. The product goes to settling tanks and the pulverized ore is shovelled into amalgamating pans (Fig. 134 *) 5 feet in diameter and 3 feet deep, together with some blue vitriol and salt. The bottom of this pan has a steam-jacket (S); the sides are of wood lined with cast-iron around the bottom. A vertical shaft, passing through a central cone (C), carries mullers (M) to stir and grind the charge. Wings (W) on the sides of the pan assist the stirring by directing the pulp toward the centre. Removable iron plates (P) on the mullers and on the inside bottom of the pan take the wear of grinding. The pulp is heated to 80° C. by live steam run into it, and is kept hot by steam passed into the jacket (S). All the pulverizing may be done in the stamp

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* After Richards, Ore Dressing, Vol. I. New York, 1903.

battery; but when grinding is necessary, it lasts ½ to 4 hours, during which the sulphides, arsenides, and antimonides of silver are converted into chloride by the bluestone and salt. Iron, worn from the grinding plates, or added as borings, reduces the silver chloride: — $2\,AgCl + Fe = 2\,Ag + FeCl_2$. After these reactions are completed, quicksilver is sprinkled in, and stirring (without grinding) continued for 3 to 8 hours more. The pulp must be of the right consistency to keep the quicksilver distributed through the mass. When the mercury has taken up the silver, the diluted charge goes to a settler, and the silver amalgam runs out through a small pipe at the bottom. The amalgam is strained, retorted, and the silver melted down as for gold (p. 631).

The Reese River process is used for ores (arsenic and antimony) which do not easily amalgamate. The ore is crushed dry and given a chloridizing roast previous to amalgamation. This either removes arsenic and antimony, or so changes them as to permit satisfactory amalgamation. The amalgam is treated the same as for gold.

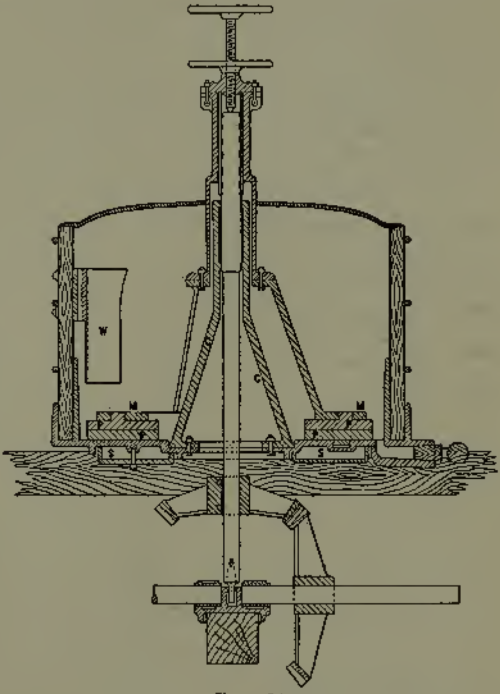

Fig. 134.

The tailings (waste) are often concentrated by mechanical methods to recover any amalgam and undecomposed sulphides and arsenides which still retain precious metals. The amalgam is added to that previously obtained, while the sulphides, etc., are generally sold to smelters.

Leaching processes have been considerably used for silver ores. In the Augustin process the ore, after a chloridizing roast, is extracted by a hot solution of common salt, and the silver precipitated by metallic copper. Patera used sodium "hyposulphite" (thiosulphate) as a solvent of the silver chloride, and precipitated the silver as sulphide with sodium sulphide. Russell improved on this by treating with a double thiosulphate of sodium and copper after the sodium thiosulphate leaching; this "extra solution" dissolves some of the unchloridized silver minerals better than the single salt. Sodium carbonate is added to precipitate lead before throwing down the silver sulphide. The metal is recovered from the latter as from the slimes obtained in electrolytic copper refining (p. 617).

GOLD

The chief occurrence of gold is in the native state enclosed in quartz, with iron pyrite or other gangue; some is obtained from tellurides of gold in certain districts. While it is seldom visible to the naked eye in pyrite, the microscope frequently shows the metal in thin scales on the parting planes; yet it may, in some cases, be chemically combined.

Some gold is obtained from **placers** by washing the gravel through long sluices filled with riffles. These are made with cobble-stones, wooden blocks, or iron formed into various shapes to produce eddies into which the particles of gold settle on account of their high specific gravity (15.6 to 19.5), while the sand and gravel are carried along by the water. Mercury is sometimes placed in the riffles to amalgamate the gold. The more common methods of recovery are by amalgamation, or cyaniding. Small amounts of gold are found in many copper and lead ores and are recovered in the regular smelting processes. The baser metals act as "carriers" and the precious metal is obtained in refining operations. Gold ores or concentrates are often added to the furnace charge even when they do not contain either copper or lead. When high in silica, such ores are desirable, as they may be used instead of barren quartz in copper-converting (p. 616).

Chlorination, formerly an important process of extraction, has rapidly fallen into disuse. Amalgamation is especially suited to ores carrying free gold in fairly coarse particles (free milling). In most other cases, cyaniding is the best process. In recent years such improvements have been made in cyanide work that it can now be applied to almost all types of ores.

In the ordinary **amalgamation process** the ore is crushed to 1-inch pieces by Blake or Gates breakers and fed to gravity stamps. Figure 135 shows two 5-stamp batteries. (A) is the cast-iron mortar, into the back of which the ore is fed with water. The stamps (S) are raised, one after another, by cams (T) on the horizontal shaft near the top, and fall by gravity. Usually each stamp weighs 800 pounds or more, and drops 80 to 110 times a minute through a distance of 5 to 9 inches. In the front of the


FIG. 135.

mortar is a screen with holes 0.02 to 0.04 inch (0.5 to 1.0 mm.) in diameter, through which the water carries the finely ground ore to the amalgamated plates. These are sheets of copper, which have been thoroughly coated with quicksilver or a silver amalgam, and fastened to a long sloping table. The bright particles of gold, and any silver passing over these plates, easily amalgamate with and are held by the mercury, while quartz, pyrite, etc., run off. Particles of gold that are coated with iron-rust (as often happens) will not amalgamate; but an advantage of stamps over most other fine grinders is that they rub off such coatings. Grease also hinders amalgamation, and special care must be used to prevent it dripping from any of the machinery.

A small amount of mercury is put into the stamp battery at intervals, or a little is occasionally sprinkled on the outside table plates, in order to keep the amalgam of proper consistency. If the amalgam is too thin, due to excess of mercury, it will easily wash off; if too thick, from too little mercury, it will not catch the gold.

Once every 24 hours, stamping is stopped long enough to scrape the amalgam from the plates. This amalgam often encloses fine particles of ore, iron, and other dirt, from which it is freed by grinding in a mortar with some extra quicksilver, or by other mechanical means. It is then strained through chamois skin or fine canvas by squeezing. A thick, "hard" amalgam, rich in precious metals, remains in the chamois, while the excess of mercury, with but little gold or silver, passes through and is used again. The hard amalgam is distilled in a large iron retort, the mercury vapor passing off through a water-cooled condenser and dropping into a vessel of water, while the gold and silver remain in the retort. The precious metals are then melted in a graphite crucible with borax, soda, nitre, etc., to remove the base metals that have been amalgamated.

The ore running off of the amalgamated plates often contains auriferous pyrite or other valuable minerals. It may be cyanided directly, or treated on mechanical concentrating tables, to wash away the quartz and other useless portions, leaving the concentrates to be smelted or treated by the cyanide process to obtain their gold.

The **cyanide process** is the most important method of treatment and is extensively employed.

Potassium cyanide dissolves gold according to the equation, —

$$4\ Au + 8\ KCN + O_2 + 2\ H_2O = 4\ KAu(CN)_2 + 4\ KOH,$$

and silver by a corresponding reaction. The oxygen dissolved in the water with which the cyanide solution is prepared, and the film of air attached to the ore particles is generally sufficient for the above reaction, but frequently sulphides, organic matter, etc., in the ore or the water absorb so much oxygen that aëration is necessary. This is done by drawing off the solution from the bottom of the leaching tank and pumping it back on to the top, or by forcing air into the charge from a perforated pipe. The process is conducted in large vats, preferably of iron, as this has less effect on the solution than wood and is cheap to keep in order. The ore, if crushed with water in gravity stamps, is usually passed over amalgamated plates to catch the coarser particles of gold. As the fine slimes interfere with leaching, the ore and water are run into settling tanks to catch the sands, while the slimes overflow to be caught in larger tanks. The settling of the slimes is greatly assisted by adding some burned lime or caustic soda either in the stamp battery or after the ore leaves the latter. This coagulates the slimes and neutralizes free sulphuric acid and basic iron salts which are produced by the decomposition of pyrite, etc., and which decompose cyanide. Some ores require roasting to get satisfactory extraction, and so should be dry crushed. Roasting makes the slimes less troublesome to leach, so that they can be treated with the sands. The sands are charged into the leaching vats, where they may be washed with water to remove soluble salts, if this has not already been accomplished; and then with alkali if necessary. A solution containing 0.25 to 0.35 per cent of potassium cyanide is then run on (stronger solutions are no more effective) and allowed to stand for several hours. It may be removed and pumped back for the sake of aëration, or may be passed through a vat of fresh ore, or may be treated directly for its dissolved gold. A second treatment is given with a weaker cyanide solution to dissolve any gold remaining and to wash out the adhering "strong" solution. The last of the cyanide is removed by a water wash. When slimes are treated separately agitation is used, and the solutions are not so strong as for sands, sometimes containing 0.01 per cent or less of KCN. After sufficient agitation they are allowed to settle and the solution decanted through a siphon or through holes in the side of the tank, or the whole mass may be passed through filter-presses.

To recover the gold the solution is passed through a series of boxes filled with fine zinc shavings, or in some cases the solution is agitated with zinc dust. What gold does not drop to the bottom of the zinc boxes is washed off the shavings at the clean up. The gold slime is screened to remove bits of zinc, and then treated with dilute sulphuric acid to remove fine zinc, etc., dried, and melted in graphite crucibles with borax, soda, sand, etc. By another method the slime is mixed with litharge (PbO), a reducing agent, borax, etc., and melted in a small reverberatory furnace to produce a rich lead bullion, which is cupelled after running off the slag.

As zinc precipitation is less efficient for solutions containing very small quantities of gold than with larger quantities, the Siemens-Halske **electrical method** has been applied in South Africa to the dilute solutions obtained from slime treatment. The anodes are iron, the cathodes lead. When enough gold is deposited the cathodes are melted and cupelled. This method has been considerably displaced by the **Betty-Carter process**, which uses a zinc-lead couple obtained by treating zinc shavings (or zinc dust) with lead acetate, whereby lead is precipitated on the zinc. To make the action of this couple thoroughly effective, some strong cyanide solution is added in the precipitation boxes. Aluminum shavings may be used instead of zinc.

Gold ores almost always contain some silver, and silver ores generally contain gold; and in most processes the two metals are recovered together and subsequently "parted."

For **chlorination** the ore is first dead-roasted, because sulphides, arsenides, etc., envelop particles of gold, and consume chlorine to no purpose. Roasting converts them into porous oxides, which the chlorine gas can easily penetrate. If lime, copper minerals, or other substances are present which would absorb chlorine after roasting, salt should be added to the charge before completing the roast; this chloridizes them in a cheaper way, but salt must be added cautiously and in small amounts, for the gold chloride formed is easily lost by volatilization. The gold is most commonly chlorinated in large iron barrels lined with lead, the chlorine being generated by the action of sulphuric acid on chloride of lime. The barrel is supported horizontally by a trunnion at each end, and has a manhole on the side. Water is run into the barrel, the proper quantity of sulphuric acid added, then the ore is charged, the chloride of lime being put in last, and the cover immediately fastened on securely. Another method consists in having a lead pocket inside the barrel near the top, into which the acid is poured the last thing before putting on the cover. The object is to avoid generating chlorine till the barrel is tightly closed. The barrel is then revolved for 1½ to 6 hours, depending on the ore; this thoroughly stirs the charge, giving the gas free access to every particle, and rapidly dissolving the gold chloride ($AuCl_3$). Silver chloride that may be formed, and other substances that would coat the gold particles and thus hinder the process, are removed by the attrition. When the reaction is complete, a cock is opened to discharge the excess of gas through a pipe outside the mill, the barrel is filled with water, revolved again, and the solution poured upon a sand filter. The barrel is again filled with water, revolved, the solution poured through the filter, and then the whole charge is emptied upon the filter and washed more if necessary. The solution is run from below the false bottom of the filter-tank to a precipitating vat. At several large plants the excess of chlorine is removed by passing SO_2 from burning brimstone through the solution. Hydrogen sulphide is then introduced, precipitating the gold as sulphide, thus: —

$$2\ AuCl_3 + 3\ H_2S = Au_2S_3 + 6\ HCl.$$

After settling, the liquor is passed through a filter-press to save any suspended particles of Au_2S_3. The precipitate in the vats accumulated from a number of charges is then filtered as dry as can be, placed in iron trays, and roasted in a muffle heated from the top. This leaves metallic gold, which is melted in a crucible with a little borax and nitre to slag iron or other impurities.

The vat process is older than the above, and although it is less perfect and takes more time, it is still used in small plants. The roasted ore is moistened with just enough water to cling together when pressed in the hand, and yet to crumble easily. Chlorine, at ordinary temperatures, scarcely attacks dry gold; but if the ore is too wet it packs so hard that the chlorine cannot penetrate. The ore is then carefully charged on a filter-bed of crushed quartz on a perforated false bottom in a large wooden vat painted with tar or asphalt. When the tank is charged, a cover is luted on, or closed with a water seal, and chlorine introduced through the false bottom. The gas is commonly generated from salt, pyrolusite (MnO_2), and sulphuric acid. A small hole, left in the cover for the escape of air, is closed when the chlorine comes from it freely; then the gas is passed in for an hour or two longer to get complete saturation and produce a certain pressure. The vat stands a day or two, the chemical action being much slower than in the barrel with its constant stirring, and then the excess gas is allowed to escape outdoors or into a holder for subsequent use. Water is then run in to cover the charge and is drawn out from the bottom, a stream running into the top to maintain its level above the ore. The washing is continued till practically no more gold is dissolved. As the later washings are poor, it is well to keep them separate to be used on another batch. In this process the precipitation is commonly done with ferrous sulphate, yielding the gold as metal: —

$$2\ AuCl_3 + 6\ FeSO_4 = Au_2 + 2\ FeCl_3 + 2\ Fe_2(SO_4)_3.$$

This precipitate does not settle so well as that obtained by the use of H_2S. The gold is carefully dried and melted with borax, nitre, etc.

Liquid chlorine has been used for chlorinating gold ores; and, if cheap enough, convenience might lead to its general adoption. One mill in Colorado in a district where the cost of power to generate electricity is low used to make its chlorine by electrolyzing salt, finding it cheaper than the usual method.

Various methods of **parting** are in use. For **acid methods**, the melted alloy is either granulated by pouring into water or is cast into small, thin plates. It is then boiled with strong sulphuric acid in cast-iron pots to dissolve the silver, leaving the gold as a powder.

For complete solution of the silver, the alloy must contain 2 or 3 times as much of that metal as of gold. The silver sulphate is held in solution by the hot acid; if, after the fire is withdrawn, the temperature is lowered by adding cold acid, sulphate crystals precipitate and help to drag down the finely divided gold. After removing the solution, the residue is boiled twice with fresh acid. The gold is washed, first with dilute acid, next with boiling water to remove the last of the silver, and is then dried and melted. Some nitre and borax are used in this melting, if base metals are still present. The silver solutions are diluted with water, which at first precipitates silver sulphate that is redissolved by heating, and the metal precipitated by metallic copper. After drawing off the copper sulphate solution the silver is washed with hot water, dried, and melted.

Nitric acid also dissolves silver, leaving the gold, but is more expensive than sulphuric. The first treatment is usually with acid of 1.2 sp. gr., followed by a second treatment with strong acid to remove the last of the silver, then after diluting the solution, the silver is precipitated by salt. The silver chloride is reduced to metal by granulated zinc in very dilute sulphuric acid.

$$2\ AgCl + Zn \rightarrow 2\ Ag + ZnCl_2.$$

The **Miller process** is used in Australia for bullion that contains too little silver for acid parting, and where silver bullion with some gold is not available to produce a suitable mixture. The bullion is melted in a crucible, and chlorine is passed into it through clay tubes. At this temperature, chlorine combines with the silver, but not directly with the gold, and the silver chloride rises to the surface, leaving the pure gold. Chlorides of the base metals, except copper, pass off as fumes. When the action is completed, the silver chloride is poured off, but carries with it some small shots of gold. Some double chloride of gold and silver is contained in the silver chloride, due to slight attack on the gold. The gold is reduced from this by melting the mass with sodium carbonate and borax. The silver chloride is then cast into plates, which are laid in a wooden frame alternately with zinc plates and connected to the latter by strips of silver. The frame is placed in a zinc chloride solution, and the silver precipitated electrochemically, zinc passing into solution.

Wohlwill's electrical process is successful for parting gold bullion carrying but little silver. The metal is cast into plates and electrolyzed in a solution containing 40 to 45 gms. of gold chloride and 20 to 50 cc. of concentrated hydrochloric acid per litre. The temperature is kept at 65° to 70° C. If the acid is not present, free chlorine is evolved at the anode without dissolving the gold. A strong current (30 ampères or more per square foot) is used, and the required voltage is low, so the cost of power is small. The cathodes are pure gold sheets, arranged in multiple. The silver is converted to chloride and settles in the slimes. If the bullion contains as much as 10 per cent silver, a crust of silver chloride forms on the anode and must be rubbed off; much silver stops the action entirely. Osmium and iridium, if present, pass into the slimes; platinum accumulates in the solution, and may be precipitated with ammonium chloride. In order to keep a constant percentage of gold chloride in the solution, some is added periodically. This is necessary because a certain weight of gold is deposited at the anode for every equivalent of silver that is precipitated or of platinum dissolved. The gold deposited on the cathodes is almost chemically pure.

The **Moebius electrical process** is used frequently for silver bullion low in gold. The electrolyte is a dilute solution of silver nitrate and free nitric acid (1 per cent or less of each), and the current is 12 to 20 ampères per square foot. The anodes and cathodes are arranged in parallel, the former being hung in muslin bags to catch the gold slime. The cathodes are silver plates, but the deposit does not form coherently on them and is scraped off mechanically to prevent short circuiting.

PLATINUM

Platinum is found chiefly in the metallic state in placer deposits, usually alloyed or associated with iridium, osmium, etc., and sometimes accompanies placer gold. It also occurs in some copper and nickel ores, as sperrylite ($PtAs_5$).

After washing the ore to separate sand and gravel, any gold is removed by amalgamation. The ore is then heated with dilute *aqua regia* under pressure, the solution evaporated, and the residue heated to 125° C. to convert any iridium or palladium into sesquichlorides, and then dissolved in hydrochloric acid. Ammonium chloride is added to precipitate ammonium platinic chloride, which is decomposed by strong ignition into platinum sponge, chlorine, and ammonium chloride, the two latter passing off. The sponge may be formed into bars or sheets by compressing, strongly heating, and then hammering or rolling.

Platinum is often contained in gold received at parting works. It may be recovered by dissolving the whole mass in *aqua regia*, precipitating the platinum by ammonium chloride, and throwing out the gold by ferrous sulphate or otherwise. Another method is to melt the gold for 2 or 3 hours with twice its weight of acid sodium sulphate. The mass is poured out, cooled, and washed with hot water. The gold is dried and fused again for several hours with a small amount of saltpetre. The platinum enters the slags, which are melted with litharge and charcoal to produce a platiniferous lead button; this is cupelled to remove the lead, the remaining metal dissolved in *aqua regia*, and the platinum precipitated by ammonium chloride.

In the **Wohlwill process** of parting gold and silver, platinum accumulates in the electrolyte, and is precipitated as the double chloride of platinum and ammonium, which is ignited as above.

Platinum is a soft, heavy metal (sp. gr. 21.4), fusing at about 1753° C., and having great resistance to corrosion by chemical agents. Its coefficient of expansion is nearly the same as that of glass, so it can be sealed into tubes and bulbs for chemical apparatus and electrical purposes. When alloyed with a little iridium, its hardness and inertness are increased. Its largest uses are for chemical apparatus, sulphuric acid stills and contact mass, in electrical work and for jewelry.

MERCURY

Mercury is obtained from **cinnabar** (HgS) by a combined roasting and distillation. Lump ore is treated in shaft-furnaces heated by external fireplaces, or sometimes the fuel is mixed with the charge. Hand reverberatory furnaces are sometimes used for fine ore, but this is more often treated in a special form of shaft-furnace, shown in Fig. 136.* Ore after drying on the platform (P) goes to the feed hopper (E); then slides down the zigzag path formed by sloping shelves (S); hot gases from the fireplace (A) pass in counter-current movement to the

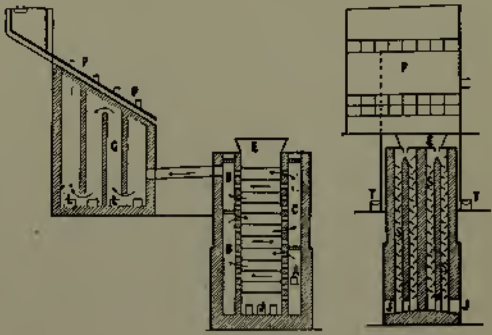

Fig. 136.

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* After Symington, Mineral Industry, Vol. VII, 585.

ore, between the shelves to (B) and back to (C); thence to (D), and from there into condensing chambers (G). The spent ore is withdrawn through (J). The excess of air from the fireplace supplies oxygen for the reaction, —

$$HgS + 2\ O = Hg + SO_2.$$

The mercury vapor and SO_2 are carried by the draught into the chambers (G), from which the condensed mercury passes through (L) into the collecting troughs (T).

In some cases the mercury is condensed in a long series of brick or cement chambers, similar to those shown in the figure; in others it passes through a series of zigzag pipes which are externally cooled by dripping water. These pipes are of iron (cemented inside to resist the corrosive action of SO_2 and SO_3), or of glazed clay, or even of wood. The condensed mercury is drawn off from the bottom bends of the pipes. At the end of the condensers there is commonly a suction fan to deliver the gases and any uncondensed fumes to the chimney. The main purpose of this fan is to insure a suction instead of a pressure in the whole apparatus, and thus prevent the poisonous mercury vapor escaping from accidental cracks.

On the walls of the condensers a considerable quantity of " soot " collects, consisting largely of fine globules of mercury mixed with carbonaceous soot, ore dust, mercuric sulphate, etc. This is mixed with lime or ashes, and is treated by stirring and pressure in specially designed pans, whereby much of the mercury is made to coalesce and passes out through holes in the bottom of the pan. The residue in the pan is returned to the furnaces, preferably being first formed into bricks.

ALUMINUM

Aluminum is produced by electrolyzing alumina (Al_2O_3) in a fused bath of cryolite ($Al_2Na_6F_{12}$) in large rectangular iron pots with thick carbon lining. The pot itself forms the cathode, while several large graphite rods suspended in the bath serve as anodes. To start the process, the anodes are lowered into contact with the pot, and powdered cryolite is gradually introduced and melted by the heat of the arc; when a large enough bath is formed, the anodes are drawn $\frac{1}{2}$ to 1 inch away from the lining of the pot. Some alumina is then stirred in, and small pieces of carbon (old electrodes) placed on the surface to prevent loss of heat by radiation. The resistance of the cryolite bath is quite high, but drops when the alumina is added, so that the voltage of the cell is 10 or less. A subsequent rise indicates that more alumina is needed in the bath, since alumina and not aluminum fluoride is decomposed. Each anode carries 250 to 300 ampères, and if a short circuit increases this, the copper rod, to which the anode is fastened, becomes very hot. The process is continuous, and at proper intervals the metal is ladled or siphoned out. The oxgyen liberated at the anode oxidizes the latter.

The quality of the product depends on the purity of the alumina used. The best grades are 99.5 to 99.9 per cent pure. The poorer grades, made from unpurified bauxite, contain 94 to 96 per cent aluminum, the rest being iron and silicon.

Bauxite (hydrated oxide of alumina with more or less iron) is the chief source of the alumina as detailed on p. 283 (Bayers' process); **cryolite** (p. 113) may also supply a little.

Aluminum is a rather soft white metal, of low specific gravity (2.56), melting at 655° C. It is not readily oxidized by the air, nor is it corroded by common organic acids, and hence is suitable for cooking vessels. It alloys readily with copper, tin, zinc, and nickel; the bronzes containing it are stronger and less readily corroded than ordinary copper alloys. It is also used to deoxidize steel in casting, thus improving the quality of the castings. It is, however, difficult to solder, a fact which has limited its uses very much.

Aluminum alloys with copper, nickel, zinc, etc., are made direct as follows: a rectangular chest of fire-brick is lined with charcoal which has been treated with limewater to coat the particles with lime. Large carbon electrodes pass through opposite ends of the chest and nearly meet in the centre. A mixture of alumina and carbon is packed around the electrodes, and strips of copper or whatever metal is to be used for alloy are laid in the mixture. A cover of small charcoal is put in and a brick cover luted over all. The electric current heats the charge, and the electrodes are then gradually drawn apart so as to heat all parts of the chest. This movement of the electrodes is accomplished automatically by a shunt circuit which operates the vibrating armature of an electromagnet, after the manner of the automatic feed of an arc lamp, and thus maintains a constant strength of current. The aluminum appears to be produced, not by electrolysis, but by the reducing action of the carbon at the extremely high temperature of the electric arc, for the process is as successful with an alternating as with a direct current.

NICKEL

Practically all the world's nickel comes from the nickeliferous pyrrhotite (Fe_9S_{10}) of the Sudbury district, Ontario, and the garnierite (hydrated silicate of magnesia, nickel, and iron) produced in New Caledonia. Some sulphides, arsenides, and antimonides of nickel, *e.g.* nickel blend, NiS, kupfernickel, NiAs, etc., are found in Saxony and Bohemia. The Sudbury ore contains chalcopyrite ($CuFeS_2$), and the average assay is about 2 per cent each of Ni and Cu.

The ores are heap-roasted, and smelted for matte (sulphide of nickel, copper, and iron) and slag in blast-furnaces like those used in ordinary copper smelting, p. 613. Most of the iron is later removed from the matte in converters (see p. 615), leaving a product with about 80 per cent Ni + Cu and nearly 20 per cent S. Oxide and sulphide of nickel do not react to give metal as in the case of ordinary copper matte ($Cu_2S + 2\ CuO = 4\ Cu + SO_2$). Hence metallic nickel cannot be produced in the converter; it would all pass into oxide (provided the charge did not freeze). In the **Orford process** the 80 per cent matte is smelted in blast-furnaces with salt-cake (Na_2SO_4) and coke; the salt-cake is reduced to Na_2S. When the resulting matte settles and cools, the NiS is found at the bottom, while the Cu_2S, FeS, and Na_2S are largely combined in "tops," these two products being easily broken apart. If the tops are left to weather, their Na_2S changes to NaOH; and upon melting with another portion of nickel-copper matte, the caustic passes again into Na_2S, and another separation of NiS is obtained. The bottoms may require a second smelting with salt-cake to remove the remaining iron and copper. The nearly pure NiS is dead-roasted, and the resulting NiO is reduced to metal by fusing with charcoal in graphite crucibles.

In the **Mond process**, the Bessemerized matte, nearly free from iron, is dead-roasted, crushed to pass a 60-mesh screen, and treated with warm dilute sulphuric acid, which dissolves much of the copper and a little nickel. The residue is sent through a reducing tower which is 25 feet high, contains 14 hollow shelves, and has mechanical rabbles to move the ore from one shelf to the next. The upper seven shelves are heated to 250° C. by burning producer gas inside of them. Water gas is passed through the furnace in contact with the ore, and reduces the NiO to nickel. The lower seven shelves are cooled by passing water through them, and the ore is brought to 50° C. It then goes to a volatilizing tower (similar to the reducer, but not arranged for heating), through which carbon monoxide is passed. This forms nickel carbonyl (NiC_4O_4), which is volatile and passes through a filter to remove dust, and then into a decomposing cylinder filled with granules of nickel and maintained at 200° C. by passing hot air through internal flues. The $Ni(CO)_4$ decomposes at this temperature, depositing its metal on the particles already present, while the CO is removed by a fan and returned to the volatilizer. The grains of nickel are continuously but slowly withdrawn from the bottom of the decomposer and screened, the small particles being sent back. Care is used that the temperature of the reducing tower does not get much above 250° C.; at higher temperatures Fe_2O_3 is reduced to iron, which forms a carbonyl in the volatilizer, to be carried along with the nickel carbonyl and deposit its metal in the decomposing tower. The ore from the volatilizer returns to the reducing tower, and the cycle between these two must be repeated several times to obtain a satisfactory extraction.

In the **Browne electrolytic process**, the copper-nickel matte is crushed to 1 mm., given a dead roast, and then reduced by charcoal in a reverberatory furnace to metallic nickel and copper; half of this is cast into anodes, the other half is granulated in water. The granules are chloridized in a " shot tower " by treating with water, chlorine, and a little hydrochloric acid, producing $NiCl_2$, Cu_2Cl_2, and a little $FeCl_2$. Common salt is also used to dissolve the Cu_2Cl_2. This solution serves as electrolyte for the anodes; copper and any silver deposit on the cathode, while nickel remains in solution. For all the nickel dissolved from the anodes, a molecular equivalent of copper deposits on the cathodes; hence the electrolyte becomes gradually impoverished in copper; and when the solution finally flows out of the tanks, it contains only 1 part of copper to 80 of nickel. This copper is precipitated by Na_2S and returned to the roasting furnace. The small quantity of $FeCl_2$ is then oxidized with chlorine gas, and $Fe(OH)_3$ precipitated by adding NaOH. The decanted solution is continuously evaporated in a special furnace until the NaCl separates; and the remaining hot solution of $NiCl_2$ is electrolyzed, using insoluble anodes (Acheson graphite), which are enclosed in porous clay tubes, open at the bottom to permit free circulation of the electrolyte. Of the chlorine collected in these tubes a small portion is used to oxidize $FeCl_2$, as mentioned above, but most of it passes to the " shot tower " to chloridize a fresh supply of metal. The NaCl from the evaporator is also returned to the shot tower. The HCl added to the latter makes up for the chlorine lost in the process. The hydrogen escapes from the tower to waste. An average analysis of Mond nickel is: 98.32 per cent Ni, 0.064 per cent Cu, 0.513 per cent Fe, 0.914 per cent C, 0.058 per cent S, and 0.034 per cent Si. Orford nickel averages about 98.6 per cent Ni, 0.3 per cent Cu, 0.7 per cent Fe, 0.2 per cent C, 0.08 per cent S, and 0.05 per cent Si. The Mond and Orford products are pure enough for steel manufacture and nickel plating.

To obtain nickel from garnierite, the latter is smelted in a low blast-furnace, either with the calcium sulphide waste from Leblanc soda manufacture, or with gypsum ($CaSO_4$, 2 H_2O), which is reduced to CaS by the coke. The calcium sulphide reacts with nickel silicate to form nickel sulphide and calcium silicate. As the ore contains considerable iron, some ferrous sulphide is also formed and enters the matte; the various silicates unite to form the slag. After the gravity separation of the matte and slag, the former is either treated in converters, or is roasted and then smelted with sand (in a blast or reverberatory furnace) to slag the iron and leave a second matte containing much nickel and little iron. As no copper is present to need separation, this matte is dead-roasted, and reduced to metallic nickel by melting with charcoal in graphite crucibles.

Nickel is a hard, lustrous, white metal which fuses at 1484° C.; its specific gravity is 8.9. It takes a high polish and is stable in dry air; when exposed to damp it tarnishes, but it is not attacked by alkalies. Cast nickel contains carbon and is not malleable. Its electrical conductivity is less than that of iron, and some of its alloys are much used in electrical work. It is extensively used for plating iron and other metals by electrodeposition. The nickel coinage consists of one part nickel to three parts copper. Over 60 per cent of the nickel now refined goes into nickel-steel. Steel containing from 2½ to 3½ per cent of nickel has unusual strength and elasticity. *Invar,* a steel with about 36 per cent of nickel, has practically no coefficient of expansion with heat. *Monel metal,* an alloy made by the direct reduction of copper-nickel matte, is stronger than ordinary steel and has valuable acid-resisting properties. Because of its great coloring power, nickel is used to make silver-white alloys with copper or with copper and zinc (*e.g.* German silver).

SODIUM

Sodium is produced from fused caustic soda by the Castner electrolytic process. In Fig. 137 * the caustic (A) is fused by gas jets (G). The current passes from the iron anode (F) to the cathode (H); and, after the process is under way, the current supplies enough heat to keep the bath fused. Oxygen is liberated at the anode, and both sodium and hydrogen at the cathode. The metal, being lighter than the electrolyte, rises into the covered receiver (C) from which it is ladled out, or it may run out continuously through a suitably arranged pipe, while hydrogen escapes through the cover; the oxygen escapes around the outside of the receiver. To prevent combination of the oxygen with the sodium as they rise, a diaphragm of wire gauze is suspended from the receiver and surrounds the cathode; also the inner diameter of the receiver is larger than the outer diameter of the cathode. As the decomposition proceeds, fresh caustic is introduced through (P).

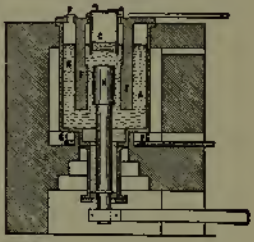

FIG. 137.

The chief uses of sodium are for the manufacture of peroxide and cyanide, and in the preparation of certain coal-tar products.

ARSENIC

There is little demand for metallic arsenic, its chief use being to harden lead used for making shot, to which it gives a spherical shape. Less than 1 per cent of arsenic is added, and this is often reduced from As_2O_3 in contact with molten lead, under a cover of charcoal.

Metallic arsenic is obtained from mispickel (FeAsS) by a system of retorts and condensers resembling those used in the distillation of zinc, but much smaller. The process is a simple decomposition according to the equation, $FeAsS = FeS + As$.

The chief metallurgical product is white arsenic (As_2O_3), which is used in the manufacture of orpiment, realgar, Paris green, Scheele's green, lead arsenate and other agricultural sprays, etc. Its chief sources are mispickel and the flue dust that results from roasting and smelting certain lead, copper, and tin ores. This flue dust is charged into a reverberatory furnace, preferably gas fired to prevent discoloring the product, and the As_2O_3 resublimed.

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* C. F. Chandler, Mineral Industry, Vol. IX (1901), 764.

ANTIMONY

Antimony is used to make hard lead for type-metal, for machinery bearings, for fans, blowers, and other apparatus used in chemical works, etc.; it is alloyed with copper and tin for similar purposes, and for pewter and Britannia ware. A good deal of antimonial lead is obtained in working up the skimmings from softening furnaces in lead refineries; but unalloyed antimony comes from stibnite, Sb_2S_3. The ore is ground moderately fine and is either roasted to oxide, which is then reduced by charcoal in crucibles, or the Sb_2S_3 is reduced directly by metallic iron, thus: —

$$Sb_2S_3 + 3\ Fe = 2\ Sb + 3\ FeS.$$

Wrought-iron scrap and turnings (often tinned iron scrap) and ore, together with common salt or salt-cake, are mixed and charged into crucibles, each holding 60 pounds or more, a sizable ball of the scrap iron placed on top of each, and a number of the crucibles lowered into a long, narrow reverberatory, through holes in the roof. The salt-cake serves to flux the gangue minerals in the ore, and also to give a good separation of the comparatively heavy ferrous sulphide from the reduced antimony. When fusion is complete, the crucibles are removed and their contents poured into cast-iron moulds. As an excess of iron is used, in order to certainly reduce all the antimony, the product contains several per cent of iron; this is removed by a second melting with a small quantity of clean stibnite liquated from the ore by a moderate heat. This leaves a little sulphur in the product, to be removed by a third fusion with some potash or soda. The mass is then poured into moulds and allowed to cool slowly before breaking off the cover of flux. When the work is successfully done, the surface of the antimony has a distinct crystalline or "starred" appearance.

BISMUTH

Bismuth is found in Saxony, Bohemia, England, Peru, Chili, and Australia, either as native metal or in connection with silver, cobalt, nickel, and arsenic ores. Bismuth glance (Bi_2S_3) and bismuth ochre (Bi_2O_3) are also found associated as ores to some extent.

The ores are commonly roasted to remove sulphur and part of the arsenic, and then may be reduced by fusing in crucibles with coal, iron, and flux; by this a speiss is formed, containing nickel, cobalt, iron, and arsenic, and beneath this layer is the metallic bismuth. The gangue minerals mostly pass into the slag which forms the top layer. The speiss has a higher melting point than metallic bismuth, and as soon as it solidifies on cooling, the bismuth is tapped off. The crude metal is then liquated on a slightly inclined iron plate, at a very moderate heat, a pure bismuth flowing away from the associated impurities, which remain on the plate as dross; or the antimony, arsenic, etc., may be removed by fusion with soda and nitre, the impurities passing into the slag. Oxidized ores are sometimes reduced by fusion with coal or iron, in crucibles or in reverberatory furnaces. Formerly the ores were liquated in slightly inclined iron tubes, but the yield was not very good. A wet process of extraction is sometimes used for carbonate and oxide ores, and for litharge obtained by cupelling argentiferous lead containing bismuth in the Pattinson process (p. 622); this consists in dissolving in hydrochloric acid and precipitating the metal by inserting metallic iron in the solution; or the solution is poured into water and the precipitated oxychloride is dried, after washing, and reduced with charcoal.

Bismuth is a reddish white, crystalline, and brittle metal, melting at about 260° C. Its specific gravity is 9.82, the hardness between 2 and 2.5, and the metal is but little attacked by atmospheric agencies. It forms easily fusible alloys with lead, tin, and cadmium (Newton's, Rose's, and Woods's metal). The commercial metal usually contains small quantities of silver, lead, copper, iron, arsenic, and sulphur. These are removed by remelting with fluxes in crucibles, or by other special treatment, before the metal is suitable for pharmaceutical purposes. The basic nitrate (subnitrate) finds considerable use in medicine as an internal remedy in case of stomach and intestinal irritation, and as powder for external application to ulcerated skin and mucous surfaces.

MAGNESIUM

Magnesium is practically all produced by the direct electrolytic reduction of fused carnallite * ($KCl, MgCl_2$), to which some common salt or fluorspar is added as flux. The iron crucible is made the negative electrode. Details of the process have not been made public, and the industry is in the control of a few firms.

The metal is used in pyrotechnics and as "flash powder" and ribbon for photographic purposes. It is a valuable deoxidizer in casting copper alloys, especially Monel metal, and its use is steadily increasing.

An alloy of magnesium with aluminum is on the market, under the name "magnalium." It is a silver-white, very light metal, and is coming into use in aviation.

Magnesium is a silver-white metal, having a specific gravity of 1.74, and melting at about 750° C. It oxidizes slowly in the air, and is attacked by hot water.

ALLOYS

While the properties of many alloys, such as strength, hardness, etc., have been known for a great while, their true nature was not appreciated till the microscope and pyrometer were brought to the aid of chemical analysis and mechanical testing. The microscopical examination of small sections that have been carefully polished, and then etched with suitable reagents, shows that the physical constitution of a metal or alloy exhibits in a very marked way the effects of mechanical or heat treatment, and often explains clearly the influence of minute quantities of an impurity. A pyrometer inserted in a metal alloy that is allowed to cool often shows a temporary halt in the cooling. This indicates that one portion of the metal is solidifying and giving out its latent heat of fusion; the cooling then continues till the whole mass is solid. These two lines of investigation have developed the modern science, *metallography*, which has shown that some alloys are definite compounds, some are solid solutions of one metal in another, some are mere mechanical mixtures, and others are combinations of these conditions.

The important metals used for ordinary alloys are copper, lead, zinc, and tin; of minor importance are nickel, aluminum, antimony, bismuth, etc. Iron alloys will not be discussed here, but nickel, chromium, tungsten, etc., are important in connection with steel. Alloys are often harder and stronger than either of the constituent metals.

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* Magnesium chloride residue from the salt industry is also said to be used.

The preparation of alloys requires care and skill. The least fusible metal is melted first and the more fusible added later, unless the former is used in only a small amount. Sometimes the heaviest metal is added last to prevent it settling to the bottom. Thorough stirring with a graphite, wooden, or iron rod is necessary before casting. To prevent oxidation, it is often necessary to cover the metal with fine charcoal. When dealing with a volatile metal, such as zinc, care must be used not to have too high a temperature, and not to keep the alloy hot too long.

Following are a few of the important alloys: —

Brass is an alloy of copper and zinc, but small quantities of lead, tin, etc., are sometimes added, either intentionally or because the raw materials are not pure. It is harder and stronger than either copper or zinc, and works much better in a lathe or other cutting machine; but it is not so ductile as the metals composing it. Copper, though possessing highly desirable physical properties (ductility, strength, etc.), cannot be successfully cast owing to oxidation; the cuprous oxide formed is soluble in the metal itself and causes brittleness and blowholes. By the addition of an electropositive metal this oxide can be removed, zinc being most frequently used, a large excess giving the best result. Common yellow metal, or Muntz metal, contains about 60 per cent copper with 40 per cent zinc. When intended for turning, drilling, or other cutting processes, the addition of about 2 per cent lead is advantageous; but for rolling or hammering, lead should be absent, as it causes the metal to crack.

Bronze is usually understood to be copper alloyed with tin up to 25 or 30 per cent, but zinc is often present, and sometimes other metals, to produce the desired qualities. It is used for a variety of purposes, such as machine parts, bells, statues, medals, etc. The metal oxidizes easily during melting, and the tin is insufficiently electropositive to reduce the cuprous oxide formed. By adding more electropositive elements, such as aluminum, phosphorus, or silicon, in small amounts, the oxide is more effectively removed, and a homogeneous dense and strong product is obtained. Aluminum bronze contains from 2 to 10 per cent aluminum; phosphor-bronze contains from 0.25 to about 2.50 per cent of phosphorus alloyed as tin phosphide. Ordinary bronze is rather brittle; but, if heated, and quickly cooled in water, it becomes quite malleable.

Bearing metal or Babbit metal, which is largely used for machinery bearings, usually contains 88.9 per cent of tin, 7.4 per cent of antimony and 3.7 per cent of copper.

Solders are used as a convenient means of uniting metals and must melt at a lower temperature than the metals to be joined. The ordinary plumber's or soft solder consists of tin and lead in varying proportions. The hard solders for uniting copper, brass, etc., contain copper and zinc, with occasionally a little tin. Silver solder is mostly silver, with a little copper and zinc; and gold solder is gold, with a little copper and silver.

Type metal usually contains 70 to 80 per cent of lead, 20 to 25 per cent of antimony, sometimes a little tin, and occasionally copper. The antimony, etc., give the necessary hardness, and cause the metal to expand on cooling so as to fill the moulds perfectly and give sharp impressions. More than 25 per cent antimony makes the metal too brittle and too hard.

Aluminum alloys are very useful where light weight is important, and some of them are also very strong.

Fusible Alloys. — The melting temperature of an alloy is usually less than the average of its component metals, and often less than the melting temperature of its most fusible constituent. For example, the most fusible alloy of copper and silver, Cu_2Ag_3 (28 per cent Cu, 72 per cent Ag), melts at 770° C., while copper melts only at 1084° C., and silver at 960° C. Some alloys, however, are less fusible than either constituent; SbAl does not melt till it reaches 1080° C., which is more than 400° above either of its metals. The most fusible commercial alloys are those used for fusible plugs on automatic sprinklers for fire protection; there are several of bismuth, lead, and tin that melt between 90° and 100° C. With 50 per cent bismuth, 27 per cent lead, 13 per cent tin, and 10 per cent cadmium, the melting point is about 60° C. Sodium and potassium, united in molecular proportions, melt at $4\frac{1}{2}$° C., their individual fusing points being 95° and 60°.

Coins. — The United States standard for gold and silver coins is 90 per cent of these metals, the rest being copper; the pure metals are too soft to withstand wear. The standard in some countries contains a little less copper than the above. The United States standard for nickels is 75 per cent copper and 25 per cent nickel; for one-cent pieces, 95 per cent copper, $2\frac{1}{2}$ per cent tin, and $2\frac{1}{2}$ per cent zinc.

REFERENCES

Metallurgy of Steel. Howe, New York, 1890.
Copper Smelting. Peters, New York, 1895.
Aluminium. Richards, Philadelphia, 1896.
Introduction to the Study of Metallurgy. Roberts-Austen, London, 1902.

Text-book of Mineralogy. Dana, New York.
Manufacture and Properties of Iron and Steel. Campbell, New York, 1903.
Metallurgy of Lead. Collins, London, 1899.
Metallurgy of Iron. Turner, London, 1900.
Metallurgy of Lead. Hofman, New York, 1901.
Metallurgy of Silver. Collins, London, 1900.
Metallurgy of Gold. Rose, London, 1902.
Metallurgy of Zinc and Cadmium. Ingalls, New York, 1903.
Metallurgy of Steel. Harbord, London, 1904.
Handbook of Metallurgy. Schnabel, translated by Louis. 2 vols., London, 1905.
General Metallurgy. Hofman, New York, 1913.
Transactions of the American Institute of Mining Engineers. New York.
Engineering and Mining Journal. New York.
Transactions of the Institute of Mining and Metallurgy. London.
Metallographist. Boston.
Metallurgie. Halle, Germany.
Mineral Industry. New York.
Mineral Resources of the United States. U. S. Geological Survey. Washington.
Mines and Minerals. Scranton.
Metallurgical and Chemical Engineering. New York.

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