CHEMISTRY OF ENGINEERING MATERIALS

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PREFACE TO THE THIRD EDITION

In the six years that have elapsed since the previous revision of this text, the new developments in the fields with which it deals have been unusually rapid, and a new revision has become necessary in order to bring the subject matter into conformity with the advances that have been made. The work of Bergius, Fischer, and others on the conversion of coal into oil by hydrogenation has changed the outlook with respect to the fuel situation. The development of the high-compression engine, with its demand for anti-knock gasoline, has caused a swinging from the liquid-phase to the vapor-phase methods of cracking petroleum intermediates. The commercial production of light, strong aluminum alloys, capable of hardening by heat treatment, has made necessary the presentation of a new theory relating to the hardening of metals. With the placing of the Aston process on a commercial basis, an entirely new principle has been injected into the age-old method of manufacturing wrought iron. The introduction of a non-ferrous alloy, harder than the sapphire, for tool bits has proven to be of great importance in industries employing machine tools. The work of Evans and his collaborators has apparently solved the baffling problem of the passivity of metals. In revising the text, these developments and many similar ones have received attention.

In the chapter on non-ferrous metals, magnesium and cadmium have been added to the industrial group; and the metallurgical processes, properties, and uses of all the metals have been described more fully. Several new pages, including more photomicrographs and more thermal diagrams, have been added to the chapter on non-ferrous alloys. The presentation of the subject of iron corrosion has been greatly improved by a discussion of the effect of primary oxide films. The chapter on foundry sands has been entirely rewritten. A section on high early-strength cements has been added to Chapter XI. The cellulose nitrate lacquers and lubricating greases, both of which have gained in importance through the growth of the automobile industry, have been treated in a manner more in keeping with their present extensive use. Through improvement in either the subject matter or in the method of presentation, most of the chapters have been modified to an important degree.

The author wishes to acknowledge his indebtedness to Liddell's "Handbook of Non-ferrous Metallurgy," Jeffries and Archer's "Science of Metals," Sutermeister's "Casein and Its Industrial Applications," and Klemgard's "Lubricating Greases." He wishes to thank all of those who have read portions of the revised manuscript, particularly Dr. Ulrich R. Evans for his helpful suggestions with respect to the treatment of the corrosion of metals. He desires also to thank the members of the Research Bureau of the Koppers Company for their help in revising the section on the by-product coking of coal. Finally, he ventures to express the hope that the new edition may be accorded a reception as kindly as was granted the two previous editions.

R. B. L.

PITTSBURGH, PA.,
January, 1931.

PREFACE TO THE FIRST EDITION

The preparation of this text has been brought about by the pressure of circumstances. The author has for nine years been conducting a course in Chemistry of Materials in the College of Industries of the Carnegie Institute of Technology, and has been considerably inconvenienced by the lack of a text. The particular object of the work is to supply information concerning the chemical properties of the materials employed in the various courses in Building Construction and Equipment, and in Machinery Construction and Operation, so that these materials might be used more intelligently and, therefore, to a better advantage. Although there are many texts on Industrial Chemistry covering the methods by which these materials are manufactured, nothing has appeared emphasizing their properties from the standpoint of the user. This is, then, the special purpose of the present text. It would naturally be understood that it is not possible to divorce entirely the discussion of the properties of any material from the discussion of the methods of its manufacture, but the latter have not been emphasized or presented in detail.

In preparing the material, the aim has been to avoid complexity of treatment in so far as possible, without becoming superficial. Although the treatment is by no means exhaustive, it is sufficiently complete to enable the student to gain a reasonably thorough knowledge of the various materials. Some theories, such as those that account for corrosion, the hardening of cements, the effect of the heat-treatment of steels, the electrochemical action in primary and secondary cells, etc., have been introduced; and although the nature of the work has made a full consideration of them inadvisable, it is believed that they have been developed in sufficient detail to avoid inexactness.

A prior course in Elementary General Chemistry has been assumed; indeed, this is considered essential not only for the study of this text, but for the understanding of any literature dealing with these or similar subjects. No special effort has been made to avoid the use of technical terms. It is considered one of the purposes of the text to explain such terms, and render them sufficiently familiar so that students whose training otherwise might be insufficient for the demand, may be encouraged to make use of reference works, scientific magazines, journals, and similar literature in which technical terms are commonly employed. In fact, the author feels that if the text accomplishes no other object than to point the way to such sources of knowledge, it will have performed a valuable service.

The references to literature, from which a considerable amount of the material of the text has been drawn, have been indicated in the footnotes and listed at the ends of the chapters in order that the student may have recourse to them to extend the study of the subject when this is desired. An effort has been made in all cases to acknowledge the source of information obtained from these writings, and if any such acknowledgment has been omitted, it has not been done designedly.

The author wishes to acknowledge his indebtedness to C. A. Coulter for his aid in preparing certain illustrations. Also, he wishes to thank the following publishers for permission to use illustrations: Charles Griffin and Company, Ltd., for photomicrographs from their treatise on Alloys by Gulliver and Law; Sauveur and Boylston for photomicrographs from Sauveur's "Metallography of Iron and Steel"; McGraw-Hill Book Company, Inc., for photomicrographs from Gardner's "Paint Technology and Tests"; and the following manufacturers for photographs and electrotypes: Harbison-Walker Refractories Company for photomicrographs and illustrations of metallurgical furnaces and coke ovens; Pratt and Lambert for photographs relating to varnish and varnish materials; The Edison Storage Battery Co. and the Electric Storage Battery Co. for electrotypes showing their products.

R. B. L.

PITTSBURGH, PA.,
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CHEMISTRY OF ENGINEERING MATERIALS

CHAPTER I

WATER FOR STEAM GENERATION

Because of the intimate connection of steam with the development of power, and because of its wide application in other ways, the whole subject of steam generation is of considerable importance. But, since the conversion of water from the liquid to the vapor phase is essentially such a simple process, the need for intelligent supervision in the development of steam from natural waters on an industrial scale is apt to be overlooked. The purpose of the present chapter is to discuss briefly the more important of the many real problems connected with the process. The difficulties that attend the successful operation of steam boilers are due in a large measure to the impurities in the waters available for use, and these must, therefore, be considered first.

Impurities in Natural Waters.—In a chemical sense, all natural waters are to some degree impure. Even rain water, which is the purest form, contains solid matter, both organic and mineral, obtained by washing out soot and wind-raised dust from the air. In fact, the generally accepted theory now is that the production of rain depends upon the presence in the air of dust particles, which serve as nuclei about which the drops may form. All waters obtained from the earth, whether from the surface or lower depths, contain dissolved substances taken up from the rocks and soils with which they have been in contact. Water from very low levels, as from deeply bored wells, is likely to contain larger quantities of dissolved substances than surface water, because of the great mass of rock through which it has percolated. In general, water from regions of granite, sandstone, and clay formations contains much less dissolved mineral matter than that from limestone regions. Further, water from rocky regions is purer than that from regions where the rock has been disintegrated to form soil, since rocks are generally less soluble than soils. Mountain waters are relatively pure because they usually come into contact with little soil. Besides the dissolved substances, water may carry a great deal of suspended matter, as silica, clay, organic material, etc. This is especially true of surface waters, such as those from rivers and other streams.

Hard Water.—Water that contains dissolved calcium, magnesium, and iron compounds, generally as the sulfates and bicarbonates, is known as "hard water." The application of this term should be confined to water containing these substances, but it is used loosely in popular language to apply to acidulated water, or to water containing any substance that will destroy soap. Soap, reacting with the calcium, magnesium, and iron compounds, forms sticky, insoluble, curdy soaps of these metals. For example, the reaction of sodium stearate, an ordinary sodium soap, with calcium sulfate is as follows:

$$2Na(C_{18}H_{35}O_2) + CaSO_4 \rightarrow Ca(C_{18}H_{35}O_2)_2 + Na_2SO_4$$

The soap continues to react with such salts in this manner until they have all been thrown out of solution; until this has been accomplished, the soap cannot form a lather.

The hardness of water is generally recognized as being of two kinds. That which is removable by boiling is said to be "temporary," that which persists after boiling is said to be "permanent."

Temporary hardness is caused by the presence of bicarbonates, especially of calcium, but also of magnesium and iron. The normal carbonates of these metals are practically insoluble in water alone, but in water that contains carbon-dioxide gas they are converted into their corresponding bicarbonates, which are much more soluble compounds. Consequently, water coming from limestone regions, where much organic matter also exists, will likely contain much of this sort of hardness. The organic matter, decaying, produces carbon dioxide, and this in the presence of water produces carbonic acid which acts on the limestone as follows:

$$H_2O + CO_2 \rightarrow H_2CO_3$$
$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

Marl is a mixture of calcium carbonate and organic matter; hence, water from marl deposits contains much calcium bicarbonate.

Permanent hardness is caused by the sulfates of calcium, magnesium, and (ferric) iron, especially the sulfate of calcium. These sulfates, in general, are not removed by boiling, although calcium sulfate is less soluble in boiling water than in water at atmospheric temperature.

Acidity of Mine Water.—In streams fed by tributaries that carry drainage from mines, or from refuse that has been removed from mines, the water may contain considerable free sulfuric acid. The acid is produced by the wet oxidation of such sulfides as marcasite or iron pyrite (FeS_2) as follows:

$$4FeS_2 + 15O_2 + 6H_2O \rightarrow 4Fe(OH)SO_4 + 4H_2SO_4$$

Reports of Water Analyses.—Although the dissolved solids, such as sulfates, bicarbonates, etc., which the water contains, may be sufficient to cause considerable trouble in a boiler, the actual amounts are small compared with the water itself. If the solids shown by analysis were reported in percentages, their true significance might not be apparent, because even in a so-called "bad" water, the total solids may be only 0.03 or 0.04 per cent. An analysis reported on this basis, would, therefore, show approximately 99.97 per cent of water, a percentage that might lead one to believe that the water is essentially pure. In order to overcome this difficulty, and to avoid showing percentages in the third or fourth place of decimals, water analyses are reported in parts per million or grains per gallon. For the purpose of comparing methods of reporting, as well as of showing the relative suitability of waters for steam generation, the following table[1] is given:

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[1] Adapted from a table quoted by Benson, "Industrial Chemistry," p. 74.

RATINGS FOR WATER CONTAINING TEMPORARY HARDNESS (GEBHARDT)

Rating	Grains per gallon	Parts per million	Per cent
Very good	Less than 8	Less than 137	Less than 0.0137
Good	12–15	206–256	0.0206–0.0256
Fair	15–20	256–342	0.0256–0.0342
Bad	20–30	342–513	0.0342–0.0513
Very bad	Over 30	Over 513	Over 0.0513

With permanently hard water, for the same ratings the numbers shown in the preceding table should be divided by four.

Grains per U. S. gallon may be converted into parts per million by multiplying the number of grains by 17.1; or conversely, parts per million may be converted into grains per U. S. gallon by multiplying parts per million by 0.0584.

Solids Deposited within the Boiler.—During the conversion of water into steam, there is deposited within the boiler both the dissolved and the suspended matter that the water carried. The deposition is due to concentration brought about by evaporation of water, to a lessening of the solubility of the dissolved substance by the increased heat and pressure, or to reactions that produce insoluble substances from others previously soluble. As already stated, calcium sulfate becomes less soluble as the temperature and pressure rise. This is shown graphically by Curve 1 in Fig. 1.[1] Because of the increased temperature, the carbon-dioxide gas is expelled from the water, and the bicarbonates revert to the normal form. This may be illustrated by the equation showing the decomposition of calcium bicarbonate, as:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

Since the normal carbonates are much less soluble than the bicarbonates, they are thrown out of solution as a result of this reaction. The effect of the presence or absence of carbon dioxide, as well as the effect of temperature changes on the solubility of the calcium and magnesium carbonates, is shown in the following table:[2]

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[1] See p. 11.

[2] BENSON, "Industrial Chemistry," p. 67.

Solubilities in Parts per Million

Substance	In water at 60°F.	In water containing carbon dioxide at 60°F.	In water at 212°F.
Calcium carbonate	12	1,100	21
Magnesium carbonate	385	27,500	nearly 0

It should be noted that with increase of temperature the solubility of calcium carbonate *increases* slightly and the solubility of the magnesium carbonate *decreases* markedly.

Physical Character of the Deposits.—Depending upon the composition of the material, the temperature and pressure within the boiler, and other factors, the precipitated solids may remain in suspension, may form a loose sediment or sludge, or may produce a hard scale. The character of the deposit, however, is determined chiefly by the composition of the material. If the amount of calcium sulfate and magnesium compounds in the water is low, or if the quantity of suspended matter is high, the scale will be soft and loose, so that it may be removed from the boiler in the form of a sludge. But if the water is clear, having but little suspended matter, and the amount of calcium sulfate and magnesium compounds is high, the scale will be hard, dense, and difficult to remove. Thus, hard scales are more objectionable than soft ones, both because of their greater insulating effect and because of the greater expense in removing them.

The location in the boiler has much to do with the composition of the scale at that point. The carbonates are found near the feed pipe where the water first comes into contact with the heat and gives up its carbon dioxide. The calcium sulfate remains dissolved until it reaches the hottest part of the boiler.

Effects of Deposits.—The substances deposited in the various ways shown in the preceding paragraphs collect on the flues, in the tubes, or on other parts of the boiler and act as heat insulators, so that heat that would otherwise be available cannot pass into the water. Because of the poor transmission when the metal is coated with scale, it becomes so overheated, even red hot, that it is soft and subject to deformation. Because of the difference in the rate at which the metal and scale expand and contract with changes of temperature, if the water in the boiler becomes low and the metal is overheated, the layer of scale may separate from the metal. Then, if cold water is run into the boiler, the scale cools quickly, contracts, and cracks. When this happens, the water pours through the crack upon the hot metal, a large volume of steam is formed, and the sudden pressure that results may be great enough to burst the boiler.

In addition to its actual insulating effect, the scale is objectionable in other ways. As the tubes become clogged, the surface area of the water exposed to the heat is lessened and the heating efficiency falls. Moreover, the boilers must be cleaned—an expensive process, especially if the scale is hard and closely adherent.

TREATMENT OF BOILER WATERS

The scale-forming tendencies of water may be overcome by suitable treatment. As a preliminary measure, the suspended matter may be removed by some purely mechanical device. Coarse substances may be taken out by screens; the more finely divided material may be removed by filtering through sand, coke, wood fiber, or similar material. To lessen the work of the filters, a great deal of the suspended matter may be got rid of by allowing the water to stand in sedimentation tanks or basins.

The dissolved solids are less easily removed. Three general methods are employed for this purpose, namely: cold-water softening, in which the water is treated with chemical reagents in the cold; hot-water softening, which consists of heating with or without the use of chemical reagents;[1] and the conditioning of the water within the boiler.

Cold-water Softening.—In this process the soluble bicarbonates, sulfates, and chlorides are removed by converting them into the more insoluble normal carbonates and hydroxides by the use of "soda ash" (sodium carbonate) and lime. In order to convert the bicarbonates into the normal form, it is first necessary

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[1] For descriptions of commercial softeners of various types, see Christie, "Water Purification and Its Use in the Industries," and *Jour. Ind. Eng. Chem.*, **3**, 326, May, 1911.

to neutralize the carbonic acid present. For the removal of calcium bicarbonate, then, the reactions are as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$
$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

Calcium sulfate is converted into the normal carbonate, thus:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

The dissolved magnesium salts are converted into magnesium hydroxide, according to the following equations:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$
$$Mg(HCO_3)_2 + 4NaOH \rightarrow Mg(OH)_2 + 2Na_2CO_3 + 2H_2O$$
$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$

When the water is allowed to stand, the insoluble products of the preceding reactions settle out. As they settle, suspended matter, as silica, clay, and organic material, is carried down with them. The clear water is then drawn off and used. By this method, the dissolved solids can be almost completely removed.

In order more effectively to remove the suspended solids, including both the products of reaction and mud, the so-called *coagulum method* may be employed. In this process dissolved aluminum sulfate, or ferrous sulfate, is introduced with the slaked lime and soda ash. A flocculent, gelatinous precipitate consisting of the hydroxide of the metal is formed as is illustrated by the following equation:

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O \rightarrow 3Na_2SO_4 + 2Al(OH)_3 + 3CO_2$$

As the precipitate settles, the suspended matter is carried down with it. Sometimes, when the water has become partly clarified by settling, the residual suspended material is removed by rapid filtration through thin beds of coke, excelsior, or similar substances. The sodium salts formed by the use of sodium carbonate, being soluble, remain in the water, and although they do not contribute directly to the formation of scale, they may become objectionable because, as later described, they contribute to the production of foam. If the amount of permanent hardness is very great, it is sometimes not practicable to neutralize all of it, because of the large amounts of sodium salts that would be left in the water.

In determining the amount of calcium hydroxide and sodium carbonate necessary to correct the hardness, an analysis of the water is required. The softening cannot be properly carried out without it. Since the amount of hardness may vary widely within short periods, on account of the prevalence or absence of rains, and other varying factors, the amount present should be determined often, at least once a day. If the degree of hardness is not accurately known, then the chances are very great that either too little of the reagents will be added, and the hardness will be incompletely corrected; or too much will be used, and the excess in the water will be objectionable. Calcium hydroxide itself will cause hardness, and by secondary reactions will produce scale, while the sodium carbonate, as stated before, may become a factor in the production of foam.

Rather recently an interesting method of softening water in the cold has been developed; this method is known as the *zeolite process*. A zeolite is a double silicate of alumina and soda; either the natural or artificial variety may be employed. The artificial zeolite is made by fusing together feldspar, China clay, and soda ash; the resulting glass is cooled and crushed. The zeolite possesses the property of exchanging bases with other compounds. When hard water, containing calcium and magnesium salts is filtered through it, calcium and magnesium silicates are formed and the corresponding sodium salts pass into solution. After a time the calcium and magnesium compounds accumulate in the zeolite to such an extent that it refuses to act. When this happens, it is reactivated by allowing a solution of sodium chloride to stand in contact with it. The zeolite then replenishes its sodium content, and the absorbed calcium and magnesium are given off as chlorides. When the water passing through begins to show, by the soap test, any hardness, the zeolite is regenerated. By repeating the regenerating process, the zeolite may be used for many years. Water softened by the zeolite process contains only a small amount of calcium or magnesium salts, but an objection to the process is the high sodium-carbonate alkalinity obtained when treating waters high in bicarbonates.

Hot-water Softening.—The process of hot-water softening is carried out in feed-water heaters. These are adjuncts to the boiler, designed to conserve heat that would be wasted otherwise. Although the saving of heat is the most important function of these heaters, because of the heating, bicarbonates are decomposed, and so they effect a certain amount of softening as well. In many cases the heater is specially designed to take advantage of this softening effect. The heat conserved may come either from flue gases or from exhaust steam: if it comes from the former source, the device is generally known as an economizer; if from the latter, as a feed-water heater.

Economizers consist essentially of water tubes set in the flues leading from the furnaces.[1] They are so arranged that scale may be cleaned from the inside, and soot from the outside of the tubes. Because of the source of heat, much higher temperatures can be obtained in the economizer than in the feed-water heater; in fact, the conditions of pressure in the economizer very closely approximate the conditions in the boiler itself.

Feed-water heaters, which use steam as a source of heat, are of two kinds, open and closed. Open heaters operate at atmospheric pressure, and are more serviceable in softening water than those of the closed type, because, although the sulfates are not much affected, the gases can escape and the bicarbonates are to a greater extent removed. As has been explained, the sulfates tend to produce hard, and the carbonates soft, scale; consequently, boiler scale from water that has been merely preheated, although it will not be so great in amount, will be harder than that from raw water.

In closed heaters, the water is heated by pipes which pass through them carrying steam under high pressure. Or these positions may be reversed; the water may pass through the pipes, and the steam, under pressure, about them. Suitable arrangements are provided for cleaning the scale from the tubes.

In order that the sulfates also may be removed from the water, it is necessary to treat it with sodium carbonate in much the same way as in the cold process, but because of the heat, the sulfates are converted into the corresponding carbonates more readily. After the precipitate has been formed, the water is filtered.

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[1] ROGERS and AUBERT, "Industrial Chemistry," 2d ed., p. 60.

Conditioning of Water within the Boiler.—In this method of treating the water,[1] account is taken of the changed conditions in the boiler with respect to temperature and pressure. By the use of soda ash, calcium sulfate is converted into the carbonate, which then becomes the solid phase in equilibrium with the boiler water; since the carbonate does not form an adherent scale, it may be removed by a filtering device which operates as an adjunct to the boiler.

As shown by the curves in Fig. 1, the solubility of calcium sulfate decreases rapidly, and the solubility of the normal carbonate increases slightly with increase of temperature. Although the increase in the solubility of the carbonates is not marked, there is, nevertheless, an increase, and this fact becomes an important item in conditioning water by this method. As shown by the curves, at 450°F. the solubilites of the sulfate and carbonate are not far apart, although at 250°F. there is considerable difference between them.

Since the solubility of calcium sulfate decreases with increase of temperature, it is evident, as has been before explained, that if any is deposited at all, the deposit will be formed at the point where the temperature is the highest, which means that it will crystallize upon the walls of the tube or the boiler. Since calcium sulfate is now the solid phase in equilibrium with calcium sulfate in solution,[2] as the water is evaporated in the boiler, more calcium sulfate is deposited, and a hard, compact scale grows on the heating surfaces. The calcium sulfate may, however, be converted into the more insoluble calcium carbonate by the use of soda ash, as shown by the equation on page 7, and the formation of adherent scale will be thus prevented. The solubility of calcium carbonate becomes greater with increasing temperature; consequently, it does not deposit on the hot surfaces, but tends to remain in suspension in the water. Moreover, as the equation referred to shows, sodium sulfate is formed simultaneously with the calcium carbonate, and the presence of the common sulfate ion from this source helps further to decrease the solubility of the

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[1] For a full discussion of this method of boiler-water conditioning see Hall, Fischer, and Smith, "The Prevention of Scale Formation by Boiler-water Conditioning," *Iron and Steel Eng.*, June, 1924.

[2] For a discussion of this sort of equilibrium, see page 617.

calcium sulfate in accordance with the general principle of precipitation.[1] Likewise, an increase in the carbonate ion from the sodium carbonate decreases the solubility of calcium carbonate. These facts are depicted graphically by the curves in Fig. 1. Curve 1 shows the solubility of calcium sulfate in water, while

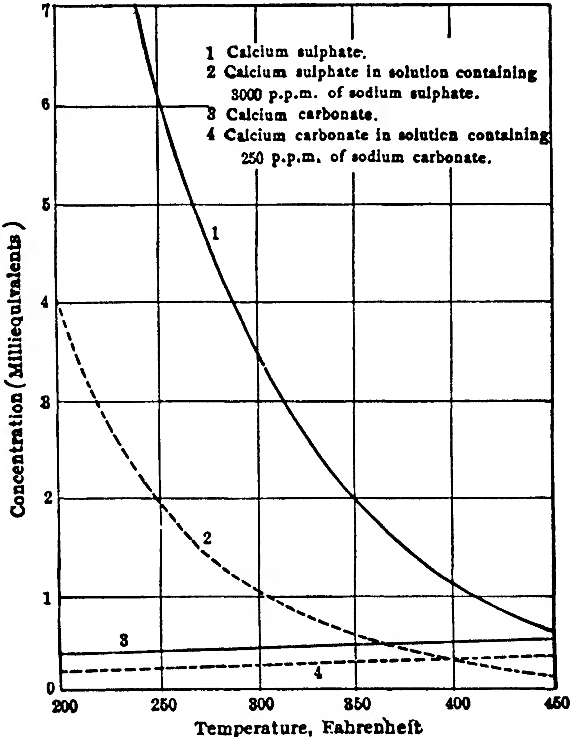

FIG. 1.—Curves showing the solubility of calcium sulfate and calcium carbonate in water and in the presence of sodium sulfate and sodium carbonate respectively.[2] (The ordinates are in milliequivalents; to change to parts per million, multiply by 68 for calcium sulfate, and by 50 for calcium carbonate.)

Curve 2 shows the comparative solubility in water containing 3,000 parts per million of sodium sulfate. Similarly, Curve 3

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[1] For a discussion of this principle, see Law of Solubility Product, in any modern text on Qualitative Analysis or Physical Chemistry.

[2] Reproduced by permission from Hall, Fischer, and Smith's article on "The Prevention of Scale Formation by Boiler-water Conditioning," *Iron and Steel Eng.*, June, 1924.

shows the solubility of calcium carbonate in water, and Curve 4 shows its lessened solubility due to the presence of 250 parts per million of sodium carbonate. In conditioning boiler water by this method, therefore, sufficient sodium carbonate is employed so that calcium carbonate in the solid phase, rather than calcium sulfate, is in equilibrium with the boiler water at the operating temperature (or pressure).

The Hydrolysis of Sodium Carbonate.—For boilers operating at 210 lb. gage pressure (385°F.) or less, sodium carbonate is a satisfactory reagent, but above this temperature it is to a large extent hydrolyzed with the formation of sodium hydroxide, as:

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$$

Due to the increasing concentration of hydroxyl ions from this source, calcium hydroxide, rather than calcium carbonate, is formed; and the concentration of the hydroxyl ions need not be markedly high before calcium hydroxide becomes the solid phase in equilibrium with the boiler water. The hydroxide of calcium, like the sulfate, decreases in solubility with an increase of temperature, and will form a scale in like manner. Therefore, for boiler pressures above 210 lb., sodium phosphate, rather than sodium carbonate, is employed because it hydrolyzes less readily. The phosphate is more expensive, but at the higher temperatures the carbonate will not serve. Although sodium hydroxide is frequently found in commercial "boiler compounds," it is not a suitable reagent for conditioning boiler water.

Removal of Precipitated Sludge and Suspended Solids.—The solid matter produced either by evaporation or by methods of conditioning the water must be removed from the boiler. This may be accomplished either by "blowing down," *i.e.*, changing a part of the water in the boiler, or by the use of a "deconcentrator," which is essentially a filtering device operated in conjunction with the boiler. In the latter case, a portion of the water is constantly being passed through the filter and then returned to the boiler. In this way the concentration of the solids is kept relatively low without the loss of heat that accompanies the blow-down method.

Boiler Compounds.—A great variety of materials is marketed under this name, the true merit of which is not infrequently

CHAPTER II

FUELS

Under the head of fuels are included all of those substances which, when burned, are capable of producing heat energy that may be utilized for domestic or industrial purposes. Fuels owe their ability to burn to the presence of two elements, carbon and hydrogen; and in the burning of all fuels the heat obtained is derived chiefly from these two constituents. In some fuels there is a small amount of sulfur which may burn and contribute to the heating value, but the quantity of heat thus derived is of little consequence. In the solid fuels, coal and coke, a great deal of the carbon exists in the free state, but in the gases, oils, and wood it is combined. Except in certain gaseous fuels, hydrogen is always in combination with other elements, usually with carbon and oxygen.

Principles of Combustion

Ignition Temperature.—In the ordinary sense, the terms "combustion" and "burning" are used synonymously to indicate the rapid union of oxygen with a combustible substance, a process that is accompanied by the evolution of heat, and generally by the production of light. Although heat is practically always produced by the union of oxygen with another substance, there may be no noticeable rise in temperature because the heat evolved may be conducted away as fast as it is formed. When the heat is produced more rapidly than it is disseminated, the temperature of the substance rises, and the speed of the reaction is increased. The increased speed of the reaction, in turn, causes the heat to be produced more rapidly, which accelerates
tion still more, until finally the ignition or kindling point
and the substance bursts into flame. The *ignition* or
ture is defined as "that temperature at which
nversely, as "tha erature below which

burning does not take place." Even when a substance is burning vigorously, if it is cooled to a temperature below its kindling point, combustion will cease. A candle flame, for example, may be extinguished by surrounding it with a coil of copper wire; a gas flame may be put out by inserting in it a mass of cold silver or copper. These metals are good heat conductors and readily chill the flame. Flames may be extinguished by a blast of air, because the moving air current carries away heat so rapidly that the temperature falls to a point below the kindling temperature of the burning substance.

Flame.—The term "flame" is generally used to describe the phenomena accompanying the rapid interaction of two or more gases. In most cases, one gas passes in the form of a stream into a larger volume of the other, and the reaction takes place at the surface of contact of the two. In the more familiar flames, some gas, such as hydrogen, coal gas, natural gas, or other gas ordinarily spoken of as combustible, reacts with oxygen of the air; and it is generally considered that it is the gas that is burned. The air takes an equal part in the reaction, however, and if a stream of it be passed into an atmosphere of so-called combustible gas with suitable ignition, the familiar flame form will appear, and the air may in the same sense be spoken of as burning. Nevertheless, in the present discussion, a flame will be considered to be produced by burning a fuel gas in free contact with air.

Although many solids burn with a flame, the flame is not produced by the burning of the solid directly. A flame always consists of incandescent gaseous matter. In a candle flame, for example, a combustible gas or vapor is continuously produced by the heat of the flame from the melted wax that ascends the wick. The flame of other burning solids, such as wood and coal, is produced in a similar manner.

Types of Flames.—When a stream of gas issues from a tube into air, the general shape of the flame is a hollow cone. The cone formation is due to the fact that the central part of the gas stream must rise higher than the outside before it can come into contact with air. The interior of the flame consists of [illegible] gases. If the end of a narrow tube be held in the [illegible] of the flame, gases may be conducted away and [illegible] This is true not only [illegible] ordinary gas fla produced by burning solids, as the candle flame, wood flame, etc. In the lower part of the flame, only the outer shell is relatively hot, a fact which may be demonstrated by holding a wire gauze in this section of the flame. The gauze will be heated only in the form of a ring. A match head may be held in the interior of the flame without being ignited, although the stick will be burned where it passes through the outer layer of the flame. Between the surface of the relatively cold interior cone and the outer margin of the flame proper, the actual burning takes place. According to the nature of the reactions that occur during burning, flames are divided into two classes, luminous and non-luminous.

Luminous Flames.—A candle flame will be considered as a typical example of the luminous flames. It consists of four parts:

1. The dark inner cone, which is common to both luminous and non-luminous flames, has just been described under Flame.

2. Surrounding the dark cone is a blue-colored layer that is best seen at the base of the flame, but which extends under the luminous part and encases the dark cone completely. In this layer or zone, the hydrocarbons are in part oxidized to carbon monoxide and hydrogen, as:

$$C_2H_4 + O_2 \rightarrow 2CO + 2H_2$$

These gases are in equilibrium with carbon dioxide and water formed at the same time, as:

$$CO + H_2O \rightleftarrows H_2 + CO_2$$

It is important to note the fact that carbon monoxide and hydrogen are produced here, since during imperfect combustion, as when the flame is chilled by striking a cold object, some of these gases may escape unburned; carbon monoxide is a very poisonous gas (see footnote on page 30).

3. The blue mantle is enclosed by the luminous cone. Although a number of investigators have worked on this subject, it is still only imperfectly known just what reactions take place in the luminous portion of the flame.[1] The fact that carbon is deposited

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[1] For a discussion of the various explanations offered to account for the luminosity of flames, see Mellor, "Modern Inorganic Chemistry," pp. 750–757, from which source the discussion here given has been in part derived.

on a cold object, as porcelain for example, is not accepted as evidence that free carbon is normally present in the flame, because changed conditions are known to exist when reactions take place in contact with solids. It has been shown, however, that when a candle flame is placed between a strong light and a screen, the luminous portion of the flame casts a dark shadow on the screen, and if the flame is caused to smoke, this shadow extends into that cast by the smoke. Because of this fact, it is believed that the luminosity of the hydrocarbon flame is due to the presence of incandescent solid matter, although luminous flames are known that contain no solids.

When hydrocarbon gases are heated in the absence of air, free carbon and dense hydrocarbons are formed; possibly reactions of a similar sort take place in the luminous cone.

According to Lewes,[1] between 800 and 1000°C., ethylene decomposes into acetylene and methane, thus:

$$3C_2H_4 \rightarrow 2C_2H_2 + 2CH_4$$

In addition to the acetylene and methane, more complex hydrocarbons are formed. At temperatures above 1200°C., acetylene breaks down into free carbon and hydrogen:

$$C_2H_2 \rightarrow 2C + H_2$$

It has been shown experimentally that luminosity is increased by preheating the air or gas and is decreased by cooling the flame.

It may be assumed, then, in some cases at least, that in the luminous cone, hydrocarbons are decomposed yielding acetylene and other hydrocarbons, together with free carbon and hydrogen.

4. The luminous cone is surrounded by a faint non-luminous mantle. It is best seen when the light from the luminous portion is suitably obstructed. In this mantle the combustion of the intermediate products is completed with the formation of carbon dioxide and water.

Non-luminous Flames.—The non-luminous, or bunsen, flame has only three parts; the luminous cone is absent. Luminosity is prevented by mixing air with the gas before it issues from the burner. Just why the admission of air causes non-luminosity is not easy to explain, and space cannot be given to it here.

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[1] Mellor, *loc. cit.*, p. 751.

It does not seem to be due alone to improved oxidation, because the introduction of nitrogen and other inert gases produces a like effect. With the same amount and same kind of gas being burned at the same rate to the same end products, the flame is smaller when non-luminous than when luminous. Thus, the non-luminous flame being more concentrated has a greater intensity, or is hotter, than the luminous flame, although the heat quantity produced by both is the same. If both were burned in the open air of a room, the temperature of the air would be increased as much by one as by the other, but if it were desired to heat an object locally, the non-luminous flame would be the more efficient.

Heat Radiated by Flames.—Since gases are poor radiators, non-luminous flames do not give off much heat by radiation. Because of this fact, when heating a room by means of a gas grate, for example, material such as fire clay forms or lattice work, asbestos matting, or asbestos wool is used. Although these substances become no hotter than the flame, they are better radiators; consequently, more heat is thrown off into the room, and a correspondingly smaller quantity passes into the flue with the products of combustion. Because a luminous hydrocarbon flame contains incandescent solid matter, it radiates heat to a greater extent than a non-luminous one. The bunsen flame radiates only about 12 per cent of the heat it produces, while a luminous flame radiates about 30 per cent.

Temperature of Flames.[1]—The temperature that may be obtained by heating a small body in a bunsen flame is said to range from 1100 to 1350°C.; in a gasoline blow-torch flame, from 1500 to 1600°C.; in the oxyhydrogen flame, about 2000°C.; and in the oxyacetylene flame, about 2400°C.

Oxidizing and Reducing Flames.—In the outer mantle of flames, especially at the tip, oxidation is completed and the temperature is very high. This portion is known as the oxidizing flame because of its ability to give up oxygen to substances that are capable of being oxidized. Metals are converted into their oxides by this flame. The inner part of the flame is called the reducing flame because that portion is seeking oxygen. It does not cause oxygen to combine with metals, but reduces

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[1] MELLOR, *loc. cit.*, p. 760.

oxides to the metallic state. The difference in this respect between the outer and inner portions of a flame may be investigated by holding a copper wire across different parts of the flame.

Conditions Necessary for Complete Combustion.—In order that combustion may be complete, two conditions must be fulfilled: there must be an excess of air; and the temperature of the fuel must be sufficiently high. Although an excess of air is desirable, this excess must not be too great, for the air in passing through the zone of combustion carries away heat and thus may retard burning by cooling the fuel. In a similar way, a cold object placed in a flame will interfere with combustion in its immediate neighborhood because of its absorption of heat. As long as the object is cold, the flame cannot touch it; there will be a clear space between the two. As the object grows hotter, the space will lessen; and when the object is as hot as the flame, an actual contact will be formed.

Ordinarily, when water is boiled in an open vessel, its temperature does not rise above 100°C. (212°F.). Since the temperature of an ordinary flame is considerably above 1000°C. (1832°F.), it is evident that the flame cannot be in contact with the bottom of the vessel. In the bunsen flame, the hottest part is just above the tip of the inner cone. Objects can be most advantageously heated by placing them at this point. If placed higher in the flame, they will heat less rapidly; if placed lower, they cool the blue-colored inner mantle in which the carbon monoxide and hydrogen are being produced. Under suitable conditions, the carbon monoxide and hydrogen formed in the inner mantle are oxidized to carbon dioxide and water in the outer mantle, but if the flame is chilled too quickly, as with a cold object, there may be insufficient time for the oxidation to take place, and some of these gases may escape unburned.

Volumes of Reacting Gases.—In accordance with Gay-Lussac's law relating to reacting gases, if all the gases are shown in the molecular form, the volume of oxygen required and the volume of the combustion products may be derived from the equation for the reaction. The volume of air may be considered to be roughly five times that of the oxygen required.

When carbon burns completely, the volume of carbon dioxide produced is the same as the volume of oxygen used, as:

$$2C + 2O_2 \rightarrow 2CO_2$$

When combustion is imperfect and carbon monoxide is formed, 2 volumes of gaseous product are made from 1 volume of oxygen, thus:

$$2C + O_2 \rightarrow 2CO$$

Two volumes of hydrogen with 1 volume of oxygen form 2 volumes of water vapor, as:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The volume of the gases is diminished one-third by the reaction, even when the water is in the form of vapor. When the vapor condenses to liquid water, the volume of the water is approximately 1/1,700 of the volume of the vapor that was formed.

In the complete burning of a hydrocarbon, both carbon dioxide and water are produced. The following equations represent the burning of methane, of which natural gas largely consists, and the second equation represents the burning of tridecane, a constituent of kerosene.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$C_{13}H_{28} + 20O_2 \rightarrow 13CO_2 + 14H_2O$$

In the first equation, 1 volume of methane gas and 2 volumes of oxygen produce 1 volume of carbon dioxide and 2 volumes of water vapor; the total volumes are the same before and after burning. In the second equation, 1 volume of the tridecane vapor and 20 volumes of oxygen produce 13 volumes of carbon dioxide and 14 volumes of water vapor, a total increase of 6 volumes. In all the volume relations stated, it is understood that the temperature and pressure after burning have been reduced to the same as before burning. Naturally, just as the burning is completed, the volumes of the combustion products are much greater than those indicated, due to the elevated temperatures caused by the heat of the reaction. In the cylinder of a gas engine, for example, the temperature of the gases produced by combustion may be easily 1600°C. If pressure were not increased, this would make the volume more than five times as great as the volume at atmospheric temperature (Charles' Law).

Explosion of Gases.—As gases are ordinarily burned, the speed of burning is determined by the rate of flow of gas from the burner, and this in turn is determined by the pressure under which it is kept in the gas holders, mains, etc., and the size of the opening through which it passes. If air or oxygen is mixed with the gas in suitable proportion prior to the time it is ignited, the rate of burning is not controlled by the rate of transportation of the gas, and the "flame wave" will pass through the mixture at very high velocity. Thus a large volume of gas may be burned almost instantaneously. When this takes place an explosion is said to have occurred. The flame or explosion wave travels at a certain maximum speed, depending upon the nature of the gas, the proportions of the mixture, etc. In a mixture of 2 parts hydrogen and 1 part oxygen by volume, the explosion wave travels at the rate of nearly 1½ miles per second, which is about 6½ times the speed of the sound wave in this mixture. Although the wave travels at a slower rate through explosive mixtures of ordinary fuel gases and air, it is apparent that the time required for it to travel through such a mixture contained in the cylinder of an engine, for example, would be very little indeed. Because of the greatly expanded condition of the products of the explosion due to the heat set free (and in some instances to an actual increase in volume), the explosion products must either occupy a greater space or exert an increased pressure.

Combustible gases mixed with air are not explosive in all proportions. If the amount of gas is above or below certain limits an explosion will not occur, even though a proper source of ignition be supplied. The approximate explosive limits for various gases and industrial mixtures of gases and vapors are shown in the accompanying table.[1] The figures represent the values observed for the upward propagation of flame in large vessels. With gases that have narrow explosive ranges, the danger of explosive mixtures being formed because of leaks in containers and conveyors is less, of course, than when the explosive range is wide.

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[1] Unless otherwise stated, percentages are as given by Coward and Jones, "Limits of Inflammability of Gases and Vapors," *U. S. Bur. Mines Bull.* 279, pp. 87 and 88, 1928.

PERCENTAGE OF GAS BY VOLUME AT ORDINARY TEMPERATURES AND PRESSURE REQUIRED FOR AN EXPLOSIVE MIXTURE WITH AIR

Gas	Lower explosive limit; gas, per cent	Upper explosive limit; gas, per cent	Explosive range; gas, per cent
Hydrogen (H_2)	4.1	74.0	69.9
Carbon monoxide (CO)	12.5	74.0	61.5
Methane (CH_4)	5.3	14.0	8.7
Ethane (C_2H_6)	3.2	12.5	9.3
Propane (C_3H_8)	2.4	9.5	7.1
Butane (C_4H_{10})	1.9	8.5	6.6
Acetylene[*] (C_2H_2)	3.0	80.0	73.0
Benzene (C_6H_6)	1.4	8.0	6.6
Toluene ($C_6H_5CH_3$)	1.3	7.0	5.7
Ammonia (NH_3)	16.0	27.0	11.0
Hydrogen sulfide (H_2S)	4.3	46.0	41.7
Acetone	2 or 3	13.0	10.0
Gasoline[†]	1.4	6.0	4.6
Water gas[‡]	9.0	55.0	46.0
Natural gas[§]	4.8	13.5	8.7

[*] COWARD and JONES, *loc. cit.*, p. 80.

[†] The gasoline had a specific gravity of 0.689 (74°Bé) at 15°C., and a boiling range of 50 to 140°C. with 2.7 per cent residue at 140°C.

[‡] The percentage composition of the water gas used was as follows: hydrogen, 49.6; carbon monoxide, 40.8; carbon dioxide, 2.6; and nitrogen, 7.

[§] The percentage composition of the natural gas was as follows: methane, 87.4; ethane, 6.8; propane, 1.55; butane, 0.81; pentane, trace; nitrogen, 3.2; oxygen, 0.1; and carbon dioxide.

Surface Combustion.—When a previously warmed piece of platinum wire is held in a stream of mixed coal gas and air issuing from a bunsen burner, the wire begins to glow. The gas and oxygen from the air combine on the surface of the platinum and produce sufficient heat to cause the metal to become incandescent, but usually no flame results. Platinum is not the only substance that accelerates gaseous combustion in this manner; other metals and even fragments of non-metallic substances act in the same way. Because the surface of the solid promotes the reaction, combustion of this type is referred to as surface combustion.

The principle involved can be very conveniently applied in the heating of diaphragms. If a diaphragm of porous material, sufficiently coarse that gas can flow through it, is placed over a container connected to the source of a combustible gaseous mixture, and if the gas is admitted and lighted after it has passed through, it will burn with ordinary flame for a time; but as the diaphragm becomes heated, the flame gradually disappears. Finally combustion takes place at the surface of the diaphragm.

Or if a crucible is placed in a furnace and a packing of granular, highly refractory material is filled in between it and the walls of the furnace, with a suitable mixture of air and gas admitted from below and ignited, after a time combustion will proceed quietly, without flame, on the surface of the granules.

Although the term "surface combustion" should be applied only to the sort of burning described in the preceding paragraphs, as now employed in commercial usage, it may be defined as the burning of an explosive mixture of gases continuously and quietly; *i.e.*, without an explosion.[1] The method by which this burning is accomplished consists essentially of injecting the explosive mixture through a suitable orifice at a speed greater than the velocity of backfiring, and then checking the flow at the desired distance beyond the point of issuance.

An idea of the velocity of backfiring as compared to the rate of gas flow may be obtained by the use of an ordinary bunsen burner. If the burner is so adjusted that the mixture of gas and air passes through at a suitably high velocity, the flame may be carried entirely away from the burner, because the velocity of backfiring cannot equal the rate of gas flow. But if an iron ring of suitable size is fixed about 2 in. above the tip of the burner, so that the stream of mixed air and gas will pass through it, the flow may be retarded sufficiently by the ring to make the velocity of backfiring greater than the rate of gas flow above the ring. Now, if the gas is lighted at some point above the ring, the flame can travel back against the flow as far as the ring, but cannot pass below it, because there the rate of flow exceeds the velocity of backfiring. Then the base of the flame will come to rest within the ring. Here the combustion will be intense.

In practice one of the commonest methods of retarding the flow consists of placing in the path of the jet a baffle consisting of a bed of broken refractory material. A furnace of this sort is known as the impact type of furnace. The stream of mixed gas

[1] *Machinery*, **18**, 677, May, 1912.

and air is injected through the furnace wall and caused to strike downward upon this bed which lies on the furnace bottom. In another method, velocity reduction is obtained by giving the stream of mixed air and gas a rotary expanding motion as it enters the furnace chamber. Through contact with the furnace atmosphere the velocity of the expanding stream is retarded, and combustion takes place at the point where the rapidity of flow and the velocity of backfiring are equal. The location of this point may be regulated by suitable adjustment, thus intensifying the production of heat at the desired place in the furnace. A noteworthy feature of the process is that, with a suitably proportioned mixture, additional air is not required in the furnace chamber, and oxidizing conditions need not be maintained there.

The advantages claimed for the process are: (1) that combustion is greatly accelerated and concentrated just where desired; (2) that combustion is complete with a minimum excess of air; (3) that the attainment of very high temperatures is possible; and (4) that, because a large amount of radiant energy is developed, the transmission of heat to the object to be heated is very rapid.

The Burning of Pulverized Coal.—An important recent development affecting the consumption of fuel in the United States has been the greatly increased use of powdered coal. When employed in this manner the coal is first dried, either by the flue gases or by independent rotary driers, and then is ground so that at least 65 per cent will pass through a 200-mesh screen, and not more than 10 per cent will remain on a 100-mesh screen. In this condition it is blown into the furnaces, where a very high efficiency is obtained in burning it. In metallurgical furnaces the substitution of pulverized coal has resulted in the saving, on an average, of one-third of the coal required when burning it in other ways. A disadvantage is the large amount of ash that is blown from the stack.

The Effect of Moisture in Fuel.—By the evaporation of moisture in fuel, heat is lost as the latent heat of steam; 966 heat units are carried away by each pound of evaporated water. On the other hand it is said that a certain amount of benefit is derived from moisture in the coal, and, for boiler purposes, coal is sometimes intentionally wetted. The idea is based upon the fact that the resultant steam is decomposed, producing carbon monoxide and hydrogen, in accordance with the following equation:

$$H_2O + C \text{ (hot)} \rightarrow H_2 + CO$$

As these gases afterward burn, the zone of intense heat is extended farther into the boiler tubes with the result that much more heat is absorbed.

It would appear, then, that the presence of moisture in a fuel employed for the heating of a shell-type boiler would be a distinct disadvantage; but with the tubular-type boiler it is possible that the presence of moisture may have the opposite effect.

Smoke.—There are two general kinds of smoke. The first kind, which is of a whitish or greenish color, consists mainly of hydrocarbons. It can be seen rising from the hot wick, when a candle is blown out, or from coal when it is first placed on a fire, or from half-dried brush or weeds, when an attempt is made to ignite them. The smoke from a cigar or other tobacco belongs to the same class. Hydrocarbon smoke can be burned quite easily. If a lighted match is applied to the upper part of the stream of smoke that rises from a blown-out candle, a flame will travel back through the ascending column and reignite the wick. Hydrocarbon smoke contains practically no free particles of carbon. Microscopic examination shows that it consists of small vesicles, or balloon-like structures, the skins of which consist of liquids distilled out of the burning substances. The vesicles are filled with gases such as nitrogen, oxygen, carbon dioxide, hydrogen, and the hydrocarbons, methane, ethylene, etc. They float in air until they are brought forcibly into contact with some surface and are caused to burst, which sets the contents free. The skins of the vesicles produce a deposit generically known as "tar."

The second kind of smoke is the heavy black cloud. It consists of minute particles of carbonaceous material produced by the cooling of a luminous flame. Although this smoke rises usually from long-flame coals, it may be produced by any luminous flame that is cooled sufficiently by radiation before it has come into contact with enough air to complete the combustion.

The tendency toward the production of smoke when the air supply is insufficient, may be shown by the following experiment suggested by Kent:[1]

> Take a lighted, central-draft kerosene lamp and adjust the wick to such a point that the lamp gives a rather short and clear, white light, without a trace of smoke. Now, without altering the adjustment of the wick, gradually obstruct the opening at the bottom of the central-draft tube and observe the result. The flame grows longer, and its whiteness changes to yellow and then to red. It begins to smoke; and finally when the flame has risen to nearly the top of the chimney, a dense column of black smoke and soot is given off. We learn from this experiment that with the same consumption of fuel, *i.e.*, the oil supplied by the wick, the flame may be short and intensely hot; or very long, of a low temperature, smoky, and sooty. While the flame is lengthening, and before it becomes smoky, the combustion may be complete, but it is not effected in as short a space as with the original supply of air. For a given supply of fuel, a short flame means rapid and complete combustion; a longer flame, delayed combustion; and a very long flame, imperfect combustion.

In the long flames the incandescent solids are given a chance to radiate heat for a longer period, and finally become cold and black; in other words, produce smoke. In general, then, the mechanism of the process may be summarized as follows: the hydrocarbons distilled from the fuel become ignited and burn with a luminous flame; the flame is cooled by radiation until combustion ceases.

In steam generation, one of the common causes of smoke is *bad stoking.* A thick layer of coal is thrown upon the fire, and the tarry matters at once begin to distill from it in great abundance. It is very probable that these volatile products will not even be ignited, because, after ascending through the cold layer of coal, they are then separated by it from the heat, and consequently escape unburned, thereby producing smoke, which in this case is mainly not carbon but tarry matter. But if these products do become ignited, because they are being produced in such great quantity, air cannot find entrance rapidly enough to burn them. Consequently, their flame gradually cools by radia-

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[1] "Steam Boiler Economy," p. 9.

tion and produces smoke, which now will be a heavy black cloud containing much carbon.

The *smokiness of bituminous coal* is due to the fact that it contains such a large proportion of volatile substances or gaseous constituents. These gases consist largely of hydrocarbons and pass off readily before they can be completely burned. The loss is avoided by the use of *mechanical stokers* that feed the coal slowly and steadily, thus turning it into coke before it reaches the fire. This method allows the gases that are thus produced to be burned only slowly as they are set free. Downdraft or underfeed furnaces are very efficient because the hydrocarbons must pass through the furnace bed of hot coals and are consequently burned. Ordinarily the loss of fuel by smoke is about 10 lb. per ton.

An idea of the *composition of the soot fall* resulting from general atmospheric smoke will be furnished by the following analysis of a deposit collected from the roof of a greenhouse after the falling of a snow: carbon, 39.00 per cent; hydrocarbons, 12.30 per cent; organic bases, 1.20 per cent; sulfuric acid, 4.33 per cent; ammonia, 1.37 per cent; metallic iron and magnetic oxide, 2.63 per cent; other mineral matter chiefly silica and ferric oxide, 31.24 per cent; water, not determined.

The composition of the soot fall varies greatly with the locality. In the Pittsburgh district, where blast furnaces are especially numerous, the soot fall is very rich in iron oxide. An analysis[1] of a year's sample of soot fall collected in the business district of Pittsburgh during the year beginning April, 1912, showed the following: tar, 2.19 per cent; ash, 75.84 per cent; fixed carbon, 21.97 per cent. The iron oxide (Fe_2O_3) in the ash was 32.08 per cent, which in the whole deposit amounts to 24.30 per cent.

Analysis of Flue Gases.—In order to insure the complete combustion of any fuel, more air than the amount theoretically required must be passed through the combustion chamber. Although an excess of air is necessary, the excess should not be too great because all air passing through the fire box is heated and an undue loss of heat may be thus entailed. An analysis of the escaping gases, commonly called a flue-gas analysis, will

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[1] *Met. Chem. Eng.*, **12**, 247, April, 1914.

determine whether or not the proper amount of air is being admitted. The amount of oxygen present shows the amount of excess air passing through the fire. The presence of carbon monoxide or methane shows incomplete combustion and insufficient air.

ASH

Source and Composition.—The ash of any fuel is the mineral residue left after the combustion of the fuel is complete. In the case of coal, the ash is made up both of the mineral matter present in the plant of which the coal was formed, and of the earthy matter mixed with the coal during its formation. Silica, alumina, lime, magnesia, and the oxide and sulfide of iron are the principal constituents of coal ash. Although the proportions of these constituents vary widely, silica usually predominates. Those coals are best the ashes of which are nearly pure white and contain but little alkali and lime as well as iron oxide, since these materials may cause the ash to fuse. It is interesting to note that coal ashes contain relatively very little potash, usually only a fractional part of 1 per cent, while the ashes of certain woods, especially certain hard woods, may contain as much as 15 per cent or more.

Clinkering of the Ash.—Clinkers are formed by the fusion of the ashes. This fusibility depends in considerable measure upon the ratio that exists between the basic oxides and the silica present. Ashes that are high in either basic oxides or silica are not readily fusible. Those in which the constituents are present in the proper ratio to form the normal silicate, fuse the most readily as a rule.

The presence of iron pyrite (FeS_2) in the coal is closely connected with the formation of clinkers. During the burning of the coal, a portion of the sulfur in this compound is oxidized and the pyrite is largely converted into ferrous sulfide (FeS). This sulfide is fusible at low temperatures, and as it melts, it entangles other substances and serves as a starting point for fusions that would not occur without this aid. It depends much on the state of division of the pyrite and its distribution through the coal, whether or not the ash will clinker. High sulfur, as shown by an analysis, does not necessarily mean clinkering tendencies, although this is generally the case. The sulfur, however, may be present in the form of organic compounds and then it has no tendency to induce the formation of clinkers.

Sometimes the unskillful use of the poker may cause the formation of clinkers because channels may be formed in the bed of coals through which the draft ascends as a blast, causing very high temperatures to be produced at such points.

THE HEATING VALUE OF FUELS

Heat Units.—A previous topic contains a statement of the temperatures developed by various flames. It must be remembered, however, that the degree of heat indicated by a specified temperature is a measure of heat intensity, and is not a measure of quantity or amount of heat. The intensity of heat in the flame of an ordinary match, for example, is high, but the quantity of heat produced is relatively little. Heat quantity is measured in terms of heat units. There are three such units in use:

A British thermal unit (B.t.u.) is the amount of heat necessary to raise the temperature of 1 lb. of water from 39 to 40°F.

A centigrade unit (c.u.) is the amount of heat required to raise the temperature of 1 lb. of water from 4 to 5°C.

A calorie (cal.) is the amount of heat required to raise the temperature of 1 kg.[1] of water from 4 to 5°C.

Heating Power of Fuel Constituents.—One pound of *carbon* in burning to carbon dioxide produces 14,500 B.t.u. One pound of carbon in burning to carbon monoxide produces 4,450 B.t.u. If this carbon monoxide should all escape,[2] as a portion of it may, 10,050 heat units would be lost. If it could all be retained and burned, however, the heat thus set free, together

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[1] The small calorie is based on 1 g.

[2] Precaution should always be taken to prevent carbon monoxide from escaping into the air from any source, because the breathing of even a very small quantity of the gas is a serious menace to health. Carbon monoxide acts as a poison by forming a compound with the haemoglobin of the red corpuscles of the blood, thus preventing the blood from carrying oxygen from the lungs to the tissues. Even 0.05 per cent, if breathed for 30 min., will produce dizziness upon exertion; 0.1 per cent inability to walk; 0.2 per cent loss of consciousness. Less than 1 per cent in air causes death when breathed for about 10 min.

with that produced when the carbon monoxide was formed, would equal the heat produced by burning the carbon to carbon dioxide.

When 1 lb. of *hydrogen* burns to form water, 62,000 B.t.u. are liberated.

When a *hydrocarbon* such as methane (CH_4) burns, carbon dioxide and water are formed. One pound of methane contains ¾ lb. of carbon and ¼ lb. of hydrogen. Three-fourths of a pound of carbon in burning to CO_2 produces 10,875, and ¼ lb. of hydrogen, 15,500 B.t.u., or a total of 26,375 B.t.u.[1]

Combined oxygen in a fuel is always undesirable. According to Dulong's formula, when calculating the thermal value of a fuel, the oxygen is considered as being in combination with hydrogen in the proportion to form water, 8:1. Thus, each 8 parts of oxygen by weight render unavailable 1 part of hydrogen. It is customary to express hydrogen as H minus ⅛O, but it has been shown[2] that in some highly oxygenated coals as much as two-thirds of the oxygen is in combination with carbon. In such cases, of course, the thermal value calculated according to Dulong's formula will not represent the true value, although the error is not great.

The Available Heating Value of a Fuel.—In the ordinary use of a fuel, the total heating power is never available. Heat is lost in many ways. For example, the losses that occur when coal is employed under a steam boiler may be summed up as follows:

1. The latent heat absorbed in evaporating the water in the coal. This includes moisture, combined water, and water formed during combustion. If the coal is very wet, the loss of heat resulting from this cause will be considerable.

2. Heat represented by the unburned fuel removed with the ashes.

3. Heat lost through the escape of fuel in the form of smoke, since this contains a notable percentage of carbon and hydrocarbons.

4. Heat lost through the formation of carbon monoxide instead of carbon dioxide.

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[1] The heat of formation of CH_4 must be subtracted, 2,500 B.t.u. per lb.

[2] PORTER and OVITZ, "Volatile Matter in Coal," *U. S. Bur. Mines Bull.* 1, 1910.

5. Heat lost through radiation.
6. Heat carried out the stack by the hot flue gases.[1]

These losses vary, of course, with the kind of coal, the type of boiler and stoker, and other factors, but the total loss may at times amount to 50 per cent of the total heating power of the fuel.

The Evaporating Power.—Since 1 lb. of carbon, in burning completely, produces 14,500 B.t.u., and 966 B.t.u. are required to evaporate 1 lb. of water, the evaporative power of 1 lb. of carbon is represented by 14,500/966, or 15 lb. This number of pounds of water is converted from water at 212°F. to dry steam at the same temperature.

In the case of hydrogen, since the combustion forms water which must be evaporated, the weight of water produced must be subtracted from the theoretical evaporative power of hydrogen, which is 62,000/966, or 64.1. Since 9 lb. of water are produced when 1 lb. of hydrogen burns, 9 must be subtracted from 64.1 leaving 55.1, which only may be counted as the practical evaporative power of hydrogen. It is impossible to burn 1 lb. of hydrogen without producing 9 lb. of water.

The Solid Fuels

Wood.—As a fuel, wood is of very minor importance industrially, although it is used extensively for domestic purposes. It consists mainly of three components: water; the solids of the sap; and vegetable tissue, for example, cellulose $(C_6H_{10}O_5)_x$. Because

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[1] Assuming complete combustion, the loss as sensible heat carried out the stack by the flue gases may be calculated from the formula:

$$\text{Heat lost} = W(T - t)0.24$$

where W is the weight of the stack gases, and $T - t$ is the difference between the temperature of the air entering the combustion chamber and that of the flue gases leaving it. The temperature of the flue gases usually ranges between 400 and 600°F. The value 0.24 is taken as the mean specific heat of nitrogen and carbon dioxide at constant pressure over the range 0 to 600°F. In burning 1 lb. of carbon, the theoretical weight of the gases may be calculated from the reacting weights in the following equation:

$$C + O_2 \rightarrow CO_2.$$

The weight of the oxygen required is $2\frac{2}{3}$ lb. and the weight of the carbon dioxide produced is $3\frac{2}{3}$ lb. for each pound of carbon. For each pound of oxygen, 4.320 lb. of air must be supplied.

of its high combined-oxygen content (see page 31), its heating value is not high; the heat is derived mainly from the burning of the carbon. On the basis of weight, wood is, roughly, about half as efficient as coal.

Peat.—This material is produced by the decomposition, partly bacterial fermentation, of vegetable matter in swamps and bogs. It varies through several grades from a light, porous, fibrous substance of yellowish color to the dark thoroughly decomposed peat, which is hard and compact. In some cases the peat beds have become covered with sedimentary rocks, the pressure of which has gradually transformed the peat into lignite. Although the peat bogs of the United States cover an area of about 31,000 sq. miles (estimated), peat here is very little used as a fuel. It has about the same heating value as wood.

Lignite.—In respect to formation and composition, lignite is intermediate between peat and coal. The more recent varieties resemble compact peat, and the older varieties merge into sub-bituminous coal.

Unlike coal, lignite is brown and not black, has a wood-like appearance, and is sometimes known as *brown coal.* Because it *slacks* or crumbles when exposed to the air, it deteriorates greatly during storage and long transportation.

Lignite has generally a high ash content; it ranges from 5 to 35 per cent. Another characteristic feature is its high moisture content, which so greatly reduces the heating value of freshly mined lignite. It is the partial evaporation of this moisture that causes the fuel to fall to pieces upon exposure. It has been found that by converting the lignite into the form of briquettes it produces a very satisfactory and desirable fuel,[1] although, because of its high moisture and ash content, it has only a low thermal value.

According to U. S. Geological Survey, about 150,000 sq. miles of land within the United States are underlaid with lignite. It is used to only a very limited extent, however, because of the abundance of more desirable fuels.

Sub-bituminous Coal.—This coal has been called "black lignite," but it is certainly not lignite in the sense of being woody in texture. It may be distinguished from lignite by its color

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[1] See *U. S. Bur. Mines Bull.* 14.

and structure, and from bituminous coal by the fact that it loses moisture and crumbles ("slacks") when exposed to the weather in the same way as does lignite. The slacking makes it necessary to ship it in box cars and guard against spontaneous ignition. In spite of the disadvantages mentioned, sub-bituminous coal has found a ready market in the western part of the United States, because, although high in volatile matter, it makes a clean domestic fuel and ignites readily. It is of more recent formation than the coals of the East, and contains less sulfur than the latter.

Bituminous Coal.—This, like sub-bituminous coal, has a high content of volatile matter; as much as one-third of its weight is volatilized when subjected to dry distillation. On this account, some varieties have a strong tendency to burn with a smoky flame. On the basis of their tendency to smoke and their fusing characteristic when heated, bituminous coals may be divided into three classes: (1) dry or non-coking coals which burn freely but with little smoke, and do not fuse together when heated; (2) coking coals which in burning produce a little smoke and fuse together, Connellsville coal being an example; (3) fat or long-flaming coals; those that have a great deal of volatile matter, sometimes 50 per cent, therefore producing much smoke and either fuse or do not fuse in burning. Some Nova Scotia and Illinois coals are of the third class. A variety of this third class is known as "cannel" coal.[1] Being very rich in volatile matter and generally high in hydrogen, it burns with great heat and a long flame. It is composed almost entirely of spores, spore cases, seed coats, and resinous and waxy products of plants living at the time of the existence of the coal swamp. Because of the absence of woody matters, it breaks with a conchoidal (shell-shaped) fracture.

Semi-bituminous Coal.—This coal has a lower content of volatile matter than bituminous coal, and is nearly smokeless when burned properly. The best coal of this type has a greater heating value than any other coal; it forms, therefore, an excellent fuel for steam generation and general manufacturing. It is the best of the coals for naval use because it requires less bunker

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[1] The term *cannel* (Scotch) is applied to this coal because it burns with a candle-like flame.

space per unit of heat. The well-known Pocahontas coal is an example of this type.

Anthracite Coal.—This is the densest and hardest of all varieties. Most of it is mined in eastern Pennsylvania where its peculiar quality is due to the crushing stresses produced when the rocks were thrown into the great folds that characterize this region.[1] Anthracite coal contains relatively little volatile matter; consequently it kindles with difficulty, burns with a small flame, and emits scarcely any smoke. Because of its freedom from a tendency to produce smoke and soot, it is much desired as a domestic fuel; and because it is not plentiful, it commands a higher price than other coals. Almost six times as much bituminous coal is produced in the United States as anthracite. Anthracite coal is excelled by some of the semi-bituminous coals in heating value, and it is not an economical fuel for steam generation and general manufacturing.

Coal Analyses.—Analyses of coal are of two kinds, known as (*a*) the ultimate, and (*b*) the proximate analysis. The former, being of the type of the usual organic analysis, involves the determination of the several elements separately, as carbon, hydrogen, oxygen, nitrogen, and sulfur, together with moisture and ash. The latter type of analysis, however, is employed for commercial work. As usually carried out, it involves the determination of moisture, volatile combustible matter, fixed carbon, ash, and generally sulfur. The method employed will be outlined briefly.

A gram of the finely divided coal is heated at a temperature of 100 to 105°C. for 1 hr. The loss in weight is reported as moisture. The dried coal is then heated in a covered crucible with a bunsen flame regulated according to certain specifications. The loss so determined is reported as volatile combustible matter. The residue is the "coke," and consists of the non-volatile carbonaceous matter, called "fixed carbon," and the ash. It must be understood that the original coal did not consist of free carbon and volatile organic matter, but that the dry distillation taking place in the closed crucible resulted in the formation of such substances by the decomposition of the more volatile matter in the coal. The ash is determined usually by burning another

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[1] Bacon and Hamor, "American Fuels," vol. I, p. 4.

1-g. sample heated to a high temperature in an open crucible. By subtracting the weight of the ash from the weight of the coke, the percentage of the fixed carbon may be determined. The percentage of sulfur is always determined on a separate sample. Since sulfur was present partly in the volatile matter distilled off, and partly as sulfides (or sulfates) in the ash, if all constituents shown in the report of the analysis are added together, the total will exceed 100 per cent by the amount of the sulfur reported.

Composition and Heat Values of Coals and Lignite.—Comparisons of the several types of coals that have been mentioned, made on the basis of the proximate analysis, together with heat values, are shown in the following table:

PERCENTAGE ANALYSIS OF REPRESENTATIVE COALS OF THE UNITED STATES[1]

Rank	Where mined	Moisture	Volatile matter	Fixed carbon	Ash	Sulfur	Heat value, B.t.u. per pound
Lignite............	North Dakota	40.5	26.3	27.0	6.2	0.8	6,210
Lignite............	Texas	33.5	39.5	16.2	10.8	0.6	7,140
Sub-bituminous....	Montana	11.7	36.1	40.2	12.0	1.1	9,790
Sub-bituminous....	Wyoming	16.5	32.9	45.8	4.8	0.6	10,750
Bituminous........	Washington	6.8	40.0	47.9	5.3	1.4	12,330
Bituminous........	Pennsylvania	2.7	30.4	57.8	9.1	1.3	13,610
Bituminous........	Tennessee	3.4	28.2	60.1	8.3	0.8	13,430
Semi-bituminous....	Virginia	2.7	20.0	73.9	6.0	0.5	14,495
Semi-bituminous....	Pennsylvania	3.3	12.5	77.9	6.3	1.0	14,340
Semi-bituminous....	Arkansas	1.4	14.8	76.9	6.9	1.5	14,330
Semi-anthracite....	Arkansas	2.1	9.8	78.8	9.3	1.7	13,700
Anthracite.........	Colorado	3.0	2.9	86.6	7.5	0.7	13,500
Anthracite....	Pennsylvania	2.2	5.7	86.2	5.9	0.6	13,830

Spontaneous Combustion in Stored Coal.—Spontaneous combustion is brought about by a combination between the coal substance and the oxygen absorbed from the atmosphere. When the heat that is produced in this manner is not conducted away at a sufficiently rapid rate, the temperature rises and the velocity of the oxidation reaction is accelerated. Ultimately the kindling point is reached. The tendency to become ignited spontaneously increases with the porosity of the coal; some coals absorb twice their volume of oxygen. When certain coals are powdered, they

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[1] From BACON and HAMOR, "American Fuels," pp. 37–43, and "Analyses of Samples of Delivered Coal," *U.S. Bur. Mines Bull.* 230, 1922.

will absorb as much as 2 per cent of their weight of oxygen and will ignite spontaneously in a very short time.

The presence of wood in a pile of coal adds materially to the fire risk, since the heat developed will distill tarry matter from the wood, which will ignite very readily.

Outdoor exposure of coal results in loss of heating value varying from 2 to 10 per cent. Dry storage has no advantages over open storage except that the pyrites are not oxidized so much and hence the pores are not opened allowing the hydrocarbon gases to escape. During storage all losses cease practically at the end of 5 months.

Coal submerged in water does not lose appreciably in heat value.

Modern Trends in the Utilization of Coal.—It is beginning to be apparent that coal is too valuable a commodity to be burned in the raw state, and a great deal of research is being devoted to the development of methods for its more economic utilization. To illustrate the progress that has been made, the work of Bergius, Fischer, and Patart will be mentioned.

Berginization of Coal.—As a result of many years of research, Bergius[1] of Germany, by treating coal with hydrogen, has been able to transform the coal into oil. This method must not be confused with the dry distillation of coal because in that process the yield is chiefly coke, while in the so-called berginization of coal, a synthetic reaction occurs and the coal substance is actually converted into a fluid. Since in a normal bituminous coal, the ratio of carbon to hydrogen is about 16:1, and in a hydrocarbon oil about 8:1, it is obvious that the transformation involves the addition of hydrogen.

As outlined by Bergius, in his process the coal, ground and mixed with oil to a thick paste, is pumped under a pressure of 2,200 to 3,000 lb. per square inch into the reaction vessel, which already contains some oil. Simultaneously hydrogen is introduced, and the mixture is heated to about 500°C. at which temperature the strength of the steel begins to decrease. The hydrogen required for the continuance of the process is produced

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[1] Bergius, Dr. Friedrich, "The Transformation of Coal into Oil by Means of Hydrogenation," *Proc.* First Internat. Conf. on Bituminous Coal, p. 102, *Carnegie Inst. Technol. Publ.*, 1926.

by heating the gaseous-reaction products with steam. Carbon monoxide is formed at the same time as the hydrogen, but it does not interfere. It is not necessary that the hydrogen be pure, as is required in the synthesis of ammonia and in the hydrogenation of fatty oils. Some of the oil produced by the process is employed to form the oil paste and is returned to the apparatus. If the ash does not exceed 10 per cent, from 40 to 70 per cent of the coal is liquefied, a yield of 107 to 185 gal. of oil from 1 short ton of coal. As compared to low-temperature distillation the products are as follows:[1]

Products	Berginization, per cent	Low-temperature distillation, per cent
Motor spirit	15 0	1.5
Diesel oil and creosote oil	15.0	3.0
Fuel oil, lubricating oil, pitch	20.0	4.5
Ammonia	0.5	
Water	8.0	5.0
Gas	20.0	15.0
Organic matter, insol. in benzene	11.5	
Semi-coke	....	61.0
Ash	10.0	10.0

From 1 short ton of coal, about 45 gal. of gasoline are obtained, and since it contains a very large proportion of aromatic hydrocarbons, it is of the anti-knock variety (page 60). To Europe, faced as it is with a rapidly vanishing oil supply, the berginization of coal is a process of great economic importance.

Fischer's "Synthol."—By the catalytic hydrogenation of carbon monoxide under high pressure, Fischer[2] of Germany has produced a complex mixture of higher alcohols (page 511), ketones (page 518), and aldehydes ($R \cdot CHO$, in which R is any radical) with some fatty acids (page 490). This mixture Fischer has named *synthol*. The carbon monoxide and hydrogen required for the process are obtained from water gas, which is manu-

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[1] Bergius, *op. cit.*, p. 109.

[2] Fischer, Dr. Franz, "The Synthesis of Petroleum," *Proc.* First Internat. Conf. on Bituminous Coal, etc., p. 234, 1926.

factured from coal and steam by the usual method (page 67). The catalyst is iron treated with an active alkali. Fischer says, considering the surplus of hydrogen employed, that the surprising feature of his process is that compounds containing oxygen, rather than hydrocarbons, are produced. One aim of the synthesis is to produce higher alcohols for use as motor fuels. For this purpose the lower alcohols, ethyl and methyl, are less suitable because of their higher relative content of combined oxygen (page 31).

By a modification of the process employing only atmospheric pressure, Fischer and his collaborators have produced from the same gases, carbon monoxide and hydrogen, both liquid and solid saturated, paraffin-like hydrocarbons with no oxygenated products. By proper control, a good yield of gasoline is obtained. In the words of Fischer: "We have not yet a world oil famine, but when it comes, there will be available methods of overcoming it by means of the newer chemistry of coal." A feature of importance in this method, as well as in that of Bergius, is that the cheapest grades of coal may be used.

Patart's Synthesis of Methyl Alcohol.—Patart of France has reported a method for the transformation of bituminous coal into organic technical products.[1] Starting with any kind of coal, by the method he describes, the coal is converted by the water-gas method into carbon monoxide and hydrogen, which, by the use of pressure and catalysts, are converted into methyl alcohol, other alcohols, and oxygenated organic products derived from the alcohols.[2]

COKE

Conversion of Coal into Coke.—Coke is the residue left after the dry distillation of bituminous coals; it is chiefly carbon. Not all bituminous coals, however, form coke when thus heated. Some of them produce only a loosely coherent mass; those that form coke fuse gradually as the hot zone moves forward through the coal in the coke oven, yield up their volatile constituents, and

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[1] PATART, GENERAL GEORGES, "The Industrial Transformation of Bituminous Coal into Organic Technical Products," *Proc.* First Internat. Conf. on Bituminous Coal, etc., p. 132, 1926.

[2] For a further description of this process, see p. 512.

leave a bright-gray, strongly coherent, porous product. The fusion begins between 300 and 400°C., but the final coking temperature is much higher, generally about 1000°C.

The coking results from the decomposition of the tarry constituents of the coal, and the separation of carbon or substances rich in carbon. In a general way, the changes that take place during coking are shown by the following percentage analysis of a coke and the coal (Pennsylvania bituminous) from which it was made:

	Water	Volatile combustible	Fixed carbon	Sulfur	Ash
Coal	4.50	25.40	64.25	0.87	5.85
Coke	....	0.73	90.49	0.78	8.78

Because of the loss of volatile matter, the percentage of ash in the coke is higher than in the coal; and, for the same reason, more sulfur has been removed by coking than might seem apparent from the percentage shown. It should be noted that the sulfur-to-carbon ratio has been considerably reduced.

An important advantage of coke as a fuel is its porous structure; its apparent specific gravity is about 0.9, while its true specific gravity is about 1.90; consequently, approximately 50 per cent of its volume is air space. This cellular structure enables the coke to burn more readily. Coke averages about 13,000 B.t.u. per pound.

Coking Processes.—There are two processes for making coke, named according to the character of the oven in which the distillation is carried out.

One type, the *beehive oven*, illustrated in Fig. 2, is a dome-shaped oven of brick, 12 to 13 ft. in diameter and 7 to 8 ft. high inside. It has an opening in the top through which the coal is charged and a door in one side through which the coke is removed and through which a small amount of air is admitted. The ovens are constructed in long rows, some of which are a quarter of a mile in length. Alternate ovens are charged with sufficient coal to produce, when leveled off, a layer about 2 ft. deep. Mean-while the intermediate ovens are burning at full heat and the heat from the hot ovens passing through the party wall ignites the charge in the adjacent oven. Only enough air is admitted through the door in the side to produce an amount of burning sufficient to keep the temperature at the desired point. The heat furnished by this partial combustion causes the coal to melt or fuse and give up its volatile constituents. The time that the charge is allowed to remain in the oven is usually 48 or 72 hr. The longer the time, the harder the coke, and the less residual volatile matter it will contain. The 72-hr. coke is usually that which is allowed to remain in the oven over Sunday. Because of its hardness, this coke is most desired by the foundry man.

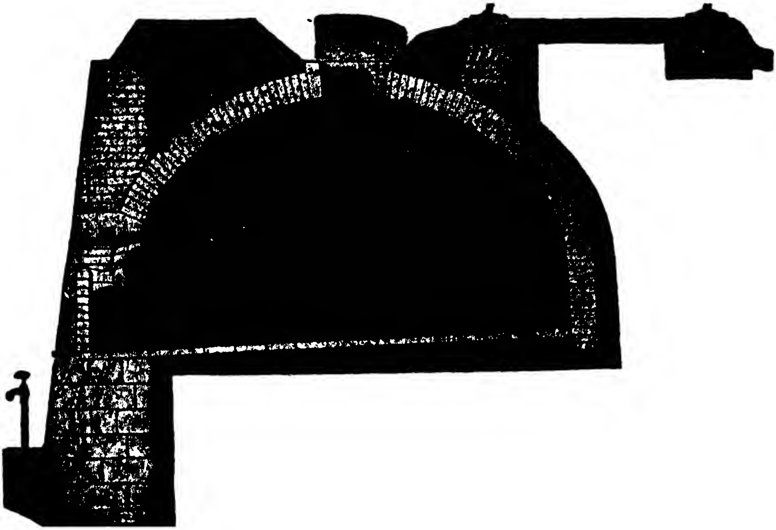

Fig. 2.—Standard American beehive coke oven.

In the beehive oven, the yield of coke is about 60 per cent of the coal charged, and averages about 5 to 5½ tons of coke per oven.

The other type of oven is the *by-product oven*, of which one well-known type is illustrated in Fig. 3. The narrow rectangular oven chambers are about 37 to 42 ft. long, 10 to 14 ft. high, and 14 to 18 in. wide. They are tightly closed so that no air is

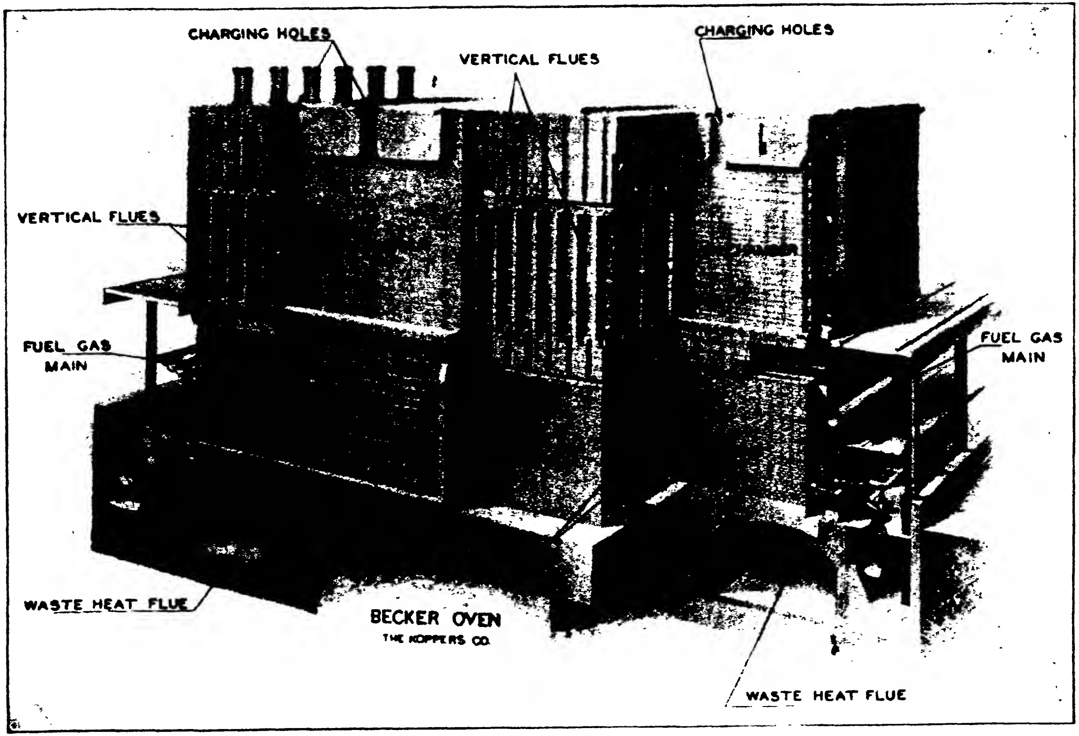

FIG. 3.—Becker by-product coke oven. Composite section through regenerators, heating flues, and oven chambers.

admitted; the heat for coking is furnished by burning gas in flues contained in the side walls of the ovens.

The ovens may be heated either by a low B.t.u. gas, such as producer gas or blast-furnace gas, or else by part of the coal gas produced in the coke oven itself. Where producer gas or blast-furnace gas is used for underfiring, the total coke-oven-gas production of about 11,000 cu. ft. per ton of coal is available for sale for city use or industrial purposes. If, on the other hand, part of the coke-oven gas is used for underfiring, the surplus gas amounts to about 6,000 to 6,500 cu. ft. of gas per ton of coal. The coking time ranges generally from 12 to 20 hr., and the coke yield is about 70 per cent of the coal charged, or about 7 to 13 tons per oven.

In the by-product coke oven the valuable by-products are saved; in the beehive oven they are allowed to escape into the atmosphere to become a great nuisance as well as a great waste. The by-products are well worth saving and have many important uses. Their recovery helps to make by-product, coke-oven operation economical.

By coking 1 ton of bituminous coal, in addition to a first-class coke, the following primary by-products are obtained:

By-products	Yield per Ton of Coal
Total gas (with producer gas or blast-furnace gas underfiring)	about 11,000 cu. ft. of 575 B.t.u.
Surplus gas (with coke-oven gas underfiring)	6,000 to 6,500 cu. ft. of 575 B.t.u.
Tar	9 to 12 gal.
Ammonium sulfate	23 to 26 lb.
Light oil	2.75 to 3.5 gal.

In the purification of the by-product-oven gas by means of a liquid-contact process, the Koppers Company obtains practically pure sulfur in a form much finer than the commercial precipitated sulfur. This finely divided sulfur has been found to possess superior qualities as a fungicide.[1] Among the other interesting and valuable by-products recovered by the liquid-purification processes are the thiocyanates of ammonium, sodium, and calcium.

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[1] RAMSBURG, C. J., "Present Trends in By-product Gas and Coke Industry," *Mining Cong. Jour.*, p. 69, February, 1930.

Starting with ammonium thiocyanate, a new synthetic resin has been made, which can be molded in a manner similar to bakelite. A transparent variety of this resin is capable of transmitting ultraviolet light and may become a substitute for glass. Sodium thiocyanate has been found to be a good germination accelerant in the growing of potatoes, and calcium thiocyanate is a solvent for cellulose.[1]

Production by Processes.—Fortunately, the coking of coal by the beehive-oven process is rapidly becoming less common, and a constantly increasing amount is being made by the by-product-oven process, as the following figures show.[2]

Year	Percentage of total production of coke	
	By-product-oven coke	Beehive-oven coke
1909	15.91	84.09
1914	32.47	67 53
1919	56.90	43.10
1923	66.00	34.00
1927	91.5	8.5

More than 15 per cent of all the coal mined in America is converted into coke by the by-product-oven process.

Comparison of Cokes.—The beehive-oven coke, which has a clean, silvery-gray appearance, usually occurs in long, slim pieces, commonly designated as "fingery" coke. The by-product-oven coke, of a gray-black cast, occurs in short, thick pieces. The difference in surface appearance is affected by the manner of quenching. In the beehive oven, the coke is quenched within the oven; as little water as possible is used. In the case of the by-product oven the red-hot coke is pushed out into a coke car which carries it to the quenching station where it is showered for a definite short period of time by a spray of water. The coke is then exposed on an inclined wharf, to allow the remaining

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[1] Ramsburg, C. J., *op. cit.*, p. 70.

[2] From "Mineral Resources of the United States," U. S. Geol. Survey.

internal heat to drive off surface moisture. No matter how quickly the coke may be quenched after being forced from the oven, contact between the air and the highly heated coke will have occurred. This causes a certain amount of surface oxidation which destroys the luster of the coke.

The size and shape of the lumps of by-product-oven coke is an advantage. Since the lumps are generally of a uniform size, the space between them is greater; therefore, the furnace blast can pass with greater ease. The prejudice against by-product-oven coke, which was strongly marked until a few years ago, has been overthrown by the actual demonstration that such coke, when properly made and used, is actually superior to beehive-oven coke.[1]

Coke as a Metallurgical Fuel.—The greatest amount of coke produced is used as a metallurgical fuel, chiefly for iron. For this purpose, it is far more desirable than coal, because it contains less sulfur, and because it is able to support the weight of the charge, which soft coal cannot do.

Coke is less desirable than charcoal, however, because it contains more sulfur, phosphorus, and ash. But because of the greater cost of charcoal its use is limited; coke is far more widely used. The fact that coke is stronger than charcoal is also an important consideration, for, since it can support a greater weight, higher furnaces can be built.

From the coke practically all of the phosphorus and some of the sulfur are taken up by the iron; the ash must be cared for as slag. The sulfur content of coke is its most objectionable feature. This varies from 0.5 per cent in the best cokes to 2 per cent in inferior cokes. In the ordinary good coke the sulfur will vary from 0.5 to 1.25 per cent. Phosphorus is generally not high, usually under 0.05 per cent; 0.03 per cent is the maximum allowable for use with irons required to have a low phosphorus content.

The ash of coke varies from 6 per cent in extremely good cokes to 14 to 16 per cent in those of poor quality. Usually the ash ranges from 8 to 12 per cent. The ash of a coke may be materially decreased by washing the coal prior to coking, and a low ash content is of great importance in the economical operation of metallurgical furnaces.

[1] BACON and HAMOR, "American Fuels," p. 121.

LIQUID FUELS

Burning of Liquid Fuels.—Liquid fuels burn much more rapidly than solids but not so rapidly as vapors and gases. Although the burning of liquid fuels is rapid under proper conditions, it cannot be made to proceed rapidly upon an unbroken surface. Oils are most conveniently and efficiently burned when "pulverized" or "atomized."

The pulverizing may be accomplished by directing a jet of compressed air or steam across a jet of oil at a definite angle. It is more advantageous to use compressed air because this helps to introduce the required amount of oxygen needed in burning the oil. It is more convenient to use steam, however, since with it no special compressing apparatus is required as is needed in the case of air. In most of the stationary boiler work, burners of the steam "atomizing" type are used; air is employed only in special cases. Mechanical devices for pulverizing the oil are also used to some extent.

Advantages of Liquid Fuels.—Some of the chief advantages pertaining to the use of liquid fuels may be summed up as follows:

The fuel can be more easily stored and moved. It can be fired mechanically, which eliminates the cost of labor in stoking. The fire may be regulated to develop a most intense heat in a very short time, and then can be cut off in a moment. There is an absence of dust, ashes, and clinkers. Less heat is lost by way of the stack owing to the clean condition in which the boiler tubes may be kept.

Another advantage of liquid fuel is its high calorific value per pound. The average heat value of the coals is probably in the neighborhood of 13,000 B.t.u. per pound, while for fuel oil it is probably about 19,000 B.t.u. per pound.

It is very necessary that the fuel oil be free from water; the heating value of the oil is reduced 13.14 B.t.u. for each 1 per cent of water. Water in a fuel oil is difficult to remove, since the densities of the two are not far apart.

Materials Used as Liquid Fuels.—The liquid fuels employed in the United States consist to some extent of the heavy, black petroleum oils found in California, Texas, Oklahoma, and other states, as well as the tarry residuum left in the refining of lighter crudes; but a great deal of liquid fuel is made up of the so-called intermediate oils. The intermediates are those products obtained in the refining of crude petroleum between the naphthas and kerosenes on the one hand and the lubricating oils on the other. Although they are used in a different manner, the naphthas (gasolines) and kerosenes are also liquid fuels; the naphthas have an especially great economic importance. Before entering upon any further discussion of the properties of the liquid fuels, it will be advisable to consider the characteristics of the crude petroleums and the methods of refining them.

CRUDE PETROLEUMS

Origin of Petroleum.—It has been suggested that the petroleum oils have been produced in the earth by the reactions involving only inorganic substances. In support of this view it has been demonstrated that carbonic acid and dissolved carbonates in ground waters acting on alkali metals will produce hydrocarbons, a class of compounds of which the petroleums consist almost entirely. The carbides of metals formed by reactions of fused materials in the earth have also been considered as a possible source of the oils. It is well known that acetylene is produced by the action of water on such carbides, and by the polymerization[1] and hydrogenation of acetylene petroleum-like hydrocarbons can be formed. Such hydrocarbons, however, are optically inactive, while nearly all petroleums, apparently, rotate the plane of polarized light[2] to either the right or the left. It would seem, moreover, that if petroleum originated in igneous rock (page 396), some of it should be found there, but these oils are always found in sedimentary rock (page 400).

The results of all the more recent investigations seem to indicate that petroleum has originated from the decomposition of organic material, of both animal and vegetable sources. There is reason to believe, Orton[3] says, that the oil found in the Appalachian field, which includes Pennsylvania, New York, southern Ohio, West Virginia, and Kentucky, is of vegetable origin. The

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[1] Footnote, p. 498.

[2] See any standard textbook on Physics.

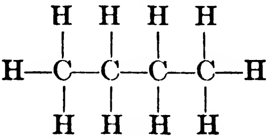
[3] "Report on the Occurrence of Petroleum, Natural Gas, and Asphalt in Western Kentucky," 1891.

California and Texas product, on the contrary, Peckham[1] states, is of animal source. It is sometimes found in rocks filled with animal remains. Engler, in working on this problem, distilled ½ ton of menhaden fish oil under a pressure of 10 atmospheres, and obtained a distillate of hydrocarbon oils, accompanied by gas, that had practically all the properties of natural petroleum. This result lends support to the theory that petroleum was formed by the action of heat and pressure on organic remains in the earth.

Petroleum Hydrocarbons.—The various crude petroleums are quite complex in structure. They are not definite compounds, but usually consist of mixtures of several series of hydrocarbons. Among the more important are the paraffin, olefin, naphthene, and aromatic hydrocarbons.

Paraffins.—The general formula for any member of this series is C_nH_{2n+2}. The series begins with methane gas (CH_4) and each member increases by CH_2, as: C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, etc., to $C_{35}H_{72}$. The first four members are gaseous. From C_5H_{12} to $C_{17}H_{36}$ are liquids; the former boils at 38 and the latter at 303°C. The remainder are solids at atmospheric temperatures; $C_{18}H_{38}$ melts at 28°C., and $C_{35}H_{72}$ at 75°C.

The paraffin series is called a *saturated* series; each molecule possesses a chain-like structure, with single "linkings" between the carbon atoms and with all other "bonds" occupied by hydrogen, as is shown by the following structural formula for the fourth member of the series, thus:



$$\begin{array}{ccccccccc}
 & H & & H & & H & & H & \\
 & | & & | & & | & & | & \\
H- & C & - & C & - & C & - & C & -H \\
 & | & & | & & | & & | & \\
 & H & & H & & H & & H &
\end{array}$$

The paraffin hydrocarbons are relatively inert chemically. It is because of their inertness that they have been named paraffin—from the Latin *parum*, too little, and *affinis*, allied, indicating that these hydrocarbons react tardily with other substances.

Olefins.—The olefin hydrocarbons are *unsaturated* compounds represented by the type formula C_nH_{2n}. The term unsaturated means that between some of the carbon atoms "double bondings"

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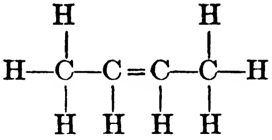
[1] *Amer. Jour. Sci.*, **48**, 389, 1894.

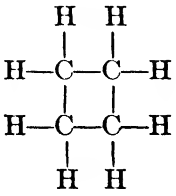
exist, an arrangement which lessens the capacity of the carbon for holding hydrogen, thus:



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & C = C & - & C & - & H \\ & & | & & \;|\quad| & & | & & \\ & & H & & H\quad H & & H & & \end{array}$$

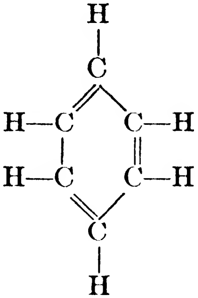
Ethylene (C_2H_4) is the simplest olefin, and the group is sometimes called the *ethylene* series. Like the paraffins, the first four olefins, C_2H_4, C_3H_6, C_4H_8, and C_5H_{10}, are gaseous at ordinary temperatures, and, except that the boiling points are a few degrees higher, the physical properties of the other members of the olefin series are very similar to the corresponding paraffins. Chemically, however, the olefins are more active than the parafins. By virtue of their "double bondings," they are able to take on additional hydrogen and to combine with other elements and compounds. They are absorbed by sulfuric acid and are converted into organic sulfates.

Naphthenes.—The naphthenes are very similar to the paraffins in chemical and physical properties, but a chemical analysis shows that the carbon-to-hydrogen ratio of the naphthenes is like that of the olefins, being represented by the type formula C_nH_{2n}. These apparently discordant facts are reconciled by the explanation that the naphthenes are "ring" compounds, whereas the paraffins and olefins are "chain-like" in character. The closing of the ring utilizes the linkings made available by the 2 missing hydrogen atoms, thus:

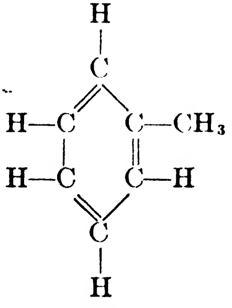


The naphthenes are sometimes called *cycloparaffins.* The formula just given is that of cyclobutane, the fourth member of the series.

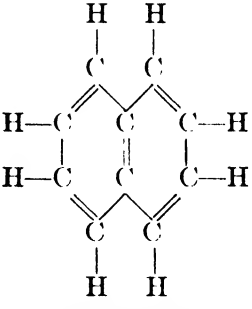
Aromatic Hydrocarbons.—In some crude petroleums, noteworthy amounts of aromatic hydrocarbons and their derivatives are found. Benzene (C_6H_6) (page 511), represented by the type formula, C_nH_{2n-6}, is one of the least complex of this class. Benzene is a six-membered carbon ring with three double bonds, thus:



Other aromatic hydrocarbons frequently occurring with benzene in petroleum are toluene ($C_6H_5CH_3$) and naphthalene ($C_{10}H_8$). Toluene may be considered as methyl benzene, and naphthalene as a product formed by the union of 2 benzene molecules with 2 carbon atoms common to each, thus:



Toluene



Naphthalene

Production.—Although petroleum has long been known in the form of seepages, pools, etc., on the earth's surface, it was not produced in quantity until 1857, for which year 2,000 bbl. are credited to Rumania. Pennsylvania reported the same amount for the year 1859. It is now produced in large quantities by a great number of countries, but about 70 per cent of the total output of the world is produced in the United States. Nearly three-fourths of the domestic production is supplied by four states, which, named in order of quantity produced, running from high to low, are California, Oklahoma, Texas and Pennsylvania. Other producing countries named in the order of lessening importance, are Russia, Mexico, Netherland East Indies, Rumania, Persia, Poland, and India.

Petroleum Types and Fields in the United States.—The petroleums of the United States may be classified under three general heads: (1) paraffin-base oils, (2) mixed-base oils, and (3) asphaltum-base oils. This classification is determined by the character of the residuum left after the more volatile portions of the oils have been removed by non-destructive distillation, that is to say, by distillation in which an effort is made to avoid, as far as is possible, any decomposition or other change in the compounds of which the petroleum consists.

The producing areas of the country, likewise, may be grouped under the heads of general fields. Although more detailed divisions are possible, the following arrangement indicates the approximate limitations of the more important producing areas:

1. Appalachian.
2. Lima-Indiana.
3. Illinois.
4. Mid-continent.
5. Louisiana and Texas Gulf Coast.
6. Wyoming.
7. California.

The Appalachian field is comprised chiefly by western Pennsylvania and eastern Ohio, but it juts into southwestern New York, West Virginia, and Kentucky. This field was the first to be developed in the United States and its production is now much less than it formerly was. Oils from this territory are typical paraffin-base oils. Both the low- and the high-molecular weight components are paraffins, but the intermediates are presumed to be largely naphthenic.[1] The oil has a low content of both sulfur and asphalt, and yields a high percentage of gasolines and kerosenes. Lubricating oils of exceptionally high quality may be prepared from it readily.

The Lima (Ohio)-Indiana petroleums contain more cyclic hydrocarbons and asphaltic substances than the Appalachian oils, and the sulfur content generally is high, about 0.5 per cent.

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[1] Gruse, "Petroleum and Its Products," p. 6.

Some of the sulfur is present in the form of compounds that possess disagreeable odors, and special methods of refining are necessary to remove them. The Illinois crudes are similar to the Lima oils but the sulfur content is lower.

As listed here, the Mid-continent field includes northern and central Texas, northern Louisiana, Oklahoma, Arkansas, and Kansas. In this wide area the character of the oils, of course, varies greatly, but they are perhaps more of the mixed-base type than any other. The asphalt content, however, is not high, especially in the oils from central and northern Texas, northern Louisiana and Kansas, and some of these petroleums have a fairly high gasoline content, are definitely of a paraffin-base character, and may be readily worked for lubricants. Some of the Texas oils are of the asphalt-base type and show a high naphthenic content.

The Louisiana and Texas Gulf Coast crudes are usually of the heavy, asphalt-base type. They generally show a high naphthene and low paraffin content. Lubricants that will withstand low temperatures without solidifying are made from these oils.

The Wyoming field produces petroleums of both the paraffin- and asphalt-base types. Some of them resemble the oils of the Appalachian field, while others are low in gasoline and kerosene, and contain so much asphaltic matter that they are unsuitable for making lubricants.

The petroleums from different parts of the California field vary considerably in character, but they are generally naphthenic in character and contain much asphalt. With some exceptions, the gasoline, kerosene, and paraffin-wax content is low. Some of the California oils contain appreciable amounts of aromatic hydrocarbons.

REFINING OF PETROLEUM

General Considerations.—Only a small quantity of petroleum is used in the crude state. It is nearly all refined by a process that consists largely of fractional distillation. The principles involved in refining the three types of oils, paraffin-base, asphaltum-base, and mixed-base, are in general not very dissimilar, but the exact treatment varies with the kind of oil and the products desired.

The paraffin-base oils, from which it is possible to obtain lubricants of superior quality, are in the main distilled with a careful avoidance of cracking or decomposition by heat. This method produces the maximum yield of a residuum suitable for the manufacture of steam-cylinder oils. Asphalt-base oils may be run with steam to a fuel-oil residuum, to a flux, or to a heavy asphalt; or if a high yield of light products, such as gasoline or kerosene, is desired, they will be run to a solid residuum or coke. In the last case, decomposition by heat is desired. The mixed-base oils may be run with steam distillation to a fuel-oil residuum or to flux, but if the oil is suitable for the production of lubricants, it may be run with little or no steam to a dry residuum or coke.

An outline of a few of the distillation processes will be given. Although these methods may be regarded as typical, it must be kept in mind that it would be difficult to find two refineries that use exactly the same process.

Refining Paraffin-base Petroleum.—The products manufactured from this oil, named in order of their density, are: (1) petroleum naphtha (which is divided into several fractions), (2) lamp oils, (3) gas-making oils, (4) fuel oils, (5) light, medium, and heavy lubricating oils, (6) paraffin, (7) asphaltum pitch, and (8) coke. The methods by which these products are separated may be divided into two general classes: (1) those employing steam distillation, and (2) those employing "dry" or destructive distillation. The products, though they differ in amount, are essentially the same in both cases.

In *steam distillation*, open steam is introduced into the retort or still by means of perforated pipes placed near the bottom, and the oil vapors, raised by the direct fire beneath the still, are swept out before they become unduly heated and decomposed. (A similar result may be obtained by distillation *in vacuo.*) The various portions of the crude oil are thus separated according to boiling point and specific gravity with practically no chemical alteration. This method is employed if it is desired to have a larger yield of lubricating oil of especially high quality.

In carrying out this process, after the mud and water have been removed by gravity in storage tanks, the oil is charged into horizontal, cylindrical steel stills that range in capacity from 200 to 1,000 bbl., and the fire is started. As soon as the temperature of the oil is well above the boiling point of water, the steam is introduced. The first product to distill off is the "crude naphtha," which usually consists of the hydrocarbons from C_5H_{12} to $C_{10}H_{22}$ inclusive. With Appalachian-field oil, this fraction may amount to as much as 24 to 40 per cent of the crude. It is collected until the boiling temperature reaches 150°C., or when the Baumé gravity (see Chap. XX) of the condensate falls to about 48 to 50°.

By a proper manipulation of valves, the distillate is now directed into another receiving tank. This is the crude kerosene distillate. It is collected between the distilling temperatures of 150 to 300°C., or until the Baumé gravity of the condensate has fallen to about 42 to 38°. The kerosene fraction may constitute from 15 to 20 per cent of the crude oil.

The next portion, usually the gas oil or fuel oil, is collected until the density of the condensate has fallen to about 36.5°Bé. This fraction usually amounts to about 10 to 15 per cent of the original crude.

The next fraction is the "wax distillate," which comprises from 16 to 22 per cent of the crude. The residue now remaining in the still is known as "steam-refined cylinder stock," and constitutes from 12 to 17 per cent of the crude. It is pumped from the still into a storage tank and later refined. (For the method of refining the wax distillate and cylinder stock, see Lubricating Oils, page 557.)

Destructive distillation is generally known as the "cracking process," because some of the heavier hydrocarbons are decomposed. This must not be confused, however, with the numerous cracking processes that have been developed during the past few years and which, as described on page 56, have been applied largely to the intermediate oils. In destructive distillation, neither steam nor reduced pressure are employed, and the distillation temperatures are considerably higher, with the result that some decomposition takes place as already stated. This method is employed if it is desired to produce a larger yield of naphthas and burning oil, rather than lubricants. The process was at one time widely used, but with paraffin-base crudes, because of the increased demand for high-grade lubricants, it is now of much less importance. Lubricating oils made from paraffin-base crudes have always been highly esteemed. After the distillation has been completed, that which remains in the still is known as "tar," and is further refined as shown under Lubricants on page 559.

Treatment of Mixed-base Petroleums.—No definite or stated method for refining mixed-base petroleums can be given, because the crude oils differ widely in their properties, and each refiner adopts methods and apparatus best suited to the particular oil being treated. If the asphaltic content is comparatively high, steam distillation will likely be employed, yielding gasoline, kerosene, gas oil, and wax distillate, and a heavy residuum known as flux. Steam is used because in this case cracking is not desired. The flux produced by this process is employed with harder asphalts in the preparation of road materials.

If the asphaltic content is comparatively low, and if the oil is suitable for the manufacture of good lubricants, it will likely be run by the cracking process, with little or no steam, to coke. In some cases, after the light and medium products have been distilled off, the asphaltic material is removed from the residue by the sulfuric-acid and fuller's-earth treatment, and then the treated product is distilled for the production of lubricants. With some oils, filtering is deferred until after the final distillation.

Production of Naphtha from Heavy Asphaltic Crudes.—In refining the heavy asphaltic oils, after the water has been removed, the treatment will depend upon whether the object is to produce lubricating oils, or whether the oil is to be reduced to asphalt. In making lubricating oils, the water-free crude is distilled to dryness. This will result in the production of the various grades of naphtha, burning oil, gas oil, light and heavy lubricating stock, gas, and coke. In the case of some asphaltic oils that also contain paraffin, a wax distillate will be produced with the lubricating stock. Sometimes a certain amount of cracking is involved; it is not difficult to bring this about because the hydrocarbons of the asphaltic crudes are relatively unstable.

Naphtha is found occasionally in unrefined oils of the asphaltic type, for example, in certain Mexican crudes. With many of the asphaltic crudes, particularly California oils, it is customary to remove the lighter portions by a method known as "topping";

the lighter hydrocarbons only are distilled off, which leaves as a residuum a heavy asphalt.

Naphthas Obtained by Cracking Gas Oil and Other Intermediates.—Perhaps more than 30 per cent of the gasoline sold in the United States is made by cracking gas oil or similar intermediate oil distilled from the crude. The processes employed for this purpose may be divided into two major classes: (1) those that treat the oil in the vapor phase; and (2) those that treat the oil in the liquid phase, with part of the liquid in contact with the vapor. Pressure and catalysts may be employed in both processes. Although until recently liquid-phase cracking was employed to the greater degree, the vapor-phase processes are now the more popular. Gasolines produced by vapor-phase methods are high in unsaturated compounds, and the research laboratories have demonstrated that the unsaturated hydrocarbons possess greater anti-knock properties (page 60) than the saturated paraffins. The introduction of high-compression motors, which demand fuels with anti-knock characteristics, has, therefore, intensified the interest in vapor-phase cracking. Cracked gasoline tends to develop an undesirable color and odor, and the problem of the producer is to keep the percentage of unsaturates as high as possible without allowing these features to render the gasoline objectionable to the consumer.

Many processes for both liquid- and vapor-phase cracking have been patented and the industry is not infrequently disturbed by questions of infringement. The technology of cracking changes rapidly, moreover, and processes that today are extensively used may soon be supplanted. In the vapor-phase method it is now a common procedure to employ a long tube through which the oil to be cracked is passed very rapidly. The velocity employed is sufficiently high to cause turbulent flow, because this type of flow minimizes the deposit of carbonaceous matter. The highest temperature, which is maintained toward the exit end of the tubular system, where it is intended that the cracking shall occur, may range from 510°C. (950°F.) to 650°C. (1200°F). Some of the oil charged passes through the system unchanged and must be returned to the retort. In a single run, 35 to 55 per cent of the charge may be recovered as yellow naphtha which is redistilled and further refined for motor fuel. The reactions by which the naphtha is produced will be considered later in the discussion of the properties of this product. A disadvantage of vapor-phase cracking is the high loss in the form of fixed gases. Perhaps 15 per cent of the total charge may be lost in this manner. The compensation for this disadvantage is, of course, the antiknock quality and the consequent higher price of the motor fuel.

Redistillation and Treatment of the Crude Naphtha.—The naphtha obtained by a "straight-run" distillation of crude oil, or by any of the destructive distillation or cracking processes, must be further refined. It is generally redistilled in a special still heated by steam coils and fitted with a fractionating column. In this way the crude naphtha is subdivided into several grades according to boiling point and density. To remove the tarry and sulfur-bearing compounds, which if allowed to remain would impart a dark color and disagreeable odor, it is agitated with sulfuric acid. After the acid treatment, it is agitated with a solution of caustic soda and then with water, after which the water is allowed to settle out. The finished product is known as "deodorized naphtha."

Commercial Names of Naphtha Subdivisions.—The several commercial grades of naphtha are known by many names, concerning which there is much confusion and, unfortunately, no uniformity of usage. Robinson[1] says that it is best to make use of but two general names—gasoline and naphtha. In this scheme the name *gasoline* is confined to the mixtures of light hydrocarbons designed for such use that they are required to be vaporized, as in a gasoline torch, stove, or automobile carburetor. On the other hand, the name *naphtha* is confined to those hydrocarbons whose use depends upon their solvent action, as when used in dry cleaning, oil extraction, or varnish making. This excludes the use of the term *benzine* entirely. And in view of the fact that this term is very similar to *benzene,* which is used to apply to a coal-tar product of entirely different nature, it is clearly evident that there would be a distinct advantage in this nomenclature.

Although the terms applied to the various divisions of the volatile portion obtained from petroleum are, by both refiners and users of these liquids, often indiscriminately employed

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[1] *Met. Chem. Eng.*, **2**, 389, July, 1913.

without much consideration of density or other properties, the following classification shows the ranges covered as they are most commonly used. It will be noted that there is considerable overlapping.

1.	Cymogene	about 108°Bé.
2.	Rhigolene	about 94 to 92°Bé.
3.	Petroleum ether	about 92 to 80°Bé.
4.	Gasoline	about 86 to 60°Bé.
5.	Naphtha	about 68 to 58°Bé.
6.	Benzine	about 66 to 60°Bé.
7.	Motor fluid	about 62 to 58°Bé.
8.	Turpentine substitute	about 62 to 52°Bé.

Naphtha is also sometimes called *ligroine* (abroad, it is called *petrol*) and the turpentine substitute is also known as "*painter's spirits*." Since, as stated before, there is no classification strictly adhered to among refiners and users, and since names, therefore, carry no definite significance, if the characteristic properties and uses of the liquids are associated with their densities and especially with their boiling points, the confusion will be lessened.

Gasoline Produced by Hydrogenation.—By the process of catalytic hydrogenation under pressure (page 37) the lowest grades of crude liquid hydrocarbons, derived from either coal or petroleum, may be converted into gasoline with a yield, measured by volume, of 100 per cent more or less.[1] The process is very similar to the berginization of coal, but when oil is used as the raw material, the hydrogenation is more easily accomplished. In the United States, plants employing this method have recently been put into operation. An important feature of the process is that the sulfur in the oil, which has always been a source of great annoyance to petroleum refiners, passes out of the reaction chamber as hydrogen sulfide with the non-condensable gases. Thus, almost sulfur-free products can be readily prepared from high-sulfur crudes.

Natural Gasoline.—The gas that issues from certain natural gas wells is known as "wet gas"; *i.e.*, it contains a certain amount of the vapor of a very volatile gasoline. By compressing and cooling, this gasoline can be extracted. From 0.5 to 2.5 gal.

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[1] *Chem. Met. Eng.*, **37**, 282, May, 1930.

of natural gasoline may be separated from 1,000 cu. ft. of gas. In another method the gasoline is extracted by passing the wet gas through oil, such as a heavy lamp oil or gas oil, which absorbs and retains the gasoline. The absorbed gasoline is then separated from the oil by distillation. Recently, a third method of separating the gasoline from the gas has been developed.[1] It has been found that the gasoline hydrocarbons are absorbed selectively by specially prepared charcoal; the gasoline is subsequently recovered from the charcoal by distillation with steam. It is said that the gasoline content is completely removed from the gas by this process.

Natural gasoline consists chiefly of the following hydrocarbons: pentane (C_5H_{12}), hexane (C_6H_{14}), and heptane (C_7H_{16}). It is too volatile to be used by itself for ordinary purposes and therefore is usually mixed with heavier hydrocarbons, in which form it is employed extensively as a fuel for stationary gasoline engines and in the aviation industry.

Gasoline Production According to Source.—In the United States, approximately 60 per cent of the gasoline produced is represented by that which was originally present in the crude oil; approximately 30 per cent is cracked distillate; and about 10 per cent is natural gasoline.

Benzol as a Motor Fuel.—Recently, mixtures of benzol (page 511) with gasoline have been employed to some extent as motor fuel. Benzol is obtained from the products resulting from the destructive distillation of coal. The ordinary commercial variety consists of about 70 per cent benzene (C_6H_6) and 30 per cent toluene ($C_6H_5 \cdot CH_3$). Although benzol has a slightly lower calorific power per unit weight than ordinary gasoline, it yields a greater amount of heat per unit volume because of its greater density. Benzol has a higher ignition temperature than gasoline, and on this account it has been found possible to employ much higher compression pressures in the engine with benzol than with gasoline, without preignition; *i.e.*, ignition before the introduction of the spark. When preignition occurs, there is a great loss of power because of the tendency to reverse the engine. The higher compression pressure that may be employed with benzol produces greater efficiency, then, but benzol has a

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[1] *Chem. Met. Eng.*, **24**, 156, 1921.

greater tendency to produce a carbonaceous deposit than has gasoline.

Detonation in a Gasoline Engine.—When kerosene is added to gasoline in considerable proportion, it causes trouble under high compression by producing a knock in the engine. This is supposed to result from the occurrence of sharp detonation rather than the normal combustion or flame propagation. Benzol, alcohol, and some other substances that burn slowly, when blended with the paraffin-series hydrocarbons,[1] tend to retard the combustion of the mixture in such a way as to minimize the knock. A mixture of 40 per cent of benzol in kerosene makes a satisfactory fuel in this respect.

Midgley and Boyd[2] of the General Motors Research Corporation have found that such compounds as diethyl selenide [$(C_2H_5)_2Se$] and tetraethyl lead [$(C_2H_5)_4Pb$] are very effective in suppressing the detonation. They report that even a single molecule of one of these compounds in over 200,000 molecules of combustible mixture of kerosene and air exerts an effect in the suppression of detonation equal to 25 per cent by volume of benzol in kerosene.

A mixture of 1,000 parts of ordinary gasoline with 1 part of a preparation known as "ethyl fluid" has been prepared with a view to suppressing the knock and is sold under the name of "ethyl gasoline." The ethyl fluid is composed of 3 parts of tetraethyl lead, 1 part of ethylene dibromide as a carrier, and a little aniline oil.

"Straight" and "Blended" Gasolines.—Since gasolines have acquired such great economic importance, it has become the practice to mix or "blend" the very light, volatile grades with heavier fractions that by themselves would be of little value, thus producing a product of a mean density, or Baumé test, that has been known to the trade as a desirable gasoline. But with the appearance on the market of such blends, the Baumé or gravity test at once ceased to be a reliable guide to the quality of

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[1] Although alcohol dissolves in gasoline to only a slight extent, the addition of benzol promotes the formation of a homogeneous mixture.

[2] "Chemical Control of Gaseous Detonation with Particular Reference to the Internal Combustion Engine," *Jour. Ind. Eng. Chem.*, **14**, 897, October, 1922.

the fluid. With gasolines that are "straight" distillates, the various grades represent fractions of the crude-oil series that were separated in order of their boiling points. Thus, the light hydrocarbons distill off at the lower temperatures and possess the lighter densities as shown by their higher Baumé readings. The medium gasoline hydrocarbons distill off at medium temperatures and may be recognized by their medium densities. In brief, since the specific gravity normally increases with the boiling points of these hydrocarbons, the Baumé readings serve to indicate, to some degree, the volatility of the liquid. But in a blend this does not follow, since a medium density may be secured by mixing two constituents, one boiling at a lower and the other at a higher temperature than a straight distillate of medium density, although hydrocarbons, such as the density would seem to indicate, may be almost entirely lacking. Hence, there is now a growing tendency to disregard density in the choice of a gasoline; the trend is toward a selection on the basis of boiling point or volatility. For this purpose a sample is distilled under special conditions, and note is taken of the temperature at which distillation begins and where it ends, particularly of the latter temperature which is known as the "end point." Also much information about the uniformity of the sample can be obtained by noting between what temperatures the bulk of the liquid distills. Blends will likely begin to distill at relatively low temperatures, have a long distillation range, and a high end point. On the other hand, straight distillates of equivalent density will generally have higher initial boiling points and lower end points; *i.e.*, the gasoline will consist of hydrocarbons of less variable volatility.

At the present time, in the production of blends it is customary to use a refinery gasoline as a base and to add (1) a certain proportion of the highly volatile natural gasoline to impart a quick-starting quality to the motor, and (2) a suitable percentage of unsaturated hydrocarbons, such as benzol or the gasoline derived from vapor-phase cracking, for the purpose of suppressing the tendency of the engine to knock under high compression. For the latter purpose, of course, the ethyl fluid may also be employed.

Does Cracked Gasoline Possess Objectionable Features?—The decomposition reactions that take place during the cracking of oils are not definitely known. According to Thorp,[1] however, reactions such as represented by the following equation may occur. The hydrocarbon ($C_{18}H_{38}$) boiling at 317°C. might decompose as follows:

$$C_{18}H_{38} \rightarrow C_{10}H_{22} + C_7H_{16} + C$$

The $C_{10}H_{22}$ boils at 173°C. and belongs with the lamp oils, while the C_7H_{16} boils at 98°C. and belongs with the naphthas. The carbon thus liberated forms a coke in the still. Possibly, the reaction may proceed in the following manner:

$$C_{18}H_{38} \rightarrow C_8H_{18} + C_{10}H_{20}$$

In this case the first product belongs to the paraffin series and boils at 125°C., while the second is a mono-olefin (unsaturated), boiling at 172°C. Diolefins also may be formed, such as erythrene [C_4H_6 ($CH_2{:}CH{\cdot}CH{:}CH_2$)] and compounds of this class are relatively unstable. The splitting does not necessarily occur near the middle of the chain; gaseous hydrocarbons may be split off. Besides, decomposition is not the only type of change occurring; polymerization and condensation are going on at the same time, so that more complex hydrocarbons may be formed. Polycyclic naphthenes and aromatics are undoubtedly present in the gasolines produced by cracking, especially when the higher temperatures are employed in the process.

Leslie says[2] that, when used as a motor fuel, a possibile objection to gasoline made by cracking processes is the olefin content, the diolefins being especially objectionable. The evidence seems to show that gasolines containing over 20 per cent of olefins cause trouble because of the formation of gummy deposits on the valve stems, valve pockets, and sometimes in the carburetor. On the other hand, these same olefins, as well as other unsaturates, are desirable because of their knock-suppressing tendency, as has been stated before.

Lamp Oils.—Returning to the distillation of the crude petroleum, after the naphtha distillate has been removed in the general refining process, the distillation of the remainder of the crude oil is continued. The distillate which passes off between 150 and

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[1] "Outline of Industrial Chemistry," p. 308.

[2] "Motor Fuels," p. 525.

about 300°C. is known as lamp oil, burning oil, illuminating oil, or kerosene. It has an average boiling point of about 230°C., and ranges from about 42 to 38°Bé. in density.

The grades of illuminating oil are designated according to their fire test. The fire test is that temperature at which the oil will give off enough vapor to support a steady flame. It is a temperature lower than its boiling point.

Boverton Redwood gives the following as the classification of illuminating oil according to fire test: (1) 110°F. fire-test oil; (2) 120°F. fire-test oil; (3) 150°F. fire-test oil; (4) 300°F. fire-test oil.

The first two grades are largely exported. The third grade is usually required by ordinance to be used in the cities of the United States. The fourth is known as "mineral-sperm," "mineral-seal," "mineral-colza" or lantern oil. It is much used in railway lanterns and switch lamps.

Any one of the preceding four grades may again be divided into three grades according to color. The first or best grade is known as "water-white" or "head-light" oil. Head-light oil is usually 150°F. fire test but not necessarily so.

The second grade, called "prime white," is a faint yellow.

The third grade, known as "standard white," is a pronounced yellow.

The tarry matters and decomposition or oxidation products to which the color is due, and which cause the flame to smoke and the wick to become clogged when the oil is used, can be removed, as is the case in the "water-white" oil, by treatment with sulfuric acid.

The oil is agitated by means of compressed air with 1 to 2 per cent of concentrated sulfuric acid for about 1 hr. The acid now containing the colored substances is allowed to settle and is then drawn off. The oil is then agitated with water, allowed to settle, then agitated with about a 1 per cent solution of caustic soda to correct any remaining trace of acidity, and finally it is again washed with water. After this it is drawn into shallow tanks exposed to light and air and allowed to settle until bright.

Because of its greater volatility and the consequent ease with which it can be converted into a "gas" for use in a gas engine, the gasoline commands a higher price than the heavier kerosene, but when compared on the basis of their heat units, the gasoline is the less efficient of the two. A gallon of 85°Bé. gasoline, when burned completely, produces 102,980 B.t.u., while a gallon of 150° fire-test kerosene produces 124,450 B.t.u.

Gaseous Fuels

Advantages and Disadvantages.—As stated previously, fuels burn more readily when converted into either a vapor or a gas. When a wax candle burns, the wax becomes a liquid which then ascends the wick, and is gasified and burned. If a fuel can be changed into a gaseous state, as an operation entirely separate from its burning, it is a long way advanced toward effective combustion. This is the idea in using a gas producer.

It must be understood that no more heat is made available per pound of fuel by gasification. On the contrary, heat is lost by the cooling of the hot gases coming from the producer, and in other ways. The use of manufactured gas under a boiler would be an economic loss.

Because the gas can be better applied, however, there is a gain in intensity. Other advantages are:

1. The temperature can be easily controlled.
2. There is but little smoke, indicating almost complete combustion, even though but little more than the theoretical amount of air is required.
3. The gas can be used for the direct production of energy, *i.e.*, in gas engines.

Besides these, there are many other advantages associated with transportation, stoking, etc., not discussed here.

Producer gas is an artificial gas resulting from the incomplete combustion of a solid fuel in a partly closed generator of special construction known as a gas producer. There are many forms of producers, each embodying usually some special feature. One of the several types is shown in Fig. 4.

The essential principle in the operation of a gas producer is to admit to the producer air in only just sufficient quantity to burn the fuel to carbon monoxide. At first carbon dioxide is formed, and this gas, together with the nitrogen admitted as part of the air, absorbs the heat produced by the burning, carries it through the fuel above, and heats the fuel to incandescence.

From this incandescent fuel, each molecule of the carbon dioxide now takes up another atom of carbon, thus forming carbon monoxide. The first reaction liberates heat and the second takes up a *part* of it. The recations are shown by the following equations:

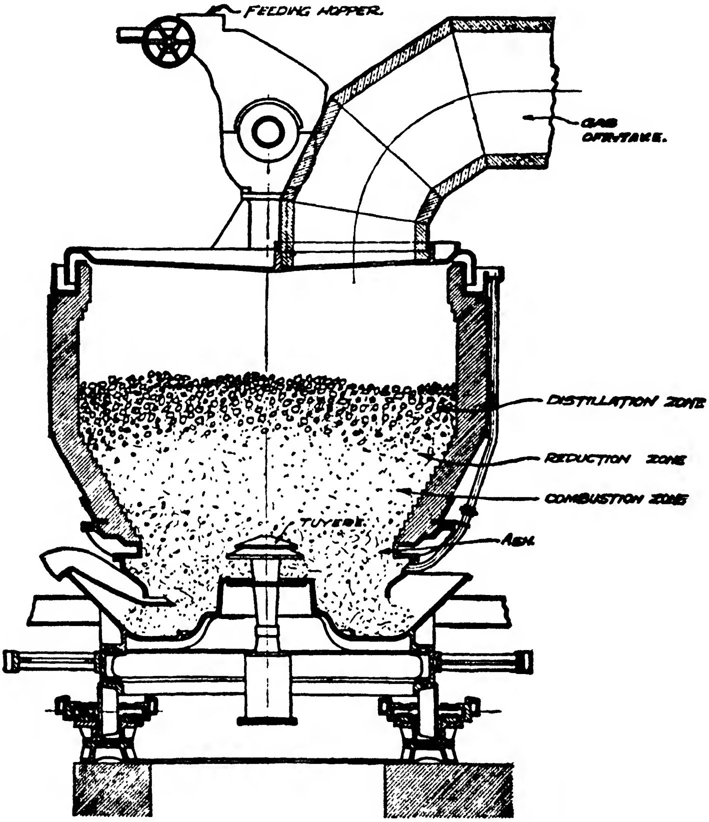

Fig. 4.—Cross-section of a gas producer.[1]

$$C + O_2 \rightarrow CO_2 \text{ (exothermic)}$$
$$CO_2 + C \text{ (hot)} \rightarrow 2CO \text{ (endothermic)}$$

The reaction represented by the former of these two equations takes place in the combustion zone, as shown in Fig. 4, and

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[1] Reproduced by permission from Bacon and Hamor's "American Fuels," vol. II, p. 918.

the latter in the reduction zone. If the reactions were complete, and were the only ones involved, the composition of producer gas would be one-third carbon monoxide and two-thirds nitrogen. As a matter of fact, this is not far from the actual composition. Other gases, however, are present. For example, not all of the CO_2 is reduced; some of it passes through unchanged. The presence of this gas in the final product is undesirable. In addition to having no fuel value it represents a loss of heat, since to produce it complete combustion must have occurred in the generating chamber so that all the heat was liberated there.

The final product or "producer gas" contains also a certain amount of free hydrogen. This comes partly from hydrogen contained in the solid fuel used, and partly from water contained as moisture in the air, which reacts with the heated carbon according to the equation:

$$H_2O + C \text{ (hot)} \rightarrow H_2 + CO$$

Producer gas frequently contains hydrocarbons that have distilled from the fuel as such.

As has been previously stated, the reduction of carbon dioxide to carbon monoxide by means of the incandescent carbon stores up only a part of the heat liberated when the carbon dioxide was formed. The heat not so taken up is equivalent to about one-third of the total heat of combustion of the solid carbon and is manifested as sensible heat in the producers. All this heat, however, need not be lost. The gases may be used direct from the producer, while they still contain much of the heat, and higher temperatures may be thus obtained; or the hot gases may be used to preheat air and steam in a *modified process*, in which steam is forced into the producer with the air. This steam reacts with the heated carbon as shown above:

$$H_2O + C \text{ (hot)} \rightarrow H_2 + CO$$

The reaction is highly endothermic and helps to store up much of the heat which would otherwise be wasted. Another gain in using the steam is that it yields the same amount of carbon monoxide in burning the carbon as when the carbon is burned with air. Then the carbon monoxide, instead of being mixed with twice its volume of nitrogen, a useless gas, is mixed with once its volume of hydrogen, which is highly combustible and heat-producing.

When air alone is used, the product is known as "air gas." When steam is blown in with the air the product is known as "semi-water gas." Because of the heat conserved and the improved quality of the gas, the process with steam is the one most commonly used.

The following analyses represent the composition of air gas made by the use of bituminous coal, and of coke, respectively:

CH_4	C_2H_4	H_2	CO	CO_2	N_2	O_2
2.5	0.4	12.0	27.0	2.5	55.3	0.3
0.4	0.0	13.2	25.3	5.4	55.2	0.6

In the first case the percentage combustible is 41.9, and in the second, 38.9.

The following is representative of a semi-water gas:

CH_4	H_2	CO	CO_2	N_2	O_2
2.0	34.0	27.0	8.0	29.0	0.0

The percentage combustible is 63.

Frazer[1] says that producer gas has the lowest calorific value of any gaseous fuel and that the temperature of its flame is the lowest of any (excepting blast-furnace gas), but that in spite of these facts, it is the cheapest artificial gas per unit of heat.

Water Gas.—The principle involved in the manufacture of water gas is essentially the same as in making semi-water gas, except that in the former, the air and steam are blown in at alternate intervals. Air is first forced through the coals in the producer until a high degree of heat is reached, which process itself makes a low-grade gas containing some carbon monoxide. When the bed of coals is sufficiently hot, the air is cut off and steam is blown in. The steam reacts with the incandescent carbon with the formation of hydrogen, and either carbon monoxide or dioxide, depending upon conditions. If the temperature of the carbon is above 1000°C., the reaction proceeds as follows:

$$C + H_2O \rightarrow CO + H_2,$$

but if the temperature falls below 1000°C., the following reaction occurs:

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

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[1] ROGERS and AUBERT, "Industrial Chemistry," p. 80.

Since both carbon monoxide and hydrogen burn with a non-luminous or blue flame, water gas is sometimes known as "blue gas."

Water gas is used either alone as a fuel or as a constituent of illuminating gas. If used for illumination, the blue gas must be enriched with hydrocarbons, in which case it is said to be *carbureted.*

The process of making water gas is modified, then, according to the purpose for which the gas is to be used.

If it is used for a fuel gas, the products of combustion resultant from the blowing in of air may serve to preheat the incoming air or steam, or may be allowed to escape.

If used for illuminating gas, the products resultant from the air blast are burned to heat a checkerwork of brick, which is used to gasify the vapors of petroleum oil used in carbureting. The blue gas is first mixed with the oil vapors and this mixture is then conducted through the hot checker work where the hydrocarbon vapors are decomposed and fixed in permanent gaseous form.

According to the primary equation of formation, a theoretical water gas would contain 50 per cent each of carbon monoxide and hydrogen. An actual analysis of the blue gas shows:

CH_4	H_2	CO	CO_2	N_2
0.1	51.5	41.0	4.0	3.4

The percentage combustible is 92.6.

Since water gas contains such a high percentage of carbon monoxide, which is practically without odor and extremely poisonous, much danger attends its use.

Blast-furnace gas is the waste gas issuing from the top of the blast furnace. It is recovered and used either in the Siemens regenerator or stove to preheat the blast for the furnace, or in gas engines. Also it may be used beneath the boilers for the production of steam for the blowing engines. It is not a rich gas and shows the following average composition:

CH_4	H_2	CO	CO_2	N_2	O_2
0.20	2.74	28.61	11.39	57.06	0.00

Only 31.37 per cent is combustible.

Coal Gas.—This is made by the dry distillation of coal in retorts. It is a somewhat expensive gas because only the volatile portion distills off leaving much of the coal in the form of a soft, non-coherent coke, which has but a low fuel value. Coal gas is rich in illuminants and is used largely as an illuminating gas. It is also used as a fuel in domestic stoves and sometimes in gas engines. The following percentage analysis shows the average composition of coal gas:

CH_4	C_2H_4	H_2	CO	CO_2	N_2	O_2
40.5	4.0	47.0	6.0	0.5	1.5	0.5

The percentage combustible is 97.5.

By-product Coke-oven Gas.—Although in some of the by-product coke-oven plants, a portion of the gas produced in the process is used to heat the ovens, it is common practice to employ a cheaper gas of lower calorific value, such as producer gas, for this purpose, and to sell the coke-oven gas for domestic and industrial uses. According to statistics of the U. S. Bureau of Mines, 125,000,000,000 cu. ft. of by-product coke-oven gas were distributed through city mains in this country during 1928, the value at the plant being 31.9 cents per 1,000 cu. ft. In more recent years there has been a large increase in the amount consumed. To give only a partial list of the American cities employing the gas for domestic uses, the following may be mentioned: Boston, Providence, New Haven, New York, Baltimore, Philadelphia, Rochester (N. Y.), Utica, Buffalo, Chicago, Milwaukee, St. Paul, and St. Louis. Because the British thermal unit standard required of the gas varies in different localities, the composition will vary accordingly, but the following analysis[1] may be regarded as typical:

CH_4	C_nH_m	H_2	CO	CO_2	N_2	O_2
28.5	2.90	53.9	7.4	1.7	0.4	5.2

The percentage combustible is 92.7.

Natural Gas.—The origin of natural gas is closely associated with the origin of petroleum. It belongs to the same series of hydrocarbons as those which make up petroleum. It consists largely of methane, which is the lowest member of its series.

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[1] Private communication from H. J. Rose, director, General Laboratory Dept., Koppers Research Corporation.

The composition of natural gas varies somewhat according to the locality from which it comes. The following shows the average of 20 analyses[1] of Pittsburgh natural gas:

CH_4	C_2H_6	CO_2	O_2	N_2
80.6	18.2	0.0	0.0	0.8

The percentage combustible is 98.8.

Natural gas has the highest kindling temperature and the highest calorific value of all the gaseous fuels.

Summary.—In order that they may be compared conveniently, the percentages of the various constituents in some of the commercial fuel gases are tabulated. It must be understood that these gases do not conform to fixed standards; the composition varies considerably, and the analyses shown must be regarded merely as typical.

REPRESENTATIVE ANALYSES OF COMMERCIAL FUEL GASES

	CH_4	C_2H_6	Illuminants, C_2H_4, etc	H_2	CO	CO_2	O_2	N_2	B.t u. per cubic foot (about)
Natural gas	80.60	18.20	0.00	0.00	0.00	0.00	0.00	0.80	1,000
Coal gas	40.50	0.00	4.00	47.00	6.00	0.50	0.50	1.50	660
Coke-oven gas	28.50	0.00	2.90	53.90	7.40	1.70	0.40	5.20	554
Oil gas	27.00	0.00	13.00	38.00	16.00	4.00	0.30	1.70	650
Producer gas (from bituminous coal)	2.50	0.00	0.40	12.00	27.00	2.50	0.30	55.30	145
Producer gas (from coke)	0.40	0.00	0.00	13.20	25.30	5.40	0.60	55.20	137
Semi-water gas	2.00	0.00	0.00	34.00	27.00	8.00	0.00	29.00	245
Water gas	0.10	0.00	0.00	51.50	41.00	4.00	0.00	3.40	330
Blast-furnace gas	0.20	0.00	0.00	2.74	28.61	11.39	0.00	57.06	98

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[1] *U. S. Bur. Mines Tech. Paper* 109, p. 13.

CHAPTER III

REFRACTORY MATERIALS FOR FURNACE LININGS

General Nature of Refractory Materials.—Although a good refractory material must possess other properties of scarcely less importance, as used in this connection, the term "refractory" means primarily the property of being able to resist fusion by heat. Besides resisting fusion, it must be able to withstand abrasion while hot and be chemically indifferent to the fused material that may come into contact with it during use.

A refractory material must be chosen with respect to the *temperature* obtained in the furnace in which it is employed. Thus, in the open-hearth steel furnace, a temperature of 1600°C. is often developed; in a blast furnace just in front of the tuyères, it may be as high as 1960°C.; while in the electric-arc furnace, the temperature may reach 3500 to 3600°C. For comparison, the melting points[1] of the common refractory materials are shown:

Material	Incipient Melting Point in Degrees Centigrade
Aluminous fire-clay brick	1400 to 1750
Silica brick	1600 to 1800
Magnesia brick	1850 to 2000
Bauxite brick	1850 to 2000
Chromite brick	2000 and above
Plumbago graphite	above 3500

Even though the material is able to resist fusion, it may not be able to withstand the *abrading action* of the furnace charge. Thus, magnesia is noticeably softened at 1500°, although still far from its melting point. The density of the brick has much to do with its resistance to mechanical abrasion. Silica bricks are

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[1] Fulton, "Principles of Metallurgy," chap. X.

relatively porous, and are not firm and tough and so yield more readily to abrasion on this account.

It is important that refractory materials have as low *heat* conductivity as possible. Although the heat conductivity of all refractory materials is relatively low, there is nevertheless a considerable difference in respect to this property. The relative values, moreover, change with the temperature as shown by the accompanying curves given by Norton.[1] The conductivity of fused alumina brick, for example, increases and that of magnesite brick decreases as the temperature rises. For furnace walls the conductivity should be as low as possible, while for muffles and crucibles it should be as high as possible. Furnace walls are often built up of several kinds of refractory materials to combine desirable features not possessed by one alone.

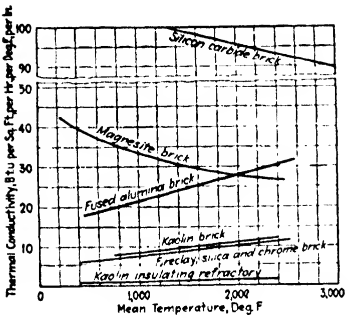

FIG. 4a.—Thermal Conductivity of Refractories. (*Norton.*)

Refractory materials should be able to withstand sudden *changes of temperature*, such as are brought about by currents of inrushing air when a furnace is emptied. Other factors being equal, there is less cracking and flaking off (spalling) under these conditions, if the material is porous, although it must be remembered that high porosity lessens the ability of the material to withstand abrasion. Magnesia bricks do not possess very high resistance to rapid temperature changes, while chromite bricks are very resistant.

If the material of the lining of a furnace is *chemically active* with the material of the charge, the lining will be removed because of the formation of [illegible]le compounds. Thus, the acid anhydride, silica, contained in a lining of silica brick, will react with lime in a basic slag producing calcium silicate, which being more readily fusible than silica, will melt and become a part of the

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[1] NORTON, "Structural Materials for Modern Heat Technology," *Chem. & Met. Engr.*, **39**, 227 (April, 1932).

slag. Other basic substances, as metallic oxides of the charge, may act in the same way as the lime. Conversely, basic anhydrides, as magnesia from a lining of this material, will react with silica carried in a highly siliceous slag. Because some materials, such as chromite, graphite, etc., are indifferent to the action of both basic and acid anhydrides, they are known as "neutral" substances.

The nature of a furnace lining is determined by the character of the slag. If the slag is basic, the lining must be basic or neutral; if the slag is acid, the lining must be acid or neutral. The character of the slag is, in turn, determined by the chemical reactions it is desired to bring about in the furnace. For example, in the open-hearth steel furnace, if it is desired to remove phosphorus from the metal of the charge, the slag must be basic; lime is used, which forms calcium phosphate with this element as it is oxidized. A siliceous slag is incapable of such action.

Classification of Refractories.—According to the reactions that may occur between linings and slags, discussed in the preceding paragraphs, refractories are divided into three classes, namely:

1. *Acid Refractories.*—This class includes the materials that consist essentially of silica, or at least contain this substance in excess of the bases present, and do not react with siliceous slags, but do react with slags rich in metallic oxides. The most important are Dinas and silica brick, gannister, and quartz. Also fire clay, which is sometimes classed as a neutral refractory, contains an excess of free silica, and to a certain extent may be considered acid.

2. *Basic Refractories.*—The materials included here are those that contain little or no free silica, and are not much affected by slags rich in metallic oxides, but are attacked by highly siliceous slags. The most common representatives are magnesite or magnesia, dolomite, lime, and bauxite.

3. *Neutral Refractories.*—Those substances that are not affected by slags rich either in silica or basic oxides are called "neutral." The most important are graphite and chromite.

Preparation.—Refractories are used in various ways, as crushed and ground material, standard bricks, shapes, and special forms. The bricks and shapes are usually formed from a stiff paste which is afterward pressed and then burned at a high temperature. Many of the properties of such refractories, as abrasion resistance, heat conductivity, etc., are not inherent in the material, but are largely dependent upon the method of manufacture. In the following paragraphs, the more important properties of the various refractories are briefly discussed.

ACID REFRACTORIES

Dinas Brick, Silica Brick.—The original Dinas brick is made from a highly siliceous sandstone occurring in south Wales. Fulton[1] gives as the composition of the best stone, the following:

	Per Cent
Silica	98.31
Alumina	0.72
Ferric oxide	0.18
Lime	0.22
Alkalies	0.18
Moisture	0.35

The bricks are molded by pressing a suitably moistened mixture consisting of the coarsely ground rock and about 2 per cent of lime. The freshly molded bricks are difficult to handle because they lack coherence. When dry they are fired at a temperature sufficiently high to cause a calcium silicate to form on the surface of the grains, which acts as a cement and binds them together. Clay is sometimes used in place of lime for this purpose. The finished bricks contain about 96 per cent of silica.

Although Dinas brick are imported into the United States, a large part of the silica bricks used here is of domestic manufacture. They are produced chiefly in Pennsylvania. The domestic bricks are manufactured in a manner similar to that described for Dinas brick, except that the binding material is generally clay.

Although silica bricks are highly resistant to heat, they are not suitable for all parts of the furnace. They are rather friable and do not stand abrasion well. They are very suitable for those locations where the heat is intense and the abrasive action low, as in the roofs of open-hearth furnaces. Their heat-insulating

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[1] *Loc. cit.*, p. 334.

value is excellent. They are much subject to spalling under sudden changes of temperature and so should not be used to line charging doors, or in furnaces that are allowed to cool down frequently, as furnaces for brass melting. Because silica is an acid anhydride, silica bricks must not, of course, be used where they will come into contact with basic slags.

Gannister.—This term was first applied to a close-grained, clayey sandstone found near Sheffield, England, but it is now used somewhat as a generic term to indicate any similar material wherever found; it is even applied to artificial mixtures prepared to conform to the requirements. Fulton gives the following as an approximate composition of gannister: quartz, 83 per cent; clay, 13 per cent; impurities and moisture, 4 per cent. The amount of clay is sufficient to form a good bond, but the amount of impurities is not sufficiently high to lower the refractoriness to any great extent. It is generally not molded into bricks, but is used to form furnace bottoms and line converters by tamping or molding it in place; the largest quantity is used probably in the acid Bessemer steel converter.

Fire Clays.—As has been pointed out before, fire clays are often classed as neutral refractories, but because of the free silica they contain they are decidedly less neutral than the true neutral refractories, as graphite and chromite; on this account they are here included among the acid materials. Like all other clays, they consist essentially of kaolin, a hydrated silicate of alumina ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) which is produced in the pure state by the weathering of pure feldspars, as described on page 368. But, because feldspar is usually associated with other minerals, its decomposition product is generally contaminated with other materials. Thus, quartz, mica, iron oxide, lime, magnesia, and other substances are almost always contained in the clays. The alkalies also are very likely to be present to some extent; they are due to incompletely weathered feldspar.

The following analyses given by Ries[1] show the relative composition of fire clays and brick clays. It will be noticed that the fluxes—iron, lime, magnesia, and the alkalies—are generally lower in the fire clays than in the brick clays.

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[1] "Building Stones and Clay Products," and "Economic Geology of the United States."

Kind of clay	SiO_2, per cent	Al_2O_3, per cent	Fe_2O_3, per cent	CaO, per cent	MgO, per cent	K_2O and Na_2O, per cent	TiO_2, per cent	H_2O, per cent
No. 1 Fireclay........	50.60	34.35	0.78	tr.	tr.	tr.	1.62	12.90
No. 1 Fireclay........	51.56	33.13	0.78	....	0.12	....	1.91	12.50
Fire-mortar clay......	67.26	23.36	1.63	0.25	......	0.65	Incl. with Al_2O_3	6.94
Common brick clay...	66.67	18.27	3.11	1.18	1.09	4.22	0.85	4.03
Pressed brick clay.....	68.28	18.83	2.60	0.70	0.13	2.29	0.27	7.23

Gowland[1] says that in the fire clays the silica generally ranges from 50 to 60 per cent or more, and the alumina from 22 to 35 per cent.[2] In almost all instances these combined constituents will comprise from 92 to 98 per cent of the clay. The other constituents are classed as fluxes, since they very noticeably lower the refractoriness. It is generally stated that the total fluxes should not exceed from 3 to 4 per cent, but this is dependent upon conditions. Thus, a very coarse-textured clay, high in alumina, may carry as much as 10 per cent of these impurities and still be a fire clay, although not of high quality. Refractoriness is also largely dependent upon the relative quantities of the fluxes, *i.e.*, upon which of them predominate. The alkalies are very objectionable, as also is iron oxide, particularly if present in the ferrous condition, or if present in the ferric state accompanied by some reducing substance as carbonaceous matter. The alkalies and iron oxide become especially objectionable if present in conjunction.

Because the alumina of the clay is a weakly basic anhydride, it does not produce an easily fusible compound with silica. With anhydrides that are more basic, such as the alkalies or lime, a compound silicate which is more easily fusible may be formed.

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[1] GOWLAND, "The Metallurgy of the Non-ferrous Metals," p. 4.

[2] Pure anhydrous kaolinite consists of silica 54 per cent, and alumina 46 per cent. Additional non-combined silica, present as quartz sand, acts as a flux to the kaolinite, and lowers the melting point until a eutectic of 90 per cent silica is reached, which melts at 1600°C. This should be remembered in making mixtures of sand and fire clay.

Iron sulfide, frequently in the form of granules of iron pyrite, may be present in fire clay. This impurity is highly objectionable, because when highly heated the sulfide is converted into ferrous oxide, which in turn combines with the silica to form an easily fusible ferrous silicate. The melted silicate retreats into the pores of the brick and leaves a black-lined cavity.

Fire clay is the furnace builder's mortar; in building substantial furnace walls, the bricks are set in fire clay.

From the standpoint of the amount used, fire clay is the most important refractory material. It is employed chiefly as bricks and other molded forms.

Basic Refractories

Magnesia.—This is the most valuable basic refractory. It is prepared by calcining magnesite at about 1700°C. Gowland[1] says that when calcined at this temperature it is practically infusible, and unlike lime has no tendency to absorb water and slake. Further, even though basic, it does not react readily with silica when used in furnace linings.

The domestic supply of magnesite is produced chiefly in California and Washington. Prior to the Great War, nearly all of the magnesite used for the manufacture of refractory materials in the United States was imported, chiefly from Austria and Greece.[2] During the war, when the foreign source of supply was cut off, attention was turned to the domestic deposits which until that time has been considered unsuitable for refractory purposes. It was found that the reason for the superiority of the imported variety as a refractory was due to the fact that it contained just the right amount of iron oxide to give it the desired abrasion resistance and wearing quality, while the domestic supply was too pure.[3] When iron ore was added to calcined domestic magnesite, it was found to give excellent service as a refractory material. Both California and Washington magnesites are now being made into high-grade refractories.

Although magnesia has no binding power of its own, strong bricks are formed of it. The bricks are made by mixing some

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[1] *Loc. cit.*, p. 10.

[2] For the world's chief producers of magnesite, see p. 130.

[3] Holmes, "General Chemistry," p. 443.

siliceous material with the magnesia and then molding the mixture under high pressure. Although magnesia bricks are hard, dense, and very refractory, they soften a great deal at temperatures much below their actual melting point. They are much poorer heat insulators than either fire-clay or silica bricks, and cannot well withstand sudden changes of temperature. They are much more expensive than fire-clay or silica bricks, a factor which causes their use to be more limited than would otherwise be the case.

Lime.—Lime has a very high melting point, about 1900°C.; it is even more infusible than magnesia. It is cheap also. It possesses one property, however, that causes it to be practically useless as a refractory material: it cannot stand exposure to the atmosphere. If a furnace lined with it were allowed to stand idle for a time, the lime would slake and disintegrate. When mixed with magnesia, however, a very satisfactory refractory material is obtained. A native material containing both lime and magnesia in suitable proportions is known as dolomite.

Dolomite is a magnesian limestone (pages 405 and 408). It contains calcium carbonate and magnesium carbonate in molecular weight proportions. Although calcined dolomite does not slake in the air like lime, it is not entirely resistant to that action. Dolomite is far cheaper than magnesia, but because of its greater tendency to react with acid oxides and its lower resistance to abrasion, it cannot be used as a substitute for magnesia in many instances.

Bauxite is a hydrated aluminum oxide ($Al_2O_3 \cdot 3H_2O$).[1] It generally contains iron oxide, silica, and titanium oxide as impurities. Depending upon the amount of ferric oxide present. bauxite is known as red or white; in the red variety, the ferri oxide amounts sometimes to 25 per cent. It is only the whit variety, in which the ferric oxide is practically absent, that used for making the most refractory bricks. The presence of not more than 6 to 8 per cent of silica is desired.[2]

Good bauxite bricks have high resistance to fusion, abrasion, and to reaction with metallic oxides and are much cheaper than magnesia bricks.

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[1] For sources of bauxite, see p. 84.

[2] Gowland, *loc. cit.*, p. 10.

For certain special work, bauxite is purified and fused in the electric furnace. It is thus formed into a product known as *alundum.* Alundum is very refractory; it has a melting point of about 2050°C., but it is too expensive for ordinary furnace use.

NEUTRAL REFRACTORIES

Chromite is a compound of iron and chromium. Its composition is shown by the formula, $FeO \cdot Cr_2O_3$ (page 141). Frequently part of the iron oxide is replaced by magnesia, and part of the chromium oxide by alumina; silica may be present as an impurity. With about 2 per cent of lime as a binding material, chromite is made into bricks.

Chromite is practically infusible at furnace temperatures; and it resists the chemical action of both acid and basic slags. It withstands abrasion and sudden changes of temperature better than any other refractory. For high-temperature metallurgy. no satisfactory substitute for chromite has been found. It cannot be used extensively, however, because of its high cost.

Graphite is an allotropic form of carbon. Two kinds are recognized—"amorphous" and "crystalline." It is only the latter that is of importance as a refractory material. The former is used chiefly for paints, lead pencils, stove polishes, etc. The finest grade of crystalline graphite comes from the island of Ceylon, although very fine grades are obtained from Siberia, Canada, and certain portions of the United States. Selected specimens of Ceylon graphite will contain from 99.7 to 99.8 per cent of carbon but generally the amount ranges from 70 to 90 per cent. The following analysis may be considered as typical:

	Per Cent
Carbon	86.66
Insoluble silica	4.22
Soluble silica	4.05
Alumina and ferric oxide	4.66
Lime and magnesia	1.01

The soluble silica and iron oxide determine its quality, since these substances lower its refractoriness.

Graphite can be prepared artificially by the Acheson process, in which anthracite coal, coke, or other forms of amorphous carbon are heated in the electric resistance furnace in a reducing atmosphere. The conversion of the carbon from the amorphous to the crystalline variety is indirect. Carbides are apparently formed first by a reaction between the carbon and the carbide-forming elements of the ash of the material, such as metals and silicon. The carbides later decompose to form graphite. The ash is ultimately almost completely sublimed from the finished product (page 567). The artificial graphite is used extensively in the manufacture of electrodes, and for practically all other purposes for which natural graphite is employed, except in the manufacture of crucibles.[1]

In manufacturing crucibles from natural graphite, it is necessary to mix with it a certain amount of good fire clay, because graphite is not plastic. The amount of clay used varies from 50 to 75 per cent, depending upon the grade of the crucible.

Graphite is the most refractory material known. It has not been fused, although it softens somewhat and vaporizes at the temperature of the electric arc—about 3700°C.[2] As a refractory material it can be used only under reducing conditions; it burns when under the influence of oxidizing flames and oxidizing fluxes.

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[1] Mantell, "Industrial Carbon," p. 49.

[2] Fulton, *loc. cit.*, p. 342.

CHAPTER IV

THE NON-FERROUS METALS

There are about 15 metals that are generally well known. Of these, iron, copper, lead, tin, zinc, and aluminum are quite common, and of great industrial importance. Iron, of course, which will be discussed in a later chapter, is by far the most important and useful; on this account it is classed by itself. In contradistinction to it, the other metals are commonly grouped under the name of the non-ferrous metals. In the present chapter the properties of the non-ferrous metals of industrial importance will be discussed.

Definition of Terms.—Among the most important items to be considered in discussing the metals and their alloys are their physical properties, whether they are hard, tenacious, brittle, ductile, malleable, etc. Before going further, it will be well to define the properties usually mentioned.

Hardness is the resistance a substance offers to the separation of its particles by the penetrating action of another substance. The term is often employed also with reference to the ability of a material to withstand abrasion and cutting, but in the methods now commonly employed to determine hardness on a numerical scale, only resistance to indentation is measured. The test processes employed for this purpose are the Brinell and scleroscope methods. In the former method, the test specimen is indented by a hardened steel ball, usually 10 mm. in diameter, under standard load, and the ratio of this load in kilograms to the area of indentation in square millimeters is used as an index of hardness. In the latter method, a small diamond-tipped hammer, guided by a glass tube, is dropped from a specified height upon the test specimen and the rebound, as measured against an arbitrary scale set back of the tube, is taken as the hardness index. From a soft body, lead for example, the hammer rebounds relatively little; the test specimen is indented, and some of the kinetic energy of the hammer is consumed in performing this work. In such cases a hammer giving a higher rebound, called a magnifier hammer, may be used.

Elasticity is that property by virtue of which a deformed body tends to resume its former shape.

The Tensile Test.—This is a test devised for the purpose of ascertaining the resistance a material is able to oppose to a force tending to pull it apart.

When applying a load to a material for the purpose of carrying out this test, if loaded within the limit of elasticity, the specimen will return to its original length if the load is removed, but when loaded beyond this point, the specimen acquires a permanent set. The maximum load that can be borne without retaining a permanent set is called the *elastic limit.* In commercial testing, the true elastic limit is often not measured, the yield point being determined instead. The *yield point* is that point at which a slight increase in load produces the first easily perceptible increase in length.

After the yield point has been noted, the loading is increased until rupture occurs. The maximum load required for complete rupture, divided by the initial area of the cross-section of the specimen, is called the *tensile strength.*

When testing non-brittle materials in tension, it is found that the specimen shows a local constriction at the point of fracture. The value obtained by dividing the decrease in area by the original area of cross-section at the point of fracture, when expressed in per cent, is called the *reduction of area.*

After breaking in tension, the two pieces of the test specimen are fitted together, and the increase in the length of the specimen is measured. The increase in length divided by the original length of that part of the specimen that was rendered liable to stretching furnishes a value, which, when expressed in per cent, is called *elongation.* The tougher the material, the greater the elongation.

Ductility.—If a material resists rupture when greatly extended in tension it is said to be *ductile.* It is by virtue of this property that a metal may be drawn into wire. To be formed in this manner, a metal must show considerable tensible strength after great deformation. Lead, for example, although readily deformed, because of its low tensile strength, cannot be drawn into wire.

Malleability is that property by virtue of which a material may be a hammered or rolled into thin sheets without rupture. This property generally increases with increase of temperature.

ALUMINUM

Historical.—Aluminum was a rare metal as late as 1850, and it was not produced commercially until 1889; nevertheless, among the non-ferrous metals, it is now outranked by only copper, zinc, and lead in annual output. The metal was first isolated in 1825 by Oersted, who reduced aluminum chloride with potassium amalgam. In 1827 Woehler repeated Oersted's experiment without success, but by modifying the procedure slightly he obtained the metal in the form of a gray powder. Eighteen years more elapsed, however, before Woehler produced the metal in a form pure enough to determine its properties. In 1855 the price of aluminum was $113 a pound. In 1886 Hall in America and Heroult in Europe, working independently, developed an electrometallurgical method, which by 1890 brought the price to $2.38 a pound. By 1900, it had dropped to 23 cts. and in 1914 the lowest price, 18 cts. was reached.

Hall's discovery was made when he was twenty-three years old, the year following his graduation from college. Without being aware of Hall's work, Heroult, a Frenchman, also twenty-three years of age, discovered the same process exactly 3 months later. Although the processes were practically identical, there was no patent litigation. In America, Hall's company began operations at Pittsburgh and later moved to New Kensington, Pennsylvania.

Occurrence.—Of all the metals, aluminum exists in the outer layer of the earth in the greatest quantity. Indeed, among all of the elements it is exceeded only by oxygen and silicon. It makes up about 8 per cent of the earth's crust, while the total quantity of iron amounts to slightly more than 5 per cent. The other common metals, as copper, lead, zinc, and tin, taken together constitute only a small fractional part of 1 per cent of the exterior portion of the earth. Aluminum oxide, called *alumina,* which when pure is white in color, is an essential ingredient of such minerals as clays, slates, mica, feldspar, and granite. Alumina forms several precious stones.

Corundum consists of anhydrous alumina. The ruby is made up of crystals of corundum colored red by a small amount of chromium. The sapphire is another variety, colored blue by traces of cobalt. *Emery* is an impure variety of corundum, containing ferric oxide. It has a granular structure and a degree of hardness only a little less than that of the diamond. Because of its hardness, it is used as an abrasive material.

Ore.—Although aluminum is very abundant in the earth, it is never found free, nor can it by present methods be obtained commercially from clay in which it exists in such great quantities. There is but one known ore, called *bauxite.* It takes its name from the village of Baux, near Arles, in France, where it first was found by Berthier. Bauxite is a hydrated aluminum oxide, generally believed to consist of a mixture of the monohydrate ($Al_2O_3 \cdot H_2O$) and the trihydrate ($Al_2O_3 \cdot 3H_2O$).[1] The chief impurities are iron oxide, silica, clay, and titania. Depending upon the iron-oxide content, the color varies considerably. Its structure is variable also, but usually it is made up of rounded concretionary grains imbedded in a clay-like mass.

The chief deposits of bauxite now being worked are located in Italy, France, British and Dutch Guiana, and the United States, of which the chief producers are Alabama, Georgia, Tennessee, and Arkansas. Formerly the best ore was obtained from France, but the vast deposits in the Guianas, controlled by the American Company, have proved to be purer than the French ore. An extensive deposit of very high-grade ore has recently been discovered in the Atlas mountains in French Morocco.

Cryolite.—The fluorides are the only aluminum-bearing minerals in which the metal is not associated with oxygen. Cryolite, a sodium aluminum fluoride, ($3NaF \cdot AlF_3$), is required in aluminum metallurgy as solvent for the bauxite. It is a white, ice-like solid, melting at 995°C. The deposit at Ivigtut, south Greenland, is the only commercial source of cryolite. Due to the high price of the native mineral, methods of preparing cryolite artificially have been developed.

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[1] EDWARDS, FRARY and JEFFRIES, "The Aluminum Industry," vol. I, p. 63.

Production of Aluminum.—Because an enormous amount of electric energy is required, and because it must be supplied at low cost, all the aluminum-reduction plants in the world derive their current from hydroelectric power plants. This fact causes the reduction plants to be located in the general vicinity of waterfalls. Power from coal is out of the question. Aluminum ores, consequently, are usually not smelted where mined. Arkansas, for example, of all the states, is the greatest producer of bauxite, but the state of New York leads in the production of aluminum. The ore is mined in Arkansas, is refined in St. Louis, and is smelted not far from Niagara Falls where power is cheap. The bauxites found in the United States, as a rule, contain from 15 to 33 per cent of water of hydration, with additional moisture mechanically held, and because ordinarily the ore must be shipped long distances, it is usually dried at the mine.

One of the problems encountered in aluminum metallurgy arises from the fact that after reduction to the metallic state, the metal can only with difficulty be refined. As a result, before reduction is started, it is necessary to prepare an alumina that is essentially pure. The purity of the metal depends upon the purity both of the oxide reduced and of the fused bath of cryolite.

In the process now usually employed in preparing the alumina, known as the Bayer process, the finely ground ore is digested in an aqueous solution of sodium hydroxide under pressure in steam-jacketed autoclaves. Sodium aluminates are formed, as illustrated by the following equation:

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

The ferric oxide, clay, and titania are not dissolved. Part of the silica dissolves, but this is precipitated as calcium silicate by the use of lime which was added to the ore for this purpose prior to grinding.

The sodium-aluminate liquor from the autoclaves is diluted, filtered, and run into tanks. A small amount of freshly prepared aluminum hydroxide is added to the liquor with the result that the sodium aluminate decomposes and precipitates aluminum hydroxide, as follows:

$$2NaAlO_2 + 4H_2O \rightarrow 2Al(OH)_3 + 2NaOH$$

The aluminum-hydroxide sludge from the bottom of the tank is drawn off and put through filter presses. Afterward, the hydroxide is calcined[1] to alumina. The sodium-hydroxide solution is concentrated by evaporation and is used again.

The reduction of aluminum oxide to aluminum by means of carbon, as is done in the case of iron, copper, lead, tin, and other commercial metals, is not practicable. Although the alumina can actually be reduced, under the conditions required for the reduction the metallic aluminum undergoes secondary reactions. It will form the carbide by combining directly with carbon, will form the oxide or carbide by reacting with carbon monoxide or dioxide, or will volatilize. If some other metal, such as copper, is present with which the aluminum can form an alloy as it is reduced, reduction with carbon may be employed. Pure aluminum, of course, cannot be obtained in this way. In 1886, and for several years thereafter, until driven from the field by Hall process, the Cowles brothers successfully prepared aluminum alloys on a commercial scale by the carbon reduction method.

In the Hall process, now almost exclusively used, the furnace employed consists of a rectangular box of mild steel lined with refractory material possessing low thermal and electric conductivity. Inside this lining is another of rammed carbon to form a cathode, electrical contact with which is made by a suitable lead. Anodes of hard-pressed carbon are suspended in the interior of the furnace.

The bath consists of melted cryolite, both natural and artificial, to which other salts, such as calcium fluoride, have been added. Since the specific gravity of melted aluminum and the melted bath are not far apart, care must be exercised to adjust the composition of the bath so that the reduced aluminum does not float; if this should happen the cell would be short-circuited. The melting point is also a factor to be considered in adjusting the composition. In the bath of fused salts the purified alumina is dissolved in a quantity varying from 10 to 20 per cent.

In the operation of the cell the alumina is dissociated by electrolysis in accordance with the following equation:

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

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[1] To *calcine* means to heat strongly to drive out volatile matter, as carbon dioxide and water, leaving a friable product. The manufacture of lime by heating limestone is a calcining process.

The separated aluminum collects on the cathode bottom, which slopes slightly toward the tap hole; periodically the metal is tapped. The oxygen, separating at the anode, reacts with the hot carbon to form carbon monoxide which burns to the dioxide as it escapes. From time to time, cryolite and alumina are added to replenish the bath.

Commercial Aluminum.—The product of the reduction cell is remelted in order to allow occluded bath salts to separate and then is cast in pigs. In this form it appears on the market as primary aluminum, of which there are three grades, as follows:

Classification	Per Cent Aluminum
1. Special	99.5+
2. Grade No. 1 (or Grade A)	99.0+
3. Grade No. 2 (or Grade B)	98 to 99

The 99+ aluminum contains on an average the following impurities:[1] copper, trace to 0.20; iron 0.25 to 0.60; and silicon, 0.15 to 0.40 per cent. A small amount of the oxide (Al_2O_3) is also normally present in commercial aluminum.

Physical Properties.—Aluminum is a silvery-white metal of high metallic luster. It melts at 659°C. (1219°F.) and boils at about 1800°C. (3272°F.). Its specific gravity is very low, about 2.70±, which is about one-third that of steel. It is very malleable; it is second only to gold in this respect. It may be rolled into sheets 0.0005 in. in thickness. It is about as hard as silver, but for commercial purposes, its hardness is much increased by alloying with it small amounts of copper. In proportion to its weight it is very strong. As cast, its tensile strength will range in the neighborhood of 13,000 lb. per square inch; it will be about twice this in unannealed sheet, even more in hard-drawn wire. It is less ductile than copper but more so than zinc or tin. The heat conductivity of aluminum is 31.33 (silver 100); its electrical conductivity is 62 (copper 100).

Pure aluminum does not cast very well. When molten it absorbs nitrogen, carbon dioxide, etc.; because these gases are expelled again on cooling they form gas flaws. Small additions of copper, nickel, and some other metals improve the casting qualities of the metal in this respect. Because aluminum has a

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[1] LIDDELL, "Handbook of Non-ferrous Metallurgy," p. 712.

tendency to be coarsely crystalline, in casting the temperature of the melted metal should be as low as practicable in order to keep the crystalline structure as fine as possible. The fine crystals increase the tensile strength. Aluminum shrinks upon solidifying from the melted state 0.2031 in. per foot. Its casting alloys, which contain about 8 per cent of copper, shrink somewhat less than this, about 0.156 in. per foot.

By the fusion process, aluminum and its alloys may be *welded.* In this process the fluxes generally used are mixtures of salts, such as the fluorides, chlorides and sulfates of potassium, sodium, lithium, calcium, and aluminum. For use, the salts are mixed with water to form a thin paste.[1] Since all successful aluminum fluxes are corrosive to the metal, after welding the flux must be thoroughly removed. According to the reference just given, this may be accomplished by washing first in hot water and then in a 5 per cent solution of either nitric or sulfuric acid, after which the acid must be removed by washing again in clean hot water.

Chemical Properties.—When strongly heated in the air, aluminum oxidizes quite considerably. Thin pieces will burn in the air with a brilliant light, resembling magnesium; aluminum oxide and some nitride are formed. In casting, however, it is not necessary to cover the melt with charcoal, because the tenacious film of oxide that is formed is protective. Zinc chloride, which melts at 365°C., is the best flux for aluminum.

Upon exposure to the ordinary atmosphere, aluminum corrodes very slowly; a thin film of the hydrated oxide is formed which is closely adherent and protective. If it were not for this protecting film, the metal would be rapidly attacked. When amalgamated with mercury, aluminum dissolves readily in pure water with the formation of aluminum hydroxide and the evolution of hydrogen. In warm, moist air the aluminum hydroxide grows out from the metal in a form like moss; it may reach a length of nearly ½ in. in a very short time. The amalgamation does not increase the activity of the aluminum; it prevents the formation of the protective film that usually interferes with its activity. Hydrogen sulfide has no action on aluminum.

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[1] Edwards, Frary, and Jeffries, "The Aluminum Industry," vol. II, p. 440.

In dilute sulfuric acid, aluminum is practically unaffected. In the hot, concentrated acid it dissolves in a manner similar to copper; sulfur dioxide is evolved. Nitric acid also affects it very little. Aluminum may be employed for handling cold nitric acid, both dilute and concentrated. It is attacked very rapidly by both hydrochloric and hydrofluoric acids in all concentrations with the evolution of hydrogen. Chlorine, bromine, and iodine all attack aluminum rapidly.

With elementary sulfur, aluminum reacts readily at moderately high temperatures; the sesquisulfide (Al_2S_3) is formed. Aluminum sulfide in not formed in the wet way by reacting with a solution of hydrogen sulfide.

In solutions of the caustic alkalies it dissolves very readily. The products formed are hydrogen and aluminates as, for example, sodium aluminate (Na_3O_3Al). Hence, solutions of the alkalies, such as caustic soda, should not be used in cleaning articles made of aluminum. The presence of a small quantity of sodium silicate inhibits the action of alkalies on this metal.

Pure Aluminum.—The purity of the aluminum produced by the Hall process does as a rule not exceed 99.5 per cent, while with other metals, such as copper, zinc, and tin, a purity as high as 99.95 per cent has long been common. Because of its peculiar chemical and metallurgical behavior, it seemed that commercial aluminum could not be refined, but recently the Hoopes electrolytic refining cell, yielding a product having a purity as high as 99.97 per cent, has come into use on a commercial scale.

In this process a layer of heavy, molten alloy of aluminum, copper, and silicon is employed in the bottom of the cell as the anode. This melted anode is covered with a layer of fused electrolyte consisting of the fluorides of sodium, aluminum, and barium. Above the electrolyte is a cathode layer of pure, melted aluminum. The layers float one above the other and remain separated because of their differences in density. An electric current passing through the cell removes aluminum from the anode alloy and deposits it with the pure aluminum of the cathode.

Properties of Pure Aluminum.—Pure aluminum has a silvery color and luster. Aluminum of ordinary purity has a characteristic bluish tinge which is probably due to its content of silicon and iron (page 87). With aluminum, silicon forms a purplish-colored constituent, and iron a gray constituent.[1]

With copper as 100, aluminum of the grade employed for electrical work has a conductivity of 61, while the electrical conductivity of pure aluminum is 64.6.

The mechanical properties of the pure aluminum also are very different from those of the metal of ordinary grade. Although its tensile strength is less, it is tougher than ordinary aluminum. The following table given by Edwards[2] shows the numerical values for these properties.

Mechanical Properties	Annealed aluminum, purity 99.4 per cent	Wrought annealed aluminum, purity 99.97 per cent
Tensile strength, lb. per sq. in.	13,000	8,465
Elongation, per cent in 2 in.	45	60
Reduction in area	80	95
Brinell hardness number (with 50 kg. pressure and 0.125 in. ball)	22	16

Aluminum of high purity has much greater resistance to ordinary corrosion than the ordinary metal. Edwards reports that a sample of 99.9 per cent aluminum sheet kept in a solution consisting of 5 parts by volume of concentrated hydrochloric acid and 95 parts of water was still bright and showed no appreciable corrosion in 6 weeks. Ordinary polished aluminum sheet in this solution will dissolve sufficiently to show a decided evolution of hydrogen in a few minutes, and will be distinctly etched in 1 hr.

Uses of Aluminum.—Because of its softness and the difficulty of making sound castings, little pure aluminum is used in the cast form. The largest quantity is employed after it has been mechanically worked in some manner, as by rolling, wire drawing, drop forging, extruding, etc. After rolling into sheets it may be

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[1] EDWARDS, "The Properties of Pure Aluminum," *Trans. Amer. Electrochem. Soc.*, **47**, 288, 1925.

[2] *Loc. cit.*, p. 296.

stamped into a variety of shapes. It is employed in the manufacture of furniture, airplanes, railroad and trolley cars, automobile bodies and pistons, electric cables and bus bars, rigid conduit, rivets, kitchen utensils, and collapsible tubes for pastes. Aluminum shingles, corrugated roofing and siding sheets, and mason-jar caps are recent products that seem to have been well received. To summarize its mechanical uses, it may be said that aluminum is employed wherever advantage may be taken of its low specific gravity, relatively high combined strength and toughness, or its high electrical and thermal conductivity. When employed because of its lightness, if more than its normal strength is also required, this may be secured by the use of aluminum alloys (page 194).

In a finely divided flake form, aluminum is employed as a pigment in paint (page 525). Aluminum paint is used as a priming coat for wood and as a protective coating on metal. For the latter purpose it is exceptionally serviceable.

Aluminum is used in deoxidizing molten iron and steel, especially in the top of the ingot when steel is poured in the ingot mold. In a similar manner it is used to prepare the metals from their oxides by heating a mixture of powdered aluminum and the oxide of the metal to be reduced. The mixture is known as thermit.

Thermit.—Finely divided aluminum is mixed with the metallic oxide in about equal proportions by volume. When the reaction between the two is started, it proceeds of itself and develops great heat; the products are a slag of aluminum oxide and the molten metal whose oxide was reduced. The reaction is started in the thermit by means of a small quantity of ignition powder placed on top of it. The ignition powder is made up of a mixture of barium peroxide and finely divided magnesium, and reacts according to the following equation:

$$BaO_2 + Mg \rightarrow BaO + MgO$$

In the thermit itself, if the sesquioxide of iron is used, the reaction is as follows:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

The mixture of iron sesquioxide with aluminum is known as "red thermit" and the magnetic oxide mixture as "black thermit"; the latter is probably the most used. The reaction with the magnetic oxide occurs thus:

$$
\begin{array}{lcccc}
 & 8\mathrm{Al} + & 3\mathrm{Fe_3O_4} \rightarrow & 9\mathrm{Fe} + & 4\mathrm{Al_2O_3} \\
(\text{Mol. wts.}) = & (217) & (696) & (504) & (409)
\end{array}
$$

In this reaction, the weights used are approximately 3 of aluminum and 10 of magnetic oxide, which produce about 7 of metallic iron and 6 of slag. In actual practice the proportions are usually 1 of aluminum and 3 of magnetic oxide. It is generally estimated that the molten metal produced is about one-half the original mixture by weight and one-quarter by volume.

The temperature produced by the heat of the thermit reaction is very great. It has been calculated by Richards[1] as 2694°C. Féry using the radiation pyrometer found the temperature of the stream of metal flowing from the crucible to be 2300°C.

The exceeding hot metal has proved to be very useful in a certain form of *welding*. For the purpose of welding, the parts to be joined are cleaned, butted together, and the joint is surrounded by a suitable mold. The ends are then heated by a gas flame playing through an opening provided in the mold for this purpose. The hot metal is allowed to flow from the reaction crucible into the mold, where the ends being joined are fused by the great heat, and upon cooling, the mass solidifies as a whole.[2] The process is applicable to wrought iron, steel, cast iron, and other metals whose oxides are capable of reduction by aluminum, as for example, nickel, manganese, and chromium.

Many metallic sulfides also react with aluminum powder; aluminum sulfide and the other metal in the free state are formed. Hence, the thermit process is much used in obtaining metals from sulfide, as well as oxide ores.

COPPER

Sources.—Copper is one of the most widely distributed of metals. It is mined in nearly every country of Europe, in Siberia, Japan, Chile, Mexico, Canada, Australia, and Africa, but considerably over half of the world's total smelter output of

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[1] *Elec. Chem. Met. Ind.*, **3**, 40, January, 1905.

[2] For methods of making welds by thermit see "Welding" by R. H. Hart; also literature issued by the Goldschmit Company.

copper is produced in the United States. As reported by "Mineral Resources of the United States," the states that lead in production, in order of decreasing importance, are Arizona, Utah, Michigan, and Nevada.

Ores.—Copper is one of the comparatively few metals that are found in the metallic state. Free or native copper, scattered through beds of amygdaloidal[1] and conglomerate rocks, is found in the upper peninsula of Michigan. The copper content of the rock is about 1 per cent. The metal is itself very pure, averaging above 99.9 per cent copper. The impurities consist of traces of arsenic, silver, iron, and nickel. Native copper from this source is known as "Lake" copper. According to the statistics of the U. S. Bureau of Mines it constitutes about 10 per cent of the domestic output.

Other copper ores belong to that which is known as the oxide group. This group includes not only the oxides proper, but other compounds containing them, such as the hydroxides, carbonates, silicates, and sulfates. Important members of this class are *cuprite* or *ruby copper* (Cu_2O); *melaconite* (CuO); *azurite*, the blue carbonate ($Cu(OH)_2 \cdot 2CuCO_3$); *malachite*, the green carbonate ($Cu(OH)_2 \cdot CuCO_3$), a great deal of which was formerly found in Arizona; and *chrysocolla* ($CuSiO_3 \cdot 2H_2O$).

About 70 per cent of the copper produced in the United States is obtained from sulfide ores. In Montana and Utah are found large deposits of this character. Important members of the sulfide group are *chalcocite* or *copper glance* (Cu_2S); *covellite* (CuS); *chalcopyrite* ($Cu_2S \cdot Fe_2S_3$); *bornite* ($3Cu_2S \cdot Fe_2S_3$); and *tetrahedrite* ($4RS \cdot Sb \cdot As_2S_3$), in which R may be Cu, Fe, Zn, or Ag_2, and which may contain 15 to 48 per cent of copper. The chalcocite and chalcopyrite have been the most important economically.

Reduction of Ores.—With but few exceptions, one of which has just been noted, the metallic content in copper ores is not high; it rarely exceeds 10 or 15 per cent, and not infrequently is as low as 2 or 3 per cent. On this account it is usually necessary to work over a large amount of earthy material. Smelting methods vary, of course, with the kind of ore, *i.e.*, whether it is native copper, or belongs to the oxide or sulfide group.

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[1] Almond-shaped or elliptically globular, generally of lava origin.

With native copper the smelting process is not difficult. The metal is first concentrated by crushing, grinding, and washing the ore. The remaining gangue, rocky or earthy matter, is then removed by heating the concentrate in a furnace in the presence of a suitable flux, usually limestone. The copper melts and collects beneath the silicate slag that is formed by the reaction between the flux and gangue. The melted metal is poured from the furnace and cast in ingots.

The oxide ores when rich in copper were formerly smelted with coke or charcoal and a suitable flux in blast furnaces similar to those employed in the iron industry (pages 220 and 223), except that the sides were jacketed with running water to keep them cool. This practice is still continued in some localities for screened ore with lumps averaging 2 in. in diameter, but now, because modern methods of concentration yield a very fine product, the blast furnace is little used. A fine concentrate cannot be worked satisfactorily in the blast furnace.

Due to the great success of flotation (described later) as a method of concentrating sulfide ores, there is at present, in handling oxide ores, a tendency to mix them with sulfide ores and then proceed with the regular sulfide process of reduction. Although the sulfide smelting process involves many more operations, the advantages of the sulfide concentrating process more than offset any objections that may be offered against later steps in the procedure.

Of the three classes of copper ores, the sulfide group is, indeed, the most difficult to smelt. The process is complicated because, in addition to the sulfur, it is necessary to remove the large quantity of iron which these ores carry. In most cases small quantities of lead, arsenic, antimony, or other elements are present, and these metals also must be eliminated. Since approximately three-fourths of the copper derived from domestic sources comes from sulfide ores, the process by which the metal is obtained from them will be discussed more fully than has been done for the preceding groups.

Due to the fact that the ores differ so greatly in composition and physical character, the smelting process differs in different localities. In general, however, the several steps are as follows:

(1) concentrating, (2) roasting, (3) smelting, (4) converting, and (5) refining.

1. **Concentrating.**—Concentration is not required in all cases; it is necessary only with low-grade ores. The older methods of concentrating ores, consisting chiefly of crushing, grinding, and washing, or levigating with water, often left as much as 30 per cent of the copper in the rejected tailings. Comparatively recently, however, a new process, known as *flotation*, has been developed in which 95 per cent of the copper is saved, and two-thirds of the ore is discarded. With 3 per cent of copper in the original ore, there will be at least 8 per cent in the concentrated product. The new process has even made it profitable to rework the rejected dumps of earlier operations. Because of its great economic value, flotation is without doubt the most important recent development of modern non-ferrous metallurgy.

The operation of the flotation process involves a peculiar phenomenon. In the liquid in which the ore is treated, the heavier mineral particles are made to rise, while the lighter rock particles, or gangue, sink. For the purposes of study, the process may be divided into three steps.

a. Oiling.—The ore, which has been ground to an impalpable fineness, is worked into a pulp or slime with water in the presence of less than 1 per cent of coal tar and creosote. Too much of this mixture must not be used, or, due to the formation of oil films of appreciable thickness, an effect entirely different from that desired will be produced. When the proper small quantity of the tar-creosote mixture is used, some change is effected on the surfaces of the metallic or sulfide particles of the ore which makes them less easily wetted by the aqueous part of the mixture. The gangue appears not to be affected by the oily reagent and is consequently wetted by the water. The selective wetting effect of the water on the gangue may be increased by the use of acids, alkalies, mercaptans, and other reagents.

b. Frothing.—The ore ground with the oily reagent and water is now introduced into a larger volume of water containing a frothing reagent and the whole mass is beaten or blown so that a froth or foam is produced. In practice the flotation process differs in many particulars. At this point, for example, in some cases the oiling reagent acts as the froth producer and in other cases it is necessary to add a "frother" such as pine oil. The required procedure is determined by experimenting with the individual ores. When the froth is formed, the oiled mineral particles adhere to the bubbles very tenaciously, and are buoyed up by them. The waste silicate matter, or gangue, settles out.

c. Skimming and Recovery.—By removing the froth from the surface of the liquid, the metalliferous portion of the ore is recovered. The froth must, of course, be of sufficient permanence to last until it can be removed, but it should then quickly die away. When the froth has subsided, the slime that remains is dewatered in some kind of thickening or filtering device. The oil is distilled and used again.

The flotation process has made it possible to smelt ores that could not be worked economically by older methods. It is claimed that the process will remove 95 per cent of the copper from an ore containing as little as 2 per cent of the metal.

2. Roasting.—The ore, concentrated or not as required, is roasted to expel the volatile oxides of arsenic and antimony as much as possible, and to oxidize about three-fourths of the sulfur present. At this stage the removal of all of the sulfur is not desired. In the roasting furnace, the charge, heated to redness but not fused, is stirred constantly, and a plentiful supply of air is admitted. After the oxidation is well started, it continues of itself without additional fuel; the heat necessary to keep the process going comes from the burning of the sulfur itself. By roasting, the sulfur content of the ore is reduced from about 33 per cent to about 8 per cent, and a part of the copper and iron sulfides are changed into oxides.

3. Smelting.—While still hot, the product of the roasting furnace is conveyed into a reverberatory furnace[1] to be smelted. In some instances, especially with coarser ores, the smelting may be carried out in a blast furnace. With the increase in the use of flotation as a method of concentrating the ore, which process yields a fine concentrate, the reverberatory furnace is gradually replacing the blast furnace in copper metallurgy. As far as the lining is concerned, the reverberatory furnace

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[1] For description and illustration of a reverberatory furnace see pages 253 and 257.

employed here is not unlike the basic, open-hearth, steel furnace (page 271); the roof and sides are lined with silica brick and the bottom, or hearth, with magnesite. The fuel employed may be oil or powdered coal. The air blast used in "atomizing" the oil or in blowing in the powdered coal, together with additional draft, is sufficient to produce a flame that is at least slightly oxidizing in character.

To the charge of roasted concentrate, known in the works as "calcine," silica (sand) is added, unless a sufficient quantity is initially present in the concentrate, in order that it may combine with the iron oxide (FeO) to form a slag. Lime, also, is generally added to form a calcium silicate which makes the slag more fusible and less sluggish. Through the medium of the slag, much of the iron in the form of iron silicate is separated from the copper.

Any iron pyrite (FeS_2) remaining in the charge is by distilling of the excess sulfur converted into ferrous sulfide (FeS). A small amount of sulfur is burned to sulfur dioxide and part of the ferrous sulfide is converted into ferrous oxide, which in turn enters the slag as previously stated.

With the remaining ferrous sulfide (FeS) the cuprous sulfide (Cu_2S) forms a heavy, melted mixture, which, because its specific gravity is about twice that of the slag, collects beneath the slag. This sulfide mixture is known as *matte*. Besides the sulfides of iron and copper, the matte contains a considerable amount of metallic copper, a little metallic iron, and any gold, silver, or other heavy metals that were present in the ore.

4. Converting.—In this stage of the process the matte is changed to metallic copper by blowing air through the melted mass while it is contained in a receptacle known as a converter. In principle, the converter employed is similar to the Bessemer converter (pages 266 and 267) used in the steel industry, except that it is as a rule wider and shallower with a greater capacity than the steel Bessemer, and that the air is introduced low on the sides, rather than in the very bottom. The copper converter, however, unlike the steel converter employed in American practice, is basic-lined; the lining consists of magnesia brick.

A charge of melted matte is conveyed into the converter, a little sand or raw ore is added, and air under a pressure of about

16 lb. to the square inch is blown through the liquid mass. The sulfur burns to sulfur dioxide, and the ferrous sulfide is transposed into ferrous oxide. As the ferrous oxide forms, it reacts with silica of the sand or with the silica and the alumina of the raw ore to form a slag. When the iron has been slagged from the matte, the blast is stopped and the slag is poured off. The blowing is then resumed. Now the copper sulfide is oxidized. The copper oxide formed reacts with unchanged sulfide to yield metallic copper. The chief reactions occurring in the converter may be summed up as follows:

First stage

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow FeSiO_3$$

Second stage

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

Approximately 5 hr. are required to complete these reactions as compared to the 15 min. required for the conversion of pig iron into steel. The yield of copper is about 99 per cent pure. It is called "blister copper" because, when cast, sulfur dioxide which was dissolved in the melted metal separates in the form of bubbles. On the surface of the solidified metal the bubbles appear as blisters.

Refining.—Because of the detrimental effect of even very small quantities of impurities on the electrical conductivity[1] of copper, the electrical industry, which consumes over half the copper produced in the United States, demands a purity of at least 99.95 per cent. To meet this requirement, the copper is subjected to a refining process.

There are two ways of refining copper: fire refining and electrolytic refining. It is only by the latter process, however, that metal sufficiently pure for the electrical industry can be produced.

In fire refining, which is the older method, the converter metal is transferred to an acid-lined furnace with a basin-shaped hearth. At first, the flame is kept strongly oxidizing in character. As soon as the sulfur has been removed, oxidation is carried on by

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[1] See Physical Properties, p. 101.

means of air jets aided by some method of mechanically agitating the melt to expose more surface. Cuprous oxide is formed, which in turn acts as an oxidizing agent for the baser metals. Their oxides then escape as a fume, or are slagged by combining with the silica of the lining. An excess of cuprous oxide is left, and must be reduced, since if allowed to remain, it causes the metal to be in a condition known as "dry," which means that it is brittle, breaking with a granular fracture, instead of being tough with a fibrous fracture. Reduction is accomplished by covering the molten charge with charcoal or coke and stirring with a pole of green wood. The wood undergoes destructive distillation, and the gases that escape, in addition to having a reducing effect, bring about a violent bubbling and stirring of the melted metal, which allows occluded oxidized bodies to rise. Over-reduction must be avoided, since the copper almost always contains traces of the oxides of arsenic, antimony, and bismuth which in their oxide state are not so objectionable; but if the reducing action of the carbon and the gases from the pole is too great, these oxides are reduced, and the resultant metals are more active in producing brittleness than the cuprous oxide itself.

Even in the electrolytic method, the metal is given a preliminary fire refining to remove as much as possible of the impurities and to secure as nearly as possible a uniform product. It is then cast in the form of slabs about 3 ft. square and 2 in. thick weighing approximately 500 lb., which are known as anode plates. It is cheaper to remove the impurities by the furnacing process than by electrolysis, and if the anodes are of uniform composition much better results can be secured in the electrolyzing bath.

In electrolytic refining there are two methods of connecting the electrodes, multiple and series.

In the former, the anodes, connected in multiple, are suspended between similarly connected thin sheets of pure copper in a warmed, constantly circulated bath of copper-sulfate solution acidified with sulfuric acid. An electric current of relatively low voltage and high-current strength is employed; the current density is about 25 amp. per square foot of cathode surface. As the electron stream passes through the system, copper at the anode surface is oxidized and passes into solution as copper ions. At the cathode surface, copper ions are discharged and adhere there as metallic copper. Thus, the anode gradually dissolves away and the cathode builds up. By suitably regulating the potential drop across the cell, it is possible to avoid dissolving a great many of the impurities contained in the copper. These impurities, together with bits of copper, drop from the anode and collect as an anode slime. The chief components of the slime are copper, silver, gold, platinum, salts of bismuth and antimony, cuprous oxide, lead sulfate, silver chloride, sulfur, selenium, and tellurium. The gold, silver, and platinum recovered from the slime constitute a noteworthy source of profit. Although metals such as iron, zinc, and nickel dissolve at the anode, the tendency of their ions to discharge at the cathode is less than the discharge tendency of the copper ions; consequently, under the operating conditions they are not plated out. By this method, cathode copper having a purity of approximately 99.955 per cent is obtained. Because the cathode plates are somewhat granular in texture and do not stand shipment well, small pieces being broken off, the copper is not marketed in this form, but is melted and cast in bars. The melting lessens the purity slightly.

In the series system there are no starting sheets; the back of each anode serves as the cathode for the preceding anode. These anodes, which may be either rolled or cast, are thin; the thick heavy slabs employed in the multiple system do not serve satisfactorily here.

Leaching.—The copper from low-grade oxidized ores and from old tailings may be extracted by a suitable solvent. From old tailings the metal may be obtained by leaching directly, whereas more recent tailings must be oxidized by roasting prior to leaching. By long continued exposure to the weather, a wet oxidation occurs which yields a soluble product. The action may be illustrated as follows:

$$CuS + 2O_2 \rightarrow CuSO_4$$

This reaction occurs in mines; as a result, some mine waters contain enough dissolved copper salts to render recovery profitable.

Ores and tailings are extracted in vats with acid-proof linings and filter bottoms. The solvents used may be sulfuric or hydrochloric acids, aqueous solutions of iron salts, ammonia water, ammonium-carbonate solution, or similar reagents.

From the solution the copper is recovered either by electrolysis or by precipitation with metallic iron.

Recovery of Dust and Fume.—In the several furnace operations in copper smelting, a great deal of dust is produced. The amount of the dust has been increased in recent years by the fineness of the concentrate supplied by the flotation process. Dust recovery is an important item of plant economy. For the most part, the flues of all the furnaces in a copper-smelting plant lead to a single mammoth stack. The point of entry to the stack then constitutes a convenient place for dust recovery.

One of the simplest methods is to establish at the base of the stack large dust chambers through which the gases pass at low velocity. In a modification of this system, wire baffles on which the dust impinges and adheres are placed in the dust chambers. While the gas stream is being diverted through another chamber, the dust is dislodged from the baffles and recovered.

For extremely fine particles, such as fumes, electrostatic precipitation, of which the Cottrell system is a well-known example, is serviceable. In one of the Cottrell installations, corrugated-steel roofing sheets, spaced 12 in. apart, with rows of small chains between them, are hung in box-like chambers. The chains are electrified with a static charge under very high tension. As the dust passes into the electric field surrounding the chains, the particles become charged and are repelled from the chains to the plates. The plates being grounded, the dust particles discharge there and collect in masses large enough to fall through the rising stream of gases.

Physical Properties.—Copper is the only reddish-colored metal. It melts at 1083°C. (1981°F.) and boils at about 2350°C. (4262°F.) Although it is sufficiently volatile to color a bunsen flame green, loss on melting is not noticeable. The specific gravity of electrolytic copper is 8.945; of the wrought metal, 8.95. If copper is heated to a red heat and cooled slowly, it becomes brittle; but if cooled quickly, it is soft, malleable, and ductile. The brittleness is due to a coarsely crystalline structure that develops during slow cooling. At a red heat it may be welded.

Although pure copper is one of the best conductors of both heat and electricity, its electrical conductivity is highly sensitive to the presence of impurities. The following percentages will serve to illustrate their effect: as little as 0.03 per cent of arsenic will lower the electrical conductivity about 14 per cent, 0.13 per cent of phosphorus will lower it 30 per cent; and 0.4 per cent of iron, 64 per cent.

Like aluminum, pure copper does not cast well. When molten it absorbs gases, such as carbon monoxide, hydrogen, and sulfur dioxide, which separate out on cooling and cause "blow-holes."

To produce sound castings having a high electrical conductivity, Weintraub[1] adds about 1 per cent by weight of boron suboxide to the molten copper, which has been heated to about 1350°C. To secure high conductivity, pure copper must be used, since the suboxide acts only as a deoxidizer. Sound castings can be made by this treatment regardless of the purity, but the conductivity is reduced in proportion to the amount and kind of impurity present. Although electrical conductivity as high as 97 per cent has been obtained in castings made in this way, it is usually about 88 to 90 per cent.

The ultimate tensile strength of copper varies greatly with the mechanical treatment to which it has been subjected. For cast copper, the tensile strength is about 25,000 lb. per square inch; when cold rolled or cold drawn (so-called hard drawn, *e.g.*, trolley wire), its tensile strength will range from 40,000 to 67,000 lb. per square inch.

For copper that is to be worked, lead is sometimes added in order that the metal may be worked more easily, but if more than about 0.5 per cent is employed, it causes the copper to be brittle. In copper alloys for casting, as much as 10 to 20 per cent may be added to cheapen the product, but this lead largely separates out in globular masses on cooling. Lead will not alloy with copper in amounts greater than 3 per cent, and the amount that will remain in solid solution is very much less, probably not over 0.1 per cent.

[1] *Gen. Elec. Rev.*, **15**, 459, 1912.

Chemical Properties.—When exposed to dry air, copper slowly turns dull, due to the formation of a thin film of the cuprous oxide. In moist air, it becomes coated with a green basic carbonate [$Cu(OH)_2 \cdot CuCO_3$] incorrectly called verdigris, which is closely adherent and protective. In the presence of atmospheric hydrogen sulfide, it is rapidly darkened by the formation of cupric sulfide, but the film is protective. On the whole, copper is quite permanent under the usual conditions of outdoor exposure.

When heated in the air, it becomes coated with a layer of the black cupric oxide (CuO) beneath which will be found a layer of the red, cuprous oxide (Cu_2O).

Although copper does not dissolve in hydrochloric and sulfuric acids with the evolution of hydrogen, both these acids attack the metal slowly in the presence of oxygen. It is very soluble in nitric acid, both dilute and concentrated. It is important to remember that many organic acids, even when dilute, act upon copper. Such acids are often found in food products, and may come into contact with copper used in making utensils for cooking. All copper compounds are poisonous.

Ammonia water slowly dissolves copper in the presence of air with formation of a double compound [$Cu(NH_3)_4(OH)_2$]; a blue-colored solution is produced.

Uses of Copper.—The largest proportion of copper produced is employed for electrical purposes. About one-fourth is consumed in making brasses, bronzes, and other copper alloys. It is used for sheeting, roofing, spouts, boilers, stills, and condensers, and other purposes where corrosion resistance with fair strength and flexibility is essential.

LEAD

Occurrence.—Lead is a very widely distributed metal; it is found in nearly every country of the world. Approximately 80 per cent of the total output of all countries, however, is produced by five of them, the United States, Mexico, Australia, Spain and Canada. Other large producers are Germany, Belgium, and India. Russia and China have immense quantities of ore, but their output is small because the deposits are not now extensively worked. In the United States, the leading states in order are Missouri, Utah, Idaho, and Oklahoma.

The production of lead in the United States has been gradually increasing for many years, but this has not been due to any recent discovery of new ore bodies. There are probably within the United States no deposits of any consequence that remain to be discovered, and the fields now being worked are slowly being exhausted. The increase in output has been due to better methods of ore dressing, especially to selective flotation. By this method it has been possible to derive lead from complex ores that were formerly considered to contain so little lead that it could not profitably be recovered.

In the last few years the rate of increase in the output of Canadian lead has been greater than that of any other country. The most of it is produced in British Columbia.

In Europe, Spain is the greatest producer of lead. It is interesting to note that Spain's lead deposits, which today rank with the greatest in the world, are the same deposits that were worked by the Romans in the third century B.C.

It seems now that Africa will make a considerable contribution to the world's future supply of lead. Important ore fields have been found in Morocco, Rhodesia, and in the Southwest Africa mandate.

Ores.—In deposits of their ores, lead and zinc are generally associated. The mixtures, of course, vary greatly in proportions. In one locality it will be lead and in another zinc that predominates, but neither metal is likely to be found entirely free from the other. Not infrequently lead mines become zinc mines at lower levels. Zinc minerals weather more readily than those of lead and are often carried by water to lower levels more rapidly and completely than lead.

Lead sulfide (PbS), called *galena* or *galenite,* is the chief lead ore. Its distribution is very wide. There are practically no important deposits of lead in which galena is not present to some extent. Silver sulfide is scarcely ever absent from galena; the amount is small, however, generally being less than 0.3 per cent.

Second in importance as an ore of lead is *cerussite,* the carbonate ($PbCO_3$), immense deposits of which are found in Colorado and Nevada. Prior to the discovery of these deposits, cerussite was considered to be of little value. During the 16 years that followed the gold strike in 1860 on the present site of the city of

Leadville at the upper end of the Arkansas River valley in Colorado, the placer miners thoughtlessly moved aside the great boulders and "heavy sands" that obstructed their work, unaware that they were part of a deposit of lead ore, extremely rich in silver, worth more by many hundreds of millions of dollars than all of the gold that would ever be removed from that district. Cerussite is a secondary formation; it has been formed by the weathering of galena. In some mines cerussite is found near the surface and galena at lower levels.

Anglesite ($PbSO_4$) and *pyromorphite* ($3Pb_3P_2O_8 \cdot PbCl_2$) are lead ores of minor importance. Other lead minerals also are found.

Metallurgy of Lead.—If the metallurgy of lead involved no more than the extraction of lead from galena or from cerussite, the process would be extremely simple. In practice, however, the process is not simple because lead ores are very complex. In addition to the zinc and silver, of which mention has already been made, in lead ores, antimony, arsenic, bismuth, cadmium, manganese, iron, nickel, cobalt, copper, gold, and other metals may be present. The process must be adapted to the recovery of some of these elements because they are valuable, while others must be removed from the lead because they affect its properties adversely.

Flotation.—In accordance with modern practice in handling ores, the sulfide ores especially, if concentration of lead ores is required it is generally done by flotation.[1] It has been found that the intimate mixtures of sulfides in lead ores may be not only parted from the gangue, but may themselves be separated by a process of selective flotation. If the flotation liquid is made faintly alkaline with soda ash, and a little sodium cyanide and zinc sulfate are added, zinc sulfide and iron pyrite may be floated without bringing up the sulfides of copper and lead. In a second treatment, by making the liquid more alkaline, the zinc sulfide is floated from the iron pyrites. The copper is removed from the lead later during refining.

General Principles of Smelting.—In accordance with the principles involved, the processes by which the sulfide ores of lead are smelted may be divided into three classes, as follows:

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[1] For a general discussion of flotation, see p. 95.

1. An oxidizing roast, with a partial removal of sulfur, yielding lead oxide and lead sulfate which later react with unchanged lead sulfide to produce sulfur dioxide and lead.
2. An oxidizing roast yielding lead oxide which is reduced to lead with carbon or carbon monoxide.
3. A precipitation of lead from lead sulfide by means of metallic iron.

In the first method the oxidation is continued until the weight of the oxygen in the oxide and sulfate together is approximately equal to the weight of the sulfur in the sulfate and unchanged sulfide. The ratio between oxygen and sulfur, in other words, is $S:O_2$. The reactions involved are as follows:

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$

Then, by further heating at a higher temperature in the relative absence of air, the following reactions ensue:

$$2PbO + PbS \rightarrow 3Pb + SO_2$$
$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2$$

The reactions of the second method are typical blast-furnace reactions. The carbon and carbon monoxide are derived from the fuel of the charge. The reduction may be represented thus:

$$PbO + CO \rightarrow Pb + CO_2$$

The lead oxide may be obtained from the sulfide by a more complete oxidizing roast than is employed in the first process. Naturally oxidized ores, such as cerussite, may of course be smelted in the blast furnace without any preliminary treatment other than crushing to the size required.

The precipitation reaction is also a blast-furnace reaction. The sulfide is reduced directly, as:

$$PbS + Fe \rightarrow FeS + Pb$$

The metallic iron needed for the reaction results from the reduction of iron compounds intimately mixed with the lead ore itself, or it may be derived from iron ore added for this purpose. If copper be present it collects in the iron-sulfide matte, while the gold and silver dissolve in the lead. Of the three principles involved in lead smelting, precipitation is probably the least important.

Leaching.—An increasing tonnage of lead is being extracted from ores by a method of brine-leaching. Galena ore, roasted to sulfate, is leached with a chlorinated solution of sulfuric acid saturated with sodium chloride. In some cases, raw ores are leached. The lead is recovered from the leach liquor by electrolytic deposition with high current density. The sponge lead that collects on the cathode is removed and pressed into cakes for melting.

Refining of Lead.—The lead obtained from practically all ores, except those found in the Mississippi valley and in parts of Germany and Spain, contains enough silver to pay for its extraction. This argentiferous lead, called base bullion, is likely to contain also other precious metals such as gold, platinum, and palladium. In refining the lead, not only must these metals be recovered, but the impurities, such as sulfur, arsenic, antimony, bismuth, tin, copper, iron, nickel, and cobalt, all of which are very detrimental in their effect on the lead, must be removed, and for the most part must be worked up into salable products.

Softening.—The base metal impurities make the lead hard and unfitted for most of its uses. The treatment employed for their removal, therefore, is spoken of as a softening process. Nearly all of these impurities fortunately combine with oxygen more readily than lead, and can be taken out by an oxidizing treatment. As their oxides are formed, they collect on the surface as a dross, which is removed by skimming. Copper and bismuth cannot be effectually eliminated in this manner. Copper, however, forms an alloy with lead that is less fusible than the lead itself. By suitably regulating the temperature of the melt, use may be made of this fact to effect its removal. Bismuth is generally separated subsequently in connection with the process of desilvering.

Desilvering.—The softened lead still contains the silver and other precious metals. There are three principal methods employed for their removal: the Pattinson, the Parkes, and the Betts.

1. The Pattinson process: This method is based upon the fact that when argentiferous lead is cooled to its solidification

range, the lead crystallizes selectively, rejecting the silver which remains in the melt. The crystals of lead are skimmed out, more silver-bearing lead is added, and the process is repeated. When the silver content of the liquid lead reaches about 500 oz. per ton it is removed from the pot and cupelled. In cupellation the metal is subjected to an oxidizing process. The lead is converted into litharge (PbO), while the silver is practically unaffected by the oxidizing attack. Gold and other metals remain with the silver.

2. The Parkes process: This method of desilvering lead is based upon two facts: (*a*) that gold and silver are more soluble in melted zinc than in lead, and (*b*) that zinc with its dissolved metals will rise and form a crust on the lead. The zinc is first brought into intimate contact with the lead by stirring, then is allowed to rise, and the crust that it forms is removed. Two or more treatments with zinc are required.

The zinc is recovered from the crust by distillation and is employed again. The relatively small amount of lead remaining with the silver is removed by cupellation.

Whether the Pattinson or Parkes method is employed depends partly upon the bismuth in the softened lead. In the Pattinson process the bismuth stays in the silver-bearing lead and is removed by cupellation; in the Parkes process the bismuth remains in the desilvered lead that goes to market. High bismuth lead, therefore, is more successfully handled by the Pattinson process. On the other hand, because the Parkes method is cheaper to operate, allows less silver to remain in the lead that is marketed, and recovers completely even traces of gold, it is the desilvering process most generally used in the United States.

3. The Betts process: Some lead, especially that with a high bismuth content, is refined by electrolysis. The scheme is very similar to that employed in the electrolytic refining of copper (page 99). The electrolyte is a solution of lead silicofluoride ($PbSiF_6$). Gold, silver, and bismuth remain unattacked at the anode, and are recovered from the anode slime. Although ordinarily the lead deposit on the cathode is spongy, if a little gelatin or some similar colloidal substance be added to the fluosilicate electrolyte, a solid cathode deposit as dense as cast

lead is secured. Only as little as 1 part of gelatine to 5,000 parts of solution is required to produce this effect.

Commercial Lead.—In commercial lead from different sources there may be a marked variation in the amount of impurities carried. The refining that non-argentiferous lead receives is sometimes scanty. It may be no more than a slow melting down and stirring with a pole of green wood or with dry steam to allow entangled slag and other oxide inclusions to rise. Some purification through oxidation, of course, will occur in this process. Lead containing over 0.05 per cent of bismuth cannot be used for "corroding" lead in the manufacture of white lead (page 469) because bismuth imparts to the white lead a grayish color. A good quality of corroding lead will contain from 99.95 to 99.99 per cent of lead. All of the usual impurities, arsenic, antimony, bismuth, zinc, and copper, increase the hardness of lead. Zinc also lessens both its resistance to acid attack, and its suitability for the manufacture of lead-tin solder.

Physical Properties.—Lead is a bluish-gray metal with a high metallic luster when freshly cut. It is the softest and heaviest of all the common metals.[1] It can readily be scratched with the finger nail when pure.

Lead is the least tenacious of the common metals; its tensile strength when cast is not over 2,000 lb. per square inch, although in hard wire the strength may reach about 3,000 lb. It is very malleable and may be readily formed into foil. When hot it may be extruded by hydraulic presses into tubes, rods, and wire. Under a pressure of 29,000 lb. per square inch, filings and shavings of it may be pressed into a solid block. Under a pressure of 75,000 lb., it appears to liquefy at ordinary temperatures.

If cooled quickly from the molten condition, lead solidifies in the ordinary amorphous condition; if cooled slowly, it forms lustrous, octahedral crystals. The crystalline form may be prepared also by electrodeposition of the metal.

Lead melts at 327°C. (621°F.) and boils at 1525°C., but it is not easy to distill it. Volatilization is noticeable, however, at comparatively low temperatures, at about 700°C., a bright red heat.

The specific gravity varies according to the mechanical treatment the lead has received; it ranges from 11.25 to 11.4. Its

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[1] Next to iron it is also the cheapest of the metals.

specific heat is 0.0314. With silver taken as 100, the conductivity of lead for both heat and electricity is approximately 8.5.

Chemical Properties.—Lead is not affected by perfectly dry air nor by water that is free from air. In the presence of both air and moisture, clean lead surfaces rapidly acquire a thin film of the basic carbonate. The film adheres closely and retards further action. Under severely corrosive conditions, as when buried in cinders, lead is rapidly attacked. In this location, a white incrustation of the carbonate, sulfite, and sulfate is produced.

Lead is quickly tarnished by atmospheric hydrogen sulfide; a layer of black lead sulfide is formed. In normally dry air the sulfide layer is protective, but if exposed to the weather the sulfide is oxidized to the sulfate which forms a whitish efflorescence.

If melted in contact with air, a dark scum or coating of the suboxide (Pb_2O) appears. If the temperature is raised to a dull-red heat the suboxide is converted into the monoxide (PbO). This oxide finds wide application in the arts, especially in paints as a drier. It is manufactured by heating lead in air, and removing the film of oxide as it forms. If produced at a temperature below the melting point of the oxide, the product, which is an extremely fine powder, is called *massicot.* When formed at a temperature above its melting point, the oxide, which solidifies as a stone-like mass, is known as *litharge.* On standing, the massive litharge crumbles into orange-yellow scales called *flake litharge,* which must be ground to a powder for use. If the litharge is heated in air to a temperature between 400 and 450°C., it is converted into *red lead* or *minium* (Pb_3O_4).

Lead is resistant to the action of the alkalies, such as caustic soda and potash. It is not much affected by cold hydrochloric or sulfuric acid; it is especially indifferent to the latter. The lead salts of these acids are insoluble in the cold, so that some protection is afforded the metal after the acid has attacked the surface slightly. Lead is quite soluble in nitric acid, and in the presence of air is noticeably attacked by acetic. Many of the relatively weak organic acids, such as are found in food products, dissolve lead slightly, so that lead should not be allowed to remain in contact with foods or beverages. All lead salts are poisonous.

According to the manner in which they act, they belong to the accumulative class, *i.e.*, small amounts taken daily seem to be stored within the system until a toxic quantity is present. Absorbed lead may remain in the body for years. Very pure water dissolves lead sufficiently to make it dangerous for continuous use. When the lead is in contact with hard water, an insoluble coating of lead carbonate and sulfate is formed on the metal; this coating prevents the water from being contaminated. With pure water, such as rain water, lead hydroxide, which is noticeably soluble, is formed. Consequently, lead pipes are suitable for conveying drinking water only when the water is hard. At the present time, however, lead pipes are used chiefly for waste lines. Stains and splashes of paints containing lead pigments should not be allowed to remain upon the skin, because lead compounds from this source are absorbed through the skin.

Uses of Lead.—From the time of the Romans, at least, lead has been used for the making of tubes or pipes; in fact, from the Latin word for lead, *plumbum*, has been derived the name "plumber." Lead is employed for chemical-laboratory and plant drains, and for chemical-proof plumbing in general. It finds extensive application as sheaths for electric cables, both overhead and underground. In the form of sheet lead it serves excellently for roofs, gutters, and cornices. Large quantities of the metal are consumed in the manufacture of the lead-plate-sulfuric-acid type of storage battery, and in the manufacture of white lead and other paint pigments.

As shown by "Mineral Resources of the United States" for 1928, the percentages of the total lead consumed in the United States that were required for its major uses were as follows:

Use	Per Cent
Storage batteries	23.64
Cable coverings	19.35
White lead	13.22
Building	10.32
Ammunition	4.26
Solder	3.98
Foil	3.76
Bearing metal	3.44
Calking	3.44
Litharge and red lead	3.33

The uses indicated account for more than 88 per cent of the total consumption. As compared with previous years, there is a distinct falling off in the amount required by the white-lead industry. Other pigments such as zinc oxide, lithopone, and titanium oxide are replacing white lead to some extent.

In addition to the solder and bearing alloys, mentioned in the preceding table and discussed on pages 208 to 216, lead enters into a great variety of other alloys, such as type alloys, some brasses and bronzes, pewter, low-melting-point alloys such as for sprinkler heads, safety plugs in boilers, fire-door releases, and fuses

TIN

Occurrence.—There is only one tin ore of any importance, the stannic oxide (SnO_2), called *cassiterite* or *tin stone*. In Cornwall and Devon, in the south of England, it has been found in comparatively large quantities. As early as 1000 B.C. these deposits were worked by the Phœnicians, and for many centuries in more modern times they were the best-known source of tin, but now the mines are almost exhausted.

At present, the chief producers of tin, named in order of importance, are the Federated Malay States, Bolivia, and the Dutch East Indies. Approximately three-fourths of the world's total production of the metal comes from these three sources. Nearly the total output of the last named source is supplied by the islands of Banca and Billiton, lying between Sumatra and Borneo. In the tin trade the terms "Straits tin," indicating Malayan tin, and "Banca tin" have long been common.

Other countries producing tin in amounts entitling them to mention here are Siam, Nigeria, China, and Australia. Tin is the one metal of major industrial importance that is not found in considerable quantity in the United States; in fact, no noteworthy deposit of this metal has been found anywhere on the North American continent.

Mining and Metallurgy of Tin. *General Considerations.*—Cassiterite, the tin ore, is found in two types of deposits: (*a*) in primary deposits in the form of veins or lodes; and (*b*) in transported alluvial (water-borne) or placer deposits. The transported deposits, of course, had their origin in the weathering of the primary deposits. The latter are practically always in, or closely connected with, granite or other acid eruptive rocks (pages 396 and 398). According to the type of deposit, tin ore is designated either as "vein tin" or "stream tin." Although the other minerals associated with tin oxide in the ore are decomposed by weathering, the cassiterite, being very stable, is practically unaffected. Due to the removal of the decomposition products by the dissolving and washing action of the transporting water, the tin ore in placer deposits is much more nearly pure than that in the original vein formations. Most of the Malayan and East Indian tin is obtained from alluvial deposits chiefly by ground sluicing, hydraulic mining, and dredging, while practically all of the ores from Bolivia, China, and Nigeria are taken out by vein mining. This fact has an important bearing on the quality of the tin coming to the market from these sources. Tin smelted from Asiatic ores is much purer than that from Bolivian and other ores.[1]

By virtue of a prohibitive export duty, all tin ores mined in Great Britain and her possessions are required to be smelted within the British Empire.[2] As a result, most of the Malayan ores are smelted at Singapore and Penang. The latter town is located on a small island just off the west coast of the peninsula. Similar restrictions operate to prevent the exporting of tin ores from the Dutch East Indies, and these ores also are smelted locally. Due to lower smelting costs, the Bolivian ores are smelted in Europe, chiefly in England and Germany.

Preparation of Ore.—Because the methods of refining the metallic tin after smelting are not very satisfactory, it is more essential with tin ores than it is with those of some other metals to deliver to the smelting furnace as pure a concentrate as possible. Inasmuch as the alluvial ores are originally relatively pure, mere concentration may be all that is required with such ores. This may be accomplished by washing in various types of simple sluicing devices. In this manner the lighter clay, sand, and gravel may be washed away. The same treatment may be applied to a few lode ores after crushing. Sometimes handpick-

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[1] See Commercial Tin, p. 116.

[2] HILL, "Tin: Its Political and Commercial Control," *Eng. Mining Jour.*, **109**, 1013.

ing methods are used. In the more modern plants, standard wet-concentrating machinery is employed.

Some tin ores, particularly those from Bolivia, contain the sulfides and arsenical compounds of such metals as lead, antimony, bismuth, copper, and iron. Washing will not remove these minerals, but they may be removed by oil flotation (page 95).

In some cases, after washing, a further purification of the ore is effected by roasting. Much of the sulfur, arsenic, and antimony may be removed directly by volatilization in this way. After roasting, washing will remove undesirable metallic compounds that could not be removed by water from the unroasted ore. Oxides formed by roasting, such as those of copper, bismuth, and iron, may be extracted by leaching with dilute solutions of sulfuric or hydrochloric acids. Roasting with sodium chloride or sodium carbonate, followed by leaching with water, is sufficiently effective in some cases. From the several methods available, the metallurgist in charge selects that one which will yield the purest product with the ore in question.

Smelting.—Compared to the metallurgical difficulties encountered in the smelting of the ores of some metals, the extraction of tin from its ores is not difficult. Tin is found in the ore as an oxide, and the oxide is readily reduced by carbon. Either the blast furnace or the reverberatory furnace may be employed. Blast-furnace smelting is much the older of the two methods.

The blast furnace employed in tin metallurgy has a rather low shaft and the blast pressure is comparatively light. The fuel may be either charcoal or coke, and the flux may be either silica or limestone as the gangue requires. The only difficulty encountered is that, if the slag is too acid, tin will be lost as a silicate of tin, and that if the slag is too basic, the tin oxide will act as an acid and will enter the slag as a calcium stannate.

If the reverberatory furnace is employed the charge will consist of ore, crushed anthracite coal, and the necessary fluxing material. The furnace may be fired with long-flame, bituminous coal or with oil. For the smelting of fine ores and concentrates, the reverberatory is preferred to the blast furnace because the dust losses are less.

Refining of Tin.—Depending upon the amount of impurities in the concentrated ore, the reduced metal obtained by smelting will require more or less refining. For this purpose either fire refining or electrolytic deposition may be employed. The former is the older method and is the one that is the most generally used.

Fire refining may involve two operations: liquating and poling.

Liquating is a type of sweating process. The impure tin is cautiously heated on a sloping hearth to a temperature a little above the melting point of pure tin. The relatively pure tin then melts and drains away, while a skeleton of impure metal remains on the hearth. The hearth residue ultimately finds its way back to the smelting furnace. If the metal obtained by liquating is not sufficiently pure, it is treated by the poling (frequently called "boiling") process.

In the poling process the tin is heated to a temperature considerably above its melting point and is stirred with a pole of green wood. The steam and gases that escape produce a violent "boiling" action, which causes the metal in the bottom of the vessel to be brought to the surface. This stirring not only allows occluded non-metallic bodies to rise but metallic impurities are oxidized as the metal comes into contact with the air. When a dross of oxides collects on the surface, it is removed by skimming. In some refineries the metal is agitated by the use of compressed air instead of the green wood.

In the electrolytic refining of tin, the method employed is similar to that used for copper and lead.[1] A product that is more than 99.9 per cent pure may be secured by the electrolytic method, but even this high purity is not equal to that obtained from some of the purer concentrates derived from Banca ores.

Reclaimed Tin.—Approximately a third of the tin consumed each year in the United States consists of that which has been recovered from waste material. Not all of the reclaimed tin appears on the market in the form of the metal, however; indeed, the largest part of it is in the form of oxide, salts, and alloys. Although this is true, the recoveries are important because they release a corresponding amount of new tin for other uses.

The largest recoveries are derived from the scruff and drosses that are formed in making tin plate and terne plate (page 357). This is to be expected because the plating industry is the largest single consumer of tin.

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[1] See pp. 99 and 108.

Some of the reclaimed metal comes from clean-scrap tin plate, such as the clippings left, for example, when stamping out discs for can tops and bottoms. Nearly all tin plate scrap is detinned by one of three methods: the electrolytic alkali, the chlorine, and the alkali-saltpeter processes.

In the first process the tin coating is removed by an aqueous solution of an alkali and recovered by electrolytic deposition. The recovered metal is in the form of a spongy, granular precipitate which can be melted to pig tin.

In the second process the scrap is placed in an autoclave and the tin is removed by dry chlorine gas. The chlorine attacks the tin readily, but has practically no action on the iron. The tin is recovered as stannic chloride which is used in weighting silk, and as a mordant in dyeing it.

In the third method, by the use of a hot aqueous solution of an alkali and an oxidizing agent,[1] tin oxide is obtained which is used either for the preparation of enamels for cast iron in making sanitary ware (page 461), or is smelted to pig tin in a reverberatory furnace.

The tin coating and solder are also sweated from old tin-coated containers. The black steel sheet that remains is then melted to make sash weights. In some cases, tin from old tin-plated containers is recovered by the chlorine process. Unless the recovery can be accomplished locally, so that freight charges can be avoided, the recovery of tin from old cans is not profitable.

Commercial Tin.—Because most of the tin on the market has been refined by the heat-treatment method, and because refining by this method cannot be relied upon to eliminate completely the impurities, the purity of the ore from which the tin was obtained has an important bearing upon the quality of the refined metal. This is true of all metals, of course, but it is especially true of tin. New tin, called primary tin, is generally sold under the name of the mining or smelting companies producing it, and their brands have a special significance in guiding the purchaser as to the quality of the metal. Tin ores from the Asiatic deposits are purer than those from other parts of the world, and, as a result, the metal reduced from such ores is recognized

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[1] "A Short History of the Detinning Industry," *Met. Chem. Eng.*, p. 187, 1917.

as being of superior quality. Banca tin is the purest variety; it is frequently 99.95 per cent pure. Bolivian tin, and reclaimed tin, called also secondary tin, may contain from 1 to 5 per cent of impurities chiefly lead, iron, copper, and antimony.

In one of the methods employed in gaging the purity of tin, the smelter heats the metal to a temperature a little below its melting point and then drops it from a specified height upon a stone slab. If the tin is pure, it splits into strands of granules. Tin that has been tested in this way and has been found to be pure is sold as *grain tin.* That which is somewhat less pure is known as *block tin.*

In this connection it should be remembered, as was indicated under the topic Reclaimed Tin, that the name "tin" employed in speaking of "tin cans" refers to tin plate (page 357), a product made by coating sheet iron or steel with a very thin layer of tin. Pure rolled tin is designated as *sheet tin* or *block-tin sheet.*

Physical Properties.—Tin melts at 232°C. (449°F.) and boils at about 2275°C.[1] It occurs in three allotropic modifications, known as the alpha, beta, and gamma forms. Alpha crystallizes in the cubic, beta in the tetragonal, and gamma tin in the rhombic system. The familiar, malleable form is the beta modification. It is stable at temperatures between 18 and 161°C.

When the beta form is cooled below 18°C., it has a tendency to change to the alpha form, a gray granular powder. The change is brought about very slowly, however, and the malleable form persists at ordinary low atmospheric temperatures, although it is then in a metastable condition. The conversion into the granular form takes place most rapidly at −48°C., but it may be noticed at −15°C. Consequently, articles made of pure tin will fall to a powder if kept at low temperatures for a long time. This phenomenon was first observed when some organ pipes in Russia, during prolonged cold weather, crumbled to dust.[2] The transition has been found to occur in cold-storage warehouses. It is hastened by "inoculation;" that is to say, the presence of some of the transformed variety accelerates the change. Consequently, when started, it spreads rapidly. It is commonly designated as the "tin pest."

[1] *Proc. Roy. Soc.*, **82**, 396.

[2] HOLMES, "General Chemistry," p. 482.

When the beta, or malleable, variety of tin is heated to above 161°C., it passes into the gamma form; it is then known as "brittle tin." A 200°C. it is extremely brittle and under the hammer can be readily converted into a powder.

It is the malleable form of tin, of course, with which we are chiefly concerned. The specific gravity of the pure metal when cast is 7.287, when rolled, 7.3; of certain commercial varieties, because of the impurities mentioned, it is somewhat higher, about 7.5. It is soft and readily worked. It is harder than lead but softer than zinc. Although malleable at ordinary temperatures, it is most malleable at about 100°C.; it may be rolled into foil 1/5000 in. thick. The tensile strength of cast tin is 3,500 lb. per square inch, of the rolled form about 5,000 lb. per square inch. Tin is ductile, but because of its low tensile strength it is not readily drawn into wire.

The presence of impurities has a noteworthy effect on the physical properties of tin. Fractional percentages of arsenic, antimony, and bismuth, as well as occluded stannous oxide, noticeably lower the tenacity of the metal. Small amounts of copper and lead increase its hardness and tensile strength but affect its malleability adversely. Iron increases the hardness and brittleness of tin.

Tin is a poor conductor of both heat and electricity. With silver taken as 100 in both cases, the electrical conductivity of tin ranges from 11.45 to 14.01, and the thermal conductivity from 14.5 to 15.2. When a bar of the metal is bent, it emits a low, crackling noise, known as the "tin cry" which is due to the friction of the crystalline particles moving over one another.

Chemical Properties.—Tin does not ordinarily corrode, or tarnish much when exposed to the atmosphere; in fact, it is about the most resistant of the common metals in this respect. On this account, it is much used to coat other metals. Above its melting point it oxidizes readily to stannic oxide (SnO_2). When heated to about 1550°C., it takes fire and burns with a white flame.

Tin is attacked at a moderate rate by cold, dilute hydrochloric acid; stannous chloride is formed. The action is much more rapid if the acid is heated. Dilute sulfuric acid dissolves tin slowly with the evolution of hydrogen, but in the hot, concentrated acid the action is rapid, and sulfur dioxide is evolved. Moderately concentrated nitric acid converts tin into the white, insoluble, hydrated metastannic acid, usually designated by $(H_2SnO_3)_5$. Aqua regia dissolves tin readily, forming stannic chloride.

Hot solutions of the caustic alkalies act rapidly upon tin; the cold solutions more slowly.

Uses of Tin.—Although the United States produces practically no tin, it consumes approximately half of the world's total annual production of over 150,000 long tons. The distribution is about as follows:[1] in manufacturing tin plate and terne plate,[2] 30 per cent; in solder, 25 per cent; in babbitt (page 209), 20 per cent; and in brass and bronze, 15 per cent. The remaining 10 per cent is employed for such purposes as making tin foil, collapsible tubes for pastes, type-metal alloys, white-metal alloys, chemical reagents, etc.

Due to its comparative costliness, an effort is being made to find substitutes for tin. Food-packing companies are experimenting with lacquered containers as a substitute for those made of tin plate. A phosphorized solder containing 98½ per cent of lead and very little tin has been found to be acceptable in place of the usual lead-tin solder (page 211) in making cans, and for automobile radiators. Cadmium is employed as a partial substitute for tin in babbitt and bearing alloys, and zirconium oxide is used to some extent instead of tin oxide in ceramic glazes.[3]

ZINC

Occurrence.—Because zinc in the metallic form is chemically active, its occurrence in nature is not free, but in the form of its compounds. Like lead, it is widely distributed. The sulfide (ZnS), called *sphalerite, zinc blende,* and *black jack,* is the chief ore. This ore generally contains also the sulfides of iron, lead, silver, and cadmium, and it may be accompanied by arsenides, antimonides, calcite, dolomite, and similar substances. Impor-

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[1] "Mineral Resources of the United States," pt. I, p. 33, U. S. Geol. Survey, 1927.

[2] Terne plate is sheet steel coated with a lead-tin alloy.

[3] "Mineral Resources of the United States," pt. I, p. 39, U. S. Geol. Survey, 1926.

tant deposits occur in the Ozarks, the upper Mississippi Valley, Montana, and other portions of the United States, at Broken Hill in New South Wales, in Tasmania, the Rhenish provinces of Germany, Silesia, and Burma.

The carbonate ($ZnCO_3$), called *smithsonite* and *zinc spar*, is second in importance. It is almost invariably associated with the carbonate of cadmium, manganese, magnesium, calcium, and iron. It occurs abundantly in Spain, Silesia, and the United States.

The mines of New Jersey yield *franklinite* [$(Fe, Zn, Mn)O \cdot (Fe, Mn)_2O_3$], *zincite* ($ZnO$) or red zinc ore (colored with ferric oxide), and *willemite* (Zn_2SiO_4). Another silicate ore of zinc is *calamine* ($Zn_2SiO_4 \cdot H_2O$).

The chief zinc producers of the world, in the order of output, are the United States, Poland, Mexico, Australia, Germany, Italy, and Canada. Oklahoma, Kansas, New Jersey, Montana, and Colorado furnish most of the domestic zinc, but important deposits occur also in Utah, Wisconsin, New Mexico, and Idaho.

Metallurgy of Zinc.—A great deal of zinc ore, like aluminum ore, is transported long distances for smelting. Concentrated zinc blende from Australia, for example, is smelted in quantity in Germany and Belgium. One of the reasons for this practice is that the sulfur dioxide resulting from roasting the blende is converted into sulfuric acid. A ton of rich concentrate, containing only 10 per cent of material other than zinc sulfide, will produce a ton of concentrated sulfuric acid. Unless the zinc is to be recovered from the roasted ore by a process of acid leaching accompanied by the electrolytic deposition of the metal, there is little use for the acid at the mine. It is more economical to transport the blende for smelting to some industrial center where the acid will be consumed in other processes, than it would be to transport the metal and acid to the industrial center. Some of the manufacturers of galvanized steel wire in America smelt the zinc ore at the wire plant. The acid produced is employed in "pickling" (cleaning) the steel, and the zinc is used in coating the wire. Few manufacturing processes are more perfectly integrated than this. Even if the sulfur dioxide were of no economic importance, some provision would have to be made to take care of it. It is destructive to vegetation and an active accelerator in the corrosion of metals; consequently, it would become an unendurable nuisance if it were allowed to escape.

General Principles.—There are two distinct ways by which zinc is extracted from its ores: the hydrometallurgical or electrolytic process, and the pyrometallurgical or retort process.

In the *electrolytic method,* the roasted ore is leached with sulfuric acid, produced from the sulfur dioxide evolved in the roasting as previously noted, and the zinc is recovered from the solution of zinc sulfate by electrodeposition of the metal. Although this method has come into use comparatively recently, during the past few years it has grown rapidly.

There are various ways by which the electrolyte may be prepared. In one of the recent methods, after roasting so that a magnetic decomposition product, zinc ferrite, is formed, the ore is separated into two parts by means of a magnetic separator. The magnetic portion, which contains some zinc oxide in addition to the zinc ferrite, is leached with sulfuric acid. The acid solution of zinc sulfate that results is then neutralized by the use of the non-magnetic portion which consists of pure zinc oxide. Due to the neutralization, the iron is precipitated as a dense ferric hydroxide, which carries down with it all of the arsenic, antimony, and silica in the ore. The zinc is then deposited electrolytically from the purified solution.

Electrodeposition has important advantages over distillation. The zinc produced is of high purity, and metals may be recovered from the ore that were lost by the older process. The chief plants of the world employing this method are located in Montana, British Columbia, Upper Silesia, and Tasmania. About one-fourth of the primary zinc produced in the United States is extracted by the electrolytic process.

The general principle of the *pyrometallurgical process* of zinc reduction differs from that of most metals; there is no fluxing of the gangue to a melted slag. The zinc oxide, which in the ore may exist as such, or may be produced by roasting the sulfide, is reduced by carbon in the usual manner, but the metal is separated from the unfused gangue by distilling it from the reaction zone. Although the term smelting is employed in the metallurgy of zinc, unless other metals, such as lead, are also recovered, there is no smelting in the sense in which this term is usually understood.

In order that zinc oxide may be reduced by carbon, it is necessary that the two be intimately mixed and heated to about 1100°C. Because zinc boils at 918°C., the zinc assumes the vapor state at the moment of reduction. Zinc vapor reacts speedily with the oxygen of the atmosphere, and also with carbon dioxide and water vapor, to form zinc oxide. The reduction, consequently, must be carried out in a closed vessel, or retort, in the presence of an excess of carbon.

The vapor must be condensed at some temperature above 420°C., the melting point of zinc, or liquid zinc that can be cast will not be obtained. If condensed at a temperature below 420°C. the zinc vapor will solidify in a very finely divided state, called *blue powder*, or *zinc dust.* The extremely minute droplets of zinc that constitute the blue powder cannot readily be melted to a solid mass. They carry a superficial coating of zinc oxide that prevents them from coalescing. When properly heated, some coalescence may be secured by rubbing, which breaks the coating.

Concentrating.—If concentration of a sulfide ore of zinc is required, it is done by flotation. The ingenious method of selective flotation has proved to be very satisfactory with zinc ores (page 105). Carbonate, silicate, and other non-sulfide ores are concentrated by magnetic separation, or in a washery by jigging and tabling.

Roasting.—Zinc sulfide is not directly reducible by carbon; consequently, the blende ores must be roasted to zinc oxide. The sulfur is converted into sulfur dioxide as previously stated. In roasting, care must be exercised to prevent as far as possible the formation of zinc sulfate.

In Europe the carbonate and silicate ores are calcined in order to drive off the carbon dioxide and water. If they are not expelled, they may yield oxygen to the zinc vapor in the retort, and thus allow the reduced zinc to revert to zinc oxide. In America the smelters have discontinued the calcination of the oxidized ores because they claim that the advantages derived from it are not commensurate with the cost.

Reduction of Ore and Distillation of Zinc.—The retorts employed in the reduction of the ore are made of earthen ware. The time you ll

charge placed in the retort consists of an intimate mixture of ore and crushed fuel. The percentage of fuel in the mixture will range from 40 to 75 per cent. The fuel in the retort may be non-coking bituminous coal, low in volatile matter, coke breeze, or anthracite coal. The last named is preferred. The fuel employed under the retorts for heating them may be coal or gas. The retort is connected to an air-cooled earthenware condenser, to which in a few plants is attached a cast-iron prolong, or secondary condenser, also air cooled. The zinc, which vaporizes at the moment of its reduction, emerges from the retort and is cooled in the condenser. In the initial stages of the operation the retorts are too cold; as a result, blue powder is formed. As the condenser becomes warmer, the zinc vapor condenses to liquid, which collects in the bottom of the condenser. Any vapor that escapes into the prolong, being suddenly cooled, also condenses to blue powder. The blue powder collected from the prolong is less oxidized than that from the condenser, and for this reason, when marketed, is always preferred by the buyer.[1] Most of the blue powder, however, is returned to the retort for redistillation. In good practice about 85 to 90 per cent of the zinc in the ore is ultimately obtained in marketable form. Of the zinc distilled, about 60 to 70 per cent is recovered directly in the liquid condition. When removed from the condenser and cast in ingots, it is known as *spelter*.

Because of the prevalence of lead in zinc ores, the spelter is usually contaminated with lead. Since zinc boils at 918, and lead at about 1500°C., in principle, the separation of these two metals by fractional distillation is not difficult, but at the temperature of 1100°C., to which the retort is heated, some lead vapor is carried along with the zinc. When working on argentiferous ores, even silver is volatilized and entrained with the vapor of the other metals. Most of the lead, however, remains in the retort, and lead may therefore be recovered from both the condensate and the retort residue.

Zinc Burning.—During the reduction of zinc ores in the normal retort process, if the vapor is allowed to escape into the air, it

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[1] Originally the zinc dust or blue powder that appeared on the market was all obtained as a by-product in the earlier stages of distillation, but now it is manufactured in furnaces especially designed and operated for its production.

will burn and produce dense clouds of zinc oxide (ZnO). The oxide may be collected by allowing it to settle in chambers or by filtering through bags. It is an extremely fine, white powder. In rubber mixtures, such as are used for automobile tires, it is employed extensively to increase the hardness, toughness, and mechanical strength. Under the name of *zinc white,* it is used as a paint pigment (page 471). The best quality of zinc oxide is obtained by burning the vapor produced in the retort distillation of metallic zinc, as described.

By another method, however, known as the *Wetherill process,* the largest proportion of the commercial zinc oxide is produced. An oxidized zinc ore is mixed with coal in a shallow layer on a furnace grate. The air for combustion is supplied under pressure. As the zinc is liberated by reduction of the ore, it vaporizes and burns in the combustion chamber of the furnace. The oxide is conducted away and is collected. If the ore is of the lead-bearing variety, a considerable amount of lead oxide and lead sulfate will be mixed with zinc oxide. As a paint pigment, this product is marketed under the name of "leaded zinc."

Refining of Spelter.—Spelter may be refined, but a large amount of it is marketed in the condition in which it is received from the condensers. Cadmium and lead, which are the chief impurities, are not objectionable in many instances for galvanizing and brass making, for which purposes much of the zinc is employed. If the spelter is refined, either liquation or redistillation may be used.

In the process of liquation, the zinc is melted at a low temperature in a reverberatory furnace. The non-alloyed and oxidized inclusions rise to the surface and are skimmed off. The lead and the zinc-iron alloy sink to the bottom from whence they are removed by means of a specially devised drain and ladling door. Zinc containing not above 1.25 per cent of lead may be prepared in this way.

Refining by redistillation may be carried out in retorts similar to those of the ordinary reduction furnace. The main difference between the processes is that in refining the retorts are heated to a temperature only a little above the boiling point of zinc. This method is very little employed, but a product 99.9 per cent pure can be obtained in this way.

Commercial Zinc.—According to the amount of impurities present, the American Society for Testing Materials[1] divides the spelters into four grades, as shown by the following specifications:

STANDARD SPECIFICATION FOR SPELTER

	Lead shall not exceed, per cent	Iron shall not exceed, per cent	Cadmium shall not exceed, per cent	The sum of the Pb, Fe, and Cd shall not exceed, per cent
A High-grade....	0.07	0.03	0.05	0.10
B Intermediate...	0.20	0.03	0.50	0.50
C Brass special...	0.75	0.04	0.75	1.20
D Prime western..	1.50	0.08		

Grades, A, B, and C shall be free from aluminum.

Chemically pure zinc is obtained by distilling pure precipitated zinc carbonate with pure carbon. It is prepared also by the electrolysis of pure zinc salts.

Physical Properties.—Zinc melts at 420°C. (787°F.), and boils at about 918°C. under atmospheric pressure. Consequently, it distills readily and considerable loss must be allowed for in making alloys.

When zinc is cooled suddenly from the melted state, it solidifies in an amorphous state, and then is quite malleable; if allowed to cool slowly, it becomes highly crystalline, and then is hard and brittle. The ordinary commercial form is partly crystalline and partly amorphous; at atmospheric temperatures it is quite brittle, especially if impure. If heated to between 100 and 150°C., it becomes malleable and ductile and may be rolled into sheets and drawn into wire. Moreover, it remains malleable and ductile when allowed to cool. When heated to somewhat above 200°C. it becomes brittle again and may be readily pulverized. In hardness, zinc ranks between copper and tin. Cast zinc has a specific gravity of 6.860 to 7.149; when wrought, from 7.2 to 7.3.

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[1] "Year Book," p. 344, 1915.

The tensile strength of cast zinc is about 5,400 lb. per square inch; this is found to be increased to about 30,000 lb. if rolled and tested in the direction of rolling. Although the strength is even greater transverse to the direction of rolling, it is more brittle in this direction. When rolled sheet zinc is used to line vats or packing cases, the increased brittleness sometimes becomes apparent; cracks develop in the angles running parallel to the direction of rolling.

Because of its great fluidity when molten, zinc casts well. It shrinks but little on solidifying. Like aluminum, the tensile strength of cast zinc is improved by pouring at as low a temperature as possible, because the crystal structure is finer under such conditions.

Chemical Properties.—When exposed to moist air, the bright luster of zinc is rather rapidly dulled by the formation of a thin film of the basic carbonate [$Zn(OH)_2 \cdot ZnCO_3$]. Because of its high solution tension (page 334), ordinary commercial zinc does not have a high corrosion resistance where conditions are at all severe. In the air, it burns readily with a bluish-white flame; dense clouds of zinc oxide are formed.

Commercial zinc is soluble in practically all of the acids. The dissolving action is hastened by the presence of lead, iron, etc. which have a lower solution tension and assume the cathode relation to zinc as explained on page 359. The rate of solution becomes less as the degree of purity increases. Absolutely *pure zinc* will not dissolve in any of the acids except nitric.

In hot caustic alkalies zinc is soluble, as:

$$Zn + 2NaOH \rightarrow Na_2O_2Zn + H_2 \text{ (compare aluminum)}$$

Uses of Zinc.—As shown by "Mineral Resources of the United States," the three chief uses for spelter in the United States are in the production of galvanized ware (page 356) such as sheets, tubes, wire, wire cloth, and shapes; in brass making (page 183); and in the manufacture of sheet zinc. At present the percentages of the total consumption employed for these purposes are about as follows:

Use	Per Cent
Galvanizing	47
Brass making	30
Rolled zinc	13

A great deal of the rolled sheet zinc finds application in the manufacture of covers for glass jars, and in the making of primary electric cells, such as the dry cell, where it serves both as container and anode. High purity is essential to good performance in the latter case. Sheet zinc is used also for roofs and gutters, washing-machine parts, vat and tank linings, table covers, and pipes.

Minor quantities of zinc are consumed in the manufacture of the paint pigments, French-process zinc oxide (page 471) and lithopone (page 473), and in the production of die castings and slush castings. The latter are hollow ornamental castings made by pouring back into the ladle the melted metal from the interior of the casting as soon as that part in contact with the walls of the mold has solidified. By this method, with subsequent plating, the so-called "French bronzes" are made. Etchings for line drawings and similar illustrations are also made of zinc.

In the United States about 8,000 tons of zinc dust (blue powder) are used annually. This is employed chiefly as a pigment in paints, especially in marine paints and in sherardizing (page 356). The United States Navy has found that a very effective smoke screen can be made by the use of zinc dust.

CADMIUM

Occurrence.—Cadmium is probably the first metal that was not discovered in an ore. It was found in 1817 by Strohmeyer who investigated a sample of zinc carbonate, which, although it contained no iron oxide, was colored yellow. No cadmium ores are known. One cadmium-bearing mineral, *greenockite*, the sulfide (CdS), has been recognized, but no workable deposit of greenockite has ever been discovered.

Cadmium is obtained commercially as a by-product in the metallurgy of zinc and to some extent of lead. It is recovered from the fume produced in roasting zinc blende, from the blue powder formed during zinc distillation, especially in the earlier stages of the process, from intermediate products in lithopone manufacture (page 473), from the tank solutions in the electrolytic method of zinc-ore extraction, from the electrolyte employed in the electrolytic refining of lead, and from lead-furnace fumes. It is more volatile than zinc or lead and may be separated from their metallurgical by-products by redistillation. It may also be recovered by electrolytic methods, or by precipitation with metallic zinc.

About 1,000 metric tons of metallic cadmium are produced annually in the United States, and a considerable amount is imported. The commercial metal, as a rule, is approximately 99.5 per cent pure.

Physical Properties.—Cadmium is a white metal with a bluish tinge, capable of taking a high polish. It is slightly harder than tin, but is softer than zinc. It is malleable and ductile, and can be readily rolled and hammered into foil and drawn into wire. If pure, it emits a creaking noise, like tin, when bent. At 80°C. it becomes so brittle that it can be pulverized under the hammer. Its tensile strength is 13,660 lb. per square inch, which is slightly more than the strength of aluminum.

Cadmium melts at 320, and boils at 778°C. Its specific gravity as cast is 8.604.

Chemical Properties.—Cadmium is not affected by dry air, but in moist air it becomes coated with a grayish-white film of the hydrated oxide. It burns readily at a red heat forming the yellowish-brown oxide CdO. It is readily soluble in nitric, hydrochloric, and sulfuric acids. Although it is noticeably affected by the relatively weak acids, such as acetic and tartaric, it is more resistant than zinc. From solutions of its salts cadmium is precipitated by zinc.

Uses.—Cadmium is used chiefly in alloys. It is employed especially in low-melting-point alloys as a complete or partial substitute for bismuth. Although they are both effective in bringing down the melting point, bismuth has a tendency to make the alloy brittle, while cadmium, on the other hand, increases the malleability and ductility. Cadmium is also much cheaper than bismuth. Nearly all of the fusible alloys employed for sprinkler heads in automatic fire extinguishers, fire alarms, electric fuses, and safety plugs in boilers contain cadmium. The other metals in such preparations are generally lead, tin, and bismuth. Several of these alloys, although they are strong and can be bent and machined, melt at temperatures much below the boiling point of water. A superior alloy under the name of cliché metal for stereotype plates also has been prepared by substituting cadmium for bismuth. In the jewelry trade cadmium is employed for producing green gold.

Cadmium is now being used as a substitute for tin in solder and in anti-friction alloys for bearings. In connection with its use in solders, it must be remembered that even small quantities of cadmium compounds are highly toxic to human beings, and that solders containing this metal, therefore, must not be employed for food containers.

Cadmium is finding a growing application as a rust-proofing coating for iron and steel. If heat treated, the coating forms an alloy with the base metal, and exhibits extraordinary adhesiveness, so that it does not crack or peel off like zinc or nickel when bruised under the jaws of a wrench or pliers. This new use is acquiring importance in the automobile industry. Bolts, nuts, and other small parts employed in automobile manufacture are plated with it, as are also refrigerator trimmings, locks, and wire products. The cadmium plating is applied by the Schoop metal-spray method (page 358), or by electrodeposition.

Like zinc, cadmium stands above iron in the electropotential series of metals, and is therefore able to protect iron in a manner similar to zinc (page 359), but because its solution tension is lower than that of zinc it is not consumed so rapidly. Cadmium presents a more attractive appearance and retains its luster better than zinc.

MAGNESIUM

Occurrence.—Compounds of magnesium are very abundant and widely distributed. The metal constitutes about 2.1 per cent of the earth's crust; only six elements, silicon, aluminum, iron, calcium, sodium, and potassium, in the order named, exceed it in quantity.[1] Unlike the ore of aluminum, which element magnesium resembles in physical properties, the compounds of magnesium occur in deposits that are not only extensive, but yield an output eminently suitable for the production of the metal.

Of the magnesium minerals, *dolomite* ($CaCO_3 \cdot MgCO_3$), a common rock, is the most abundant. In the United States it is

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[1] GANN, "The Magnesium Industry," *Ind. Eng. Chem.*, **22**, 694, July, 1930.

mined[1] in California, Colorado, Illinois, Ohio, Pennsylvania, and West Virginia; it is found also in great quantity in many foreign countries. *Magnesite* ($MgCO_3$) is mined in Austria, Australia, Czechoslovakia, British India, Greece, Italy, Russia, the United States (California and Washington), and other countries. The double chloride, *carnallite* ($KCl \cdot MgCl_2 \cdot 6H_2O$), is found in the Stassfurt deposits of Germany. Some of the other magnesium minerals are *kieserite* ($MgSO_4 \cdot H_2O$), *kainite* ($MgSO_4 \cdot KCl\ 3H_2O$), and *brucite* ($MgO \cdot H_2O$). The bittern obtained as a by-product in the purification of common salt in many localities, as at Midland, Michigan, is also used as a source of magnesium. The magnesium-salt content of the waters of many inland lakes, notably Great Salt Lake in Utah, is high.

Production of Magnesium.—Metallic magnesium is prepared commercially chiefly by two methods, the chloride and the oxide processes.

Until 1927, metallic magnesium was produced from magnesia obtained by calcining magnesite. The process used was similar to the Hall-Heroult method employed in the metallurgy of aluminum. After dissolving the oxide in a bath consisting of the fused fluorides of magnesium, barium and sodium, the metal was separated by electrolysis. Now, however, the oxide process is no longer used. In both this country and abroad, primary magnesium is obtained by the electrolysis of natural salts. In the United States, magnesium chloride recovered in the purification of sodium chloride derived from salt wells is used.

In the chloride process a melted mixture of the chlorides of sodium, potassium, and magnesium is electrolyzed. The presence of the alkali chlorides is necessary to prevent the decomposition of the magnesium chloride during heating. The electrolysis is carried out in an air-tight iron vessel, the walls of which act as the cathode, with a centrally located graphite anode. As the magnesium is plated out, it rises to the surface and is ladled out.

The metal is refined by remelting it in iron pots and fluxing it with sodium magnesium chloride to remove oxide inclusions. If especially pure magnesium is desired, it is prepared by distillation.

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[1] A better quality of this rock is obtained by mining than by quarrying from surface strata.

Because of the great consumption of electric energy, magnesium, like aluminum, is produced where power is cheap. The American Magnesium Corporation, a subsidiary of the Aluminum Company of America, prepares magnesia by calcining magnesite obtained from the Pacific coast and ships it to their works at Niagara Falls where the metal is produced.

Magnesium is marketed as ingots, sticks, bars, rods, wire, tubes, sheets, ribbon, powder, and in other forms. In 1883, the price of this metal in Europe was about $32 a pound, but in 1902 it had dropped to about $3 a pound. In 1917, the ingot sold in the United States for about $2, but at the present time the price of the 99 per cent pure metal in ingot form ranges from 85 cts. to $1.10 a pound. In Germany it has sold recently as low as 40 cts. a pound, at which price, for some uses, it is able to compete with aluminum.

Physical Properties.—Magnesium is the lightest metal used as an engineering material. The tensile strength of the cast metal is 13,000 lb. per square inch, which is the same as that of ordinary cast aluminum, but when reduction of weight is important, magnesium is preferable because of its low density of 1.74, which is a little less than seven-tenths of that of aluminum. The tensile strength of rolled and annealed magnesium is 25,000 lb. per square inch, about the same as that of a good quality of gray cast iron. Magnesium is harder than aluminum. It has a somewhat greater need for protection than that metal, and on a strength-weight basis its best alloys are only slightly better than duralumin, one of the best of the aluminum alloys.

In casting magnesium and its alloys, special care is necessary because of its tendency to oxidize readily. Also, because of its lightness, it tends to trap gases during casting with the formation of gas flaws. Because of the readiness with which the hot metal reacts with water, when casting in sand, the molds must be dried. Magnesium is readily machined and under the buffing wheel it takes a high polish. It hardens very rapidly with cold working, but it is suitably plastic and workable at 350°C. Magnesium can be welded, but because it combines with oxygen more readily than any other common metal, a special technique is required. Magnesium may be soldered, but the joints must afterward be protected to prevent them from corroding. As compared to copper, the electrical conductivity of magnesium is 38.6 on the basis of volume, and 197.7 on the basis of weight.

Magnesium is a silvery-white metal. It melts at 651°C. (1204°F.) and boils at 1120°C.

Chemical Properties.—Magnesium, when pure, does not corrode in ordinary dry air. In moist air, however, it becomes coated with a film of oxide, which is probably partly hydrated and carbonated. The film adheres well and tends to protect the metal beneath. Although magnesium and its alloys are less resistant to corrosion than aluminum and its alloys, the poor reputation of magnesium in this respect has been due largely to the fact that the metal produced in earlier years was very impure; it not infrequently contained as much as 4 to 6 per cent of occluded salts derived from the fused electrolyte. The trapped chlorides were very bad, so much so that the metal sometimes disintegrated in storage. Substantially pure magnesium has an acceptable corrosion resistance. It may be readily platec with more resistant metals. Lacquers, varnishes, and paints also furnish adequate protection.

In the form of powder or ribbon, magnesium burns readily in air. It does not burn directly to the oxides, however, but is first converted into the nitride, which then burns to the oxide.[1] The light produced by burning magnesium is especially rich in actinic rays, hence its use for flash-light in photographic work. Unless heated to temperatures far above its melting point, magnesium in massive form does not burn readily in air. Magnesium when hot exerts a strong reducing action and serves as a deoxidizing agent for other metals. It is used for this purpose in the metallurgy of both nickel and monel metal, and to some extent for brass, bronze, and nickel silver. It is able to abstract oxygen from carbon dioxide and under suitable conditions will burn in this gas.

Magnesium decomposes boiling water with the evolution of hydrogen. It dissolves freely in dilute hydrochloric, sulfuric, and nitric acids, but it resists hydrofluoric unless the acid is concentrated. It is not affected by alkalies of any concentration, even when hot, but salt solutions attack it, especially if heated,

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[1] Liddell, "Handbook of Non-ferrous Metallurgy," vol. II, p. 769.

with the evolution of hydrogen. In all cases its ability to resist the attack of reagents increases markedly as its purity increases.

Uses.—Magnesium readily forms alloys with most metals (not with iron and chromium), and much of it is consumed in this manner. Its employment in the form of sheets, wire, rods, tubes, etc., is noteworthy, however, and its use for these purposes is very rapidly increasing. The ribbon is now used chiefly for the degasification of radio tubes. Its suitability for this purpose depends upon the fact that the heated metal combines not only with oxygen but with nitrogen. The metals with which it is mostly alloyed are aluminum, zinc, manganese, cadmium, and copper, either as binary alloys or with two or more of them together. The tensile strength of these alloys ranges from 20,000 to 50,000 lb. per square inch, depending partly upon whether they are worked or cast, and since the specific gravity in most cases is well below 1.90, they are eminently suitable for airplane construction. Manganese, which raises the hydrogen overvoltage of the alloy (page 337), increases the corrosion resistance. Approximately 2 per cent of this metal can be alloyed successfully with pure magnesium.[1]

In the powdered form, mixed with an oxidizing agent, such as barium nitrate or potassium chlorate, magnesium is employed in the manufacture of flashlight powder, as has been noted, and in military pyrotechnics for the production of rockets, signals, and flares.

NICKEL

Occurrence and Ores.—In the outer crust of the earth, nickel is comparatively rare, but in the core of the earth it is believed to be plentiful. This belief is based partly on the fact that analyses of meteorites show them to contain nickel second in abundance only to iron. Because meteorites and the earth, as well as the other planets, have a common origin, and because there is some evidence that the core of the earth contains much iron, it seems reasonable to assume that in the earth's central portion nickel also abounds. In the rocky outer layer, nickel is widely distributed being found on every continent, but deposits of

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[1] GANN, "The Magnesium Industry," *Ind. Eng. Chem.*, **22**, 698, July, 1930.

nickel-bearing minerals that are rich enough and plentiful enough to be mined, occur in only a few places.

By far the most important known nickel deposits of the world are those of the Sudbury district of Ontario, Canada, where nickel-bearing iron sulfides containing not over 3 per cent of nickel are found. About 85 per cent of the world's annual production of approximately 40,000 metric tons comes from this source. A considerable amount is also obtained from a hydrated nickel-magnesium silicate found on New Caledonia, a French island lying east of Australia in the south Pacific Ocean. Although imported ores are smelted in the United States, the only nickel now produced in this country from domestic materials is a relatively small quantity in the form of nickel salts recovered during the electrolytic refining of blister copper.

Metallurgy of Nickel.—The details of the smelting process vary, of course, with the nature of the ores, but the general principles involved in the earlier stages are practically identical. The practice is very similar to that described for sulfur-bearing copper ores (page 94); *i.e.*, the ores are roasted to reduce the sulfur content, are then smelted to separate the gangue, and the resulting sulfide matte is bessemerized. The treatment given the New Caledonia ores is interesting. These ores contain no sulfur, and although as a rule the presence of much sulfur complicates a metallurgical process, in this case sulfur, usually in the form of gypsum or iron pyrites, is added to the concentrate prior to smelting. The mixture is then furnaced in much the same way as the Sudbury concentrates.

In the Sudbury district the coarser concentrates are smelted in blast furnaces, and the finer ones at a reverberatory plant. The matte delivered by the smelting furnace is then bessemerized to oxidize the iron. The iron oxide combines with a siliceous flux added for this purpose and enters the slag. The Bessemer matte consists chiefly of copper and nickel sulfides.

Extraction of Nickel from Matte.—There are two principal methods for extracting nickel from the copper-nickel matte. One is the method employed by the International Nickel Company at Port Colborne, Ontario, which is sometimes called the Orford process, and the other is the Mond process used at Clydach, Wales.

In the International Nickel Company's method, the matte is charged into a blast furnace with coke and sodium sulfate, which, by the reducing action of the carbon, is converted into sodium sulfide. The output of the blast furnace is poured into pots and allowed to cool. During solidification the mass separates into two well-defined layers. The upper layer carries the bulk of the sodium and copper sulfides while the bottom layer contains the bulk of the nickel sulfide. The two layers are separated mechanically. The top layer is "blown" in a Bessemer converter to blister copper. The bottom layer, after suitable treatment, is roasted to black nickel oxide, which is then reduced to metallic nickel in an open-hearth furnace. From the melted nickel, pigs, shot, and anodes are produced. The anodes are employed by electroplaters.

In the Mond process employed by the British nickel industry, "nickel bottoms" of the Orford process, shipped from Ontario to Wales, are ground to a fineness sufficient to pass a 60-mesh screen and then are calcined to convert the sulfides to oxides, which in turn are leached with sulfuric acid. The copper oxide is thus converted into copper sulfate, which is recovered and sold as such, while the nickel oxide remains undissolved.

The nickel is recovered from the nickel-oxide residue by an ingenious and interesting method. The oxide, heated to 300°C., is reduced to metallic nickel by hydrogen obtained from water gas (page 67). The reduced metal, after cooling to ordinary room temperature, is by treatment with carbon monoxide converted into nickel carbonyl [$Ni(CO)_4$], a liquid. When a stream of nickel carbonyl vapor is later passed through a tower filled with nickel pellets heated to 180°C., the carbonyl breaks down into nickel and carbon-monoxide gas. The nickel deposits on the pellets and the carbon monoxide is returned to the reaction chamber where the nickel carbonyl is formed. The nickel pellets are withdrawn continually from the bottom of the tower and are recharged at the top. The constant friction of the pellets against each other detaches small particles, which, acting as nuclei, grow into new pellets by accretions of nickel from the carbonyl. Before recharging, the pellets are screened, and only the smaller ones are returned to the tower. Those that are oversize are marketed.

Nickel prepared by the Mond process is about 99.8 per cent pure.

Malleable Nickel.—The form of the metal marketed as malleable nickel is prepared by deoxidizing and recarburizing in a manner very similar to that employed for steel (page 268). The deoxidation is effected by adding manganese, in the form of ferromanganese, followed by magnesium. Only a small quantity of magnesium is employed, and it must not be used in excess. By the use of charcoal, the carbon content is brought to an amount between 0.1 and 0.3 per cent. These additions are made to the metal while in the crucible or ladle just prior to casting. Only that which is sold as malleable nickel is treated in this manner.

Properties and Uses.—Nickel is a silver-white metal capable of taking a high polish. It melts at 1452°C. (2646°F.) Its specific gravity cast is 8.35; when wrought, it may vary from 8.6 to 8.9. It is almost as hard as soft steel; when it contains a small quantity of carbon, it is quite malleable, although it may be satisfactorily rolled with as little as 0.005 per cent of carbon. It is a little less ductile than soft steel, but small amounts of magnesium improve the ductility considerably. Its tensile strength when cast is 38,000 lb. per square inch, but in the worked form it excels soft steel somewhat, ranging from about 76,000 for sheets of annealed nickel to twice that for hard-drawn wire.[1] Nickel may be magnetized, but it loses its magnetism at 340°C.

Nickel is resistant to the attack of most acids, but it dissolves readily in nitric. It is very permanent upon exposure to the atmosphere; it is therefore much used to plate other metals, especially iron and brass. Over half the nickel production of the world is consumed in making nickel steel (page 320). Large quantities are used in other alloys, as monel metal and nickel silver (page 205). It is employed to a less extent in nichrome (nickel and chromium, page 144) and in manganin (nickel, copper, and manganese, page 141) both of which are used for electrical resistance wires. The United States five-cent piece is an alloy containing 25 per cent of nickel and 75 per cent of copper.

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[1] "Physical Properties of Materials," *U. S. Bur. Standards Circ.* 101, 1924.

High manganese nickel wire is practically standard for spark-plug points. The same alloy is used for suspension wires in electric light bulbs and the vacuum tube employed in radio work.[1] It is employed for these purposes principally because of its resistance to oxidation at high temperatures.

Because of its resistance to oxidation at high temperatures, and because of its corrosion resistance, nickel is used extensively for laboratory and plant equipment, such as stills, kettles, pots, and digesters. Burner parts, and parts of glass-making machinery, and annealing furnaces are made of nickel. A noteworthy amount of nickel is consumed by electroplaters in coating iron, copper, brass, and other metals and alloys to improve their appearance and corrosion resistance.

Malleable nickel is produced in many forms, such as hot- and cold-rolled sheets, hot- and cold-drawn rods and wire, seamless and welded tubes, forgings and castings.

A comparatively small amount of finely granular nickel, known as reduced nickel, made by reducing the black nickel oxide at a temperature slightly below the melting point of the metal, is consumed in manufacturing nickel salts. "Active" nickel, prepared by reducing the oxide below 300°C., is used in the hydrogenation reaction for converting fluid oils into solid fats.

COBALT

Occurrence.—Although cobalt has some uses for which it would be difficult to find a substitute equally acceptable, industrially it ranks among the metals of only minor importance. The total production of the world is not large. The chief deposits are those of Ontario, Canada; Katanga, Belgian Congo; and Queensland, Australia. The Katanga supply comes from veins of cobalt, copper, and iron sulfides, the Canadian output from cobalt arsenides and arsenosulfides, while the Australian ore consists of cobalt arsenosulfides. The chief minerals are *cobalt bloom* ($3CoO \cdot As_2O_5 \cdot 8H_2O$), *cobaltite* ($CoAsS$), and *smaltite* ($CoAs_2$). Some of the cobalt on the market is obtained as a by-product from nickel ores.

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[1] "Nickel and Its Alloys," *U. S. Bur. Standards Circ.* 100, 1924.

Properties and Uses.—Cobalt resembles nickel in many of its properties. Its silvery-white color is similar, but it may be distinguished from nickel by its slight bluish cast. It is somewhat harder than nickel, and for this reason would be superior to it for plating other metals, but at present it cannot compete with nickel because of the lower cost of the latter. The tensile strength of cobalt as cast is 35,000 lb. per square inch. Its specific gravity is 8.95, and it melts at 1480°C. (2696°F.). Cobalt is magnetic, but unlike nickel and iron, it retains its magnetism even at a white heat; the point of transition from the magnetic to the non-magnetic variety is 1150°C.

In the ordinary atmosphere, cobalt resists corrosion very well. It dissolves only slowly in all acids except nitric by which it is rapidly attacked.

The chief use of cobalt is in the making of stellite (page 206), a group of alloys consisting essentially of cobalt and chromium. In a high-speed, cutting-tool alloy of phenomenal hardness that has been recently developed, cobalt serves as a cementing material for tungsten carbide (page 206). Stellite and cemented tungsten carbide are not steels, but some of the high-speed steels, as well as some corrosion-resistant steels, contain cobalt. It is employed also in making steel for permanent magnets. The magnetic coercive force of the cobalt steel is from two to five times that of the commonly used tungsten or chromium steels, but because of the relatively high price of cobalt, such steels, compared to others, cost from four to ten times as much.[1]

Cobalt oxide is employed to a considerable extent in the ceramic industry. Glazes and enamels contain it. In enameling iron ware, cobaltic oxide renders exceptional service in causing the enamel to adhere to the metal (page 465). Blue glass is made with the aid of cobaltic oxide.

Cobalt linoleate and tungate (page 502) are very serviceable as driers for paint and varnish oils, especially oil from the soya bean.

The cobalt imported annually for consumption in the United States, as ore, metal, and oxide, does not exceed about 400 long tons.

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[1] Sanford, "Some Principles Governing the Choice and Utilization of Permanent Magnet Steels," *U. S. Bur. Standards Sci. Paper* **567**, p. 557.

MANGANESE

Importance of Manganese.—The steel produced by the Bessemer process at the time of its invention, which was announced to the British Association in 1856, was devoid of malleability. The foundation for the importance of manganese as an industrial metal was established when Bessemer was convinced by Mushet that the toughness of the new steel would be greatly improved by the addition of manganese. At the present time, there is practically no steel made by any process that does not receive the manganese treatment (page 140). The world's total annual production of manganese ore is now between three and four million long tons, and the largest part of it is consumed by the steel-making industry.

Ores.—*Pyrolusite* (MnO_2), which ranges from bluish black to grayish black in color, is the principal manganese ore. Other important ores are *braunite* ($3Mn_2O_3 \cdot MnSiO_3$), *hausmannite* ($2MnO \cdot MnO_2$), *manganite* ($Mn_2O_3 \cdot H_2O$), and *rhodochrosite* ($MnCO_3$).

Producers and Consumers.—Manganese ores are widely distributed, but about 80 per cent of the world's total output is produced by four countries, Russia, India, Brazil, and the Gold Coast of Africa. Other countries producing comparatively small amounts are the United States, Cuba, Italy, China, Chile, and the Dutch East Indies.

Although the United States produces only about 1.5 per cent of the world's total annual output of manganese, it consumes about 18 per cent, the latter percentage being equivalent to 625,000 tons. As an importer of manganese ore, this country has recently been surpassed slightly by France. Other large importers are Germany, Great Britain, Belgium, and Japan.

Production of Metallic Manganese.—As has been stated before, the largest part of all the manganese produced is consumed in the manufacture of steel. For use in this industry (page 269), the manganese is first prepared in the form of two intermediate alloys, ferromanganese and spiegeleisen. Ferromanganese contains from 75 to 81 per cent manganese, from 5 to 6 per cent carbon, and the remainder chiefly iron. Similarly, spiegeleisen is an iron alloy containing from 15 to 20 per cent manganese, and about 5 per cent carbon. Both alloys are manufactured by smelting the ore in a blast furnace of the same type as that employed in the production of pig iron (page 221).

For spiegeleisen the furnace practice is almost the same as in the iron industry, but for ferromanganese the furnace is burdened in a somewhat different manner. Because the manganese oxide has a tendency to enter the slag, a higher proportion of limestone is employed in the charge than is used in the smelting of iron ore. The slag is thus made more "limey" or basic, and manganous silicate is less likely to form. Because the manganese ore is more refractory than iron ore, a higher coke ratio also is maintained than in the production of pig iron. At the high temperature required for smelting the ore, manganese shows a marked volatility. A loss of as much as 15 per cent of the metal may result from this cause.

By the thermit process (page 91) metallic manganese may be obtained almost entirely pure. The absence of carbon in manganese so obtained is a point worthy of comment. By using this purer variety, high-manganese steel may be manufactured that is much softer and far more workable than that made from the alloy reduced by carbon.

By a patented process, ferromanganese produced in a blast furnace may also be decarbonized by treatment with manganese dioxide in an electric furnace. In this method the carbon content may be reduced from 5 or 6 to less than 1 per cent.

Properties and Uses.—Manganese is hard, steel-gray, and brittle. Because it lacks malleability and toughness, it is not employed in constructional work, except in the form of alloys. The pure metal has a specific gravity of 7.39, and melts at 1260°C. (2300°F.).

Upon exposure to the atmosphere, manganese oxidizes in a manner similar to iron, but more readily. It dissolves freely in the common mineral acids, even when dilute, with the formation of manganous salts. It is soluble in acetic acid. It reacts with boiling water to produce the hydrated manganous oxide and hydrogen. If the metal contains the carbide Mn_3C, when moistened with water, methane and hydrogen are produced.

The extensive use of manganese in the manufacture of iron and steel is due to the readiness with which it can transpose the ferrous oxide and sulfide into the corresponding manganous compounds. The resulting manganous compounds are only slightly soluble in the melted metal, and are, therefore, carried away by the slag.

Among the common non-ferrous alloys of manganese are manganese bronze, manganin, nickel-silver, and manganese brass. Manganese bronze contains on an average 16 to 17 per cent of manganese in copper. Manganin, which contains 12 to 15 per cent manganese, about 4 per cent of nickel, and the remainder copper, is used for electrical resistance. With a small per cent of manganese, nickel silver is harder and tougher than the usual variety (page 205). Manganese brass is described on page 188.

In the form of the oxide, manganese is employed as a coloring agent in the ceramic industry and for the purpose of discharging the color produced by iron in the manufacture of glass. The dioxide is used as a depolarizing agent in the manufacture of Leclanché and dry cells (pages 633 and 636).

CHROMIUM

Occurrence.—Chromium is obtained from the ore *chromite* ($FeO \cdot Cr_2O_3$), which is known also as chrome iron ore. *Crocoite* ($PbCrO_4$), *chrome ocher* (Cr_2O_3), and other chromium-bearing minerals are found occasionally, but chromite is the only one that is used commercially. At the present time the largest part of the world's supply of chromite comes from southern Rhodesia in south-west Africa. New Caledonia, Cuba, India, and Russia also produce noteworthy amounts. Extensive deposits are known in northern Asia Minor, but they are not now being worked.

Treatment of Chromite.—The uses for chromium ore may be classified broadly under four general heads: (1) as a refractory material, (2) for the manufacture of chromium compounds, (3) for the production of ferrochrome, an alloy employed in the manufacture of iron and steel, and (4) for reduction to metallic chromium. The treatment the ore receives depends, of course, upon the finished product desired.

For use as a refractory material, after suitable concentration, the ore is mixed with a little lime and made into bricks. For furnace linings in the steel industry no equally satisfactory substitute for chromite is known. Its properties as a refractory material are described on page 79, which see.

Among the chromium compounds, the chromates of sodium and potassium, and chromic oxide are important. In the production of the chromates, the ore is roasted with sodium or potassium carbonate in the presence of air. The reaction may be represented as follows:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

If the bichromate is desired, it is prepared by treating the chromate with sulfuric acid, thus:

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$$

Because the sulfate has the lower solubility, it crystallizes first from the solution. The bichromate is recovered from the remaining liquid.

Chromic oxide is obtained by heating sodium bichromate with sulfur in an iron vessel. The following reaction occurs:

$$Na_2Cr_2O_7 + S \rightarrow Na_2SO_4 + Cr_2O_3$$

Chromic oxide formed in this way is green, and having been ignited is insoluble in water. It may be employed in the production of metallic chromium by the thermit process. Chromium trioxide (CrO_3) in the form of red crystals, which dissolve readily in water, may be formed by treating dry sodium chromate with concentrated sulfuric acid. The following reaction takes place:

$$Na_2CrO_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2CrO_4$$

The concentrated sulfuric acid immediately dehydrates the chromic acid with the formation of chromium trioxide which precipitates. When this oxide is dissolved in water, it rehydrates and again forms chromic acid. A large amount of chromic acid is consumed by the chromium electroplating industry (page 144).

In the production of ferrochrome, an alloy of iron and chromium, containing 60 per cent of chromium or more, the ore is reduced with carbon in an electric furnace. The theoretical reaction may be represented as follows:

$$FeO{\cdot}Cr_2O_3 + 4C \rightarrow Fe + 2Cr + 4CO$$

Because metallic chromium combines readily with carbon, however, a considerable amount of it does not appear in the metallic form as called for by the equation, but in the form of chromium carbide (Cr_3C). In the steel industry, ferrochrome with a high-carbon content is not desired. The quality and price of the alloy, therefore, is inversely proportional to the carbon content. By treatment with chromite under a basic slag, ferrochrome may be largely decarbonized (*cf.* Ferromanganese). Another method sometimes employed for the production of low-carbon ferrochrome is the thermit reaction (page 91).

Metallic chromium also is produced from chromic oxide by the thermit process, as follows:

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

Chromium that is 99.5 per cent pure is obtained by this method; it contains some aluminum.

Properties of Metallic Chromium.—Chromium is a bluish-white metal, harder than glass. When polished it presents a brilliant, platinum-like luster which it retains indefinitely. The ordinary form of the metal is brittle, but electrolytically deposited chromium, although hard, is malleable. It has a specific gravity of 7.1, melts at 1615°C. (2939°F.),[1] and boils at 2200°C. (3992°F.). In casting chromium, it is necessary to heat it to a temperature several hundred degrees above its melting point. Like aluminum, copper, and iron, it does not flow freely when heated to just above its melting temperature.

Chromium is not attacked by atmospheric oxygen at ordinary temperatures, but at high temperatures it burns to the green trioxide, Cr_2O_3. It dissolves slowly in cold hydrochloric acid, but rapidly in the hot acid. In cold, dilute sulfuric acid it dissolves only slowly also, but in the hot, concentrated acid it dissolves rapidly with the evolution of sulfur dioxide. It is slowly attacked by cold, dilute nitric acid, but hot concentrated nitric acid does not affect it. Concentrated nitric acid renders it passive (page 340). When in the passive state it does not dissolve in its ordinary solvents, hydrochloric acid, for example.

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[1] LATIMER and HILDEBRAND, "Reference Book of Inorganic Chemistry," p. 277.

Chromium is made passive also by chromic acid and by exposure to air. The fact that air makes it passive accounts largely for its outstanding success as a plating.

Uses of Chromium.—Almost half of the chromium output is produced in the form of ferrochrome, which is employed chiefly in the manufacture of alloy steels (page 321). Chromium is used in steel because it imparts not only hardness but toughness, a combined effect that is unusual. Of no less importance is the fact that chromium has a marked effect in increasing the resistance of steel to corrosion. Much of the rustless iron and rustless steel now on the market contains chromium. In the use of this metal lies perhaps the solution of the age-old problem of the production of a cheap, workable, low-carbon steel that will indefinitely withstand corrosion. At the present time unsolved metallurgical difficulties render the process too costly.

Nichrome is an alloy of chromium and nickel; sometimes it contains iron. The composition of the following alloys is representative: (1) chromium 20 per cent, nickel 80 per cent; (2) chromium 15 per cent, nickel 60 per cent, iron 25 per cent. These alloys, known also by the trade name of "chromel," have a high electrical resistance, and do not oxidize materially when hot. They are employed in the winding of electric resistances and heating units.

Chromium is also a component of stellite (page 206).

Electroplating with Chromium.—The brilliant, platinum-like finish which may be imparted to chromium, and the passivity of the metal in air render it suitable as a decorative and protective coating for other metals. Its employment for this purpose, particularly in the automobile industry, has recently attracted a great deal of attention.

In electroplating with chromium, the electrolyte consists of a solution of chromic acid (H_2CrO_4) to which chromic sulfate [$Cr_2(SO_4)_3$], and other salts, such as the borate and phosphate, have been added. Chromium sulfate especially has a very beneficial effect. The percentage of chromic acid employed in the electrolyte varies considerably, but 25 per cent may be considered to be a representative concentration. The amount of the sulfate present will probably not greatly exceed one hundredth of the amount of the chromic acid, but according to Keeney,[1] it is apparently necessary to have chromium present in two valences in the electrolyte in order to secure good results.

In producing the deposit a very high current density is employed; it generally ranges from 100 to 125 amp. per square foot. If a very low current density is used, no chromium whatever is deposited; the electron stream merely changes the hexavalent chromium to trivalent chromium. With the high current density that is employed, in addition to the deposition of chromium, hydrogen is evolved freely at the cathode. Lead anodes are used but only a little lead dissolves.

Due to the conditions under which it is deposited, chromium plate is porous. When used alone it is not a good protection against corrosion. According to Schneidewind,[2] this is not surprising when it is considered that the best plate for decorative purposes is put on in about 3 min. and is only 2/100,000 in. thick. He states further that the average plate in many job shops is applied in 30 to 40 sec. and is only 2/1,000,000 in. thick. The reason given by Schneidewind for not applying a heavier coating is that a heavier plate not only greatly increases the cost but also defeats its own purpose because a system of fine cracks and other imperfections develops through which corrosion sets in.

Chromium can be deposited directly upon copper, brass, nickel, cobalt, steel, and most other metals, but due to the fact that the usual decorative chromium plate is not a sufficient protection for iron and steel and because of their tendency to corrode, these metals are first plated with copper and then with nickel, prior to the application of the chromium. In order to secure the brilliance desired in the finished plate, the base metal is polished to a high luster before it is placed in the chromium plating bath.

In commenting upon the abrasion resistance of chromium plate, Schneidewind states[3] that, although chromium itself, if applied in a heavy layer on a hard backing, is so hard that only the diamond or carborundum will affect it, decorative chromium plate is not hard. This lack of hardness results from the fact that the layer

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[1] Liddell, "Handbook of Non-ferrous Metallurgy," vol. II, p. 1261, footnote.

[2] "Commercial Chromium Plating," Dept. Engineering Research, Univ. Mich., *Circ. Ser.* 3, p. 9, January, 1930.

[3] *Loc. cit.*, p. 10.

is so very thin and is usually applied over comparatively soft metals. Usually, decorative chromium plate may be easily punctured or scratched.

One of the chief virtues of chromium plate lies in the fact that it does not tarnish or show spots, even in rainy weather. In view of its superior qualities in this respect, the slightly higher cost as compared to nickel plate is of little consequence.

To preclude any possibility of peeling, to which all plated ware is subject, in some instances "stainless" steel (page 322) is employed for bright work. This alloy, however, seems to show a reddish tinge and is slightly darker than the bluish-white chromium plate.

TUNGSTEN

Occurrence.—About half of the tungsten supply of the world is produced by China. Most of the ore apparently comes from Kiang-si and neighboring southeastern provinces. Little is known definitely about the character and extent of these deposits; very few white men have even seen the larger part of them, and no authoritative reports are known to have been issued. All that can be said with certainty is that China produces annually from 5,000 to 8,000 short tons of tungsten ore carrying from 65 to 70 per cent of tungstic oxide (WO_3).[1]

As a producer of tungsten, Burma is next in importance to China. The United States ranks third. Here the chief states are California, Colorado, South Dakota, and Nevada. The output of the United States is not large, probably 1,000 to 1,400 tons, caculated on the basis of a 60 per cent tungstic-oxide content. About twice as much is imported as is mined. Mining of tungsten ore in this country is possible at all only because of an extremely high duty on imports, the highest duty ever placed by the United States Government on a raw material.[2] Comparatively small quantities of tungsten ore are produced also by the Malay States, Portugal, and Bolivia.

Ores.—The most important tungsten ore is a ferrous-manganous tungstate called *wolframite* ($FeMnWO_4$). The ratio of iron

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[1] HESS, "Mineral Resources of the United States," pt. I, p. 427, U. S. Geol. Survey, 1927.

[2] HESS, *loc. cit.*, p. 435.

to manganese varies, and depending upon this fact the ore is called by various names. The high iron and low manganese ore, for example, is known as *ferberite.* Calcium tungstate, called *scheelite* ($CaWO_4$), is also an important source of the metal. Other minerals are the lead and copper tungstates, and the trioxide called *wolfram ocher* (WO_3).

Ferrotungsten.—From a tonnage standpoint the main use of tungsten is in the manufacture of steel, especially steel for tools employed at high cutting rates. For the manufacture of this steel either ferrotungsten or tungsten powder may be used.

In the production of ferrotungsten, the process is similar to that described for ferromolybdenum (page 150). If the ore is ferberite, no preliminary treatment other than concentration is necessary. The ore is reduced by carbon with the addition of a small amount of lime and fluorspar to flux the silica. The reduction proceeds readily. The product contains about 70 per cent tungsten, about 3 per cent carbon, and the remainder iron.

Metallic Tungsten.—In producing tungsten metal, the finely divided ore is first fused with sodium carbonate. The resulting sodium tungstate (Na_2WO_4) is extracted from the fused mass by means of hot water, and the solution after filtering is run into hot hydrochloric acid, by which tungstic acid (H_2WO_4) is precipitated. Upon ignition, the acid yields tungsten oxide (WO_3). The oxide is generally reduced by carbon. The reaction may be carried out in a closed steel tube or in a covered steel or fire-clay crucible. The temperature employed is about 1100°C. Because the temperature used is much below the melting point of tungsten, the metal is secured in the form of fine granules or powder. Metallic aluminum, zinc, and magnesium are also employed for the reduction of tungstic oxide, but the purest metal is obtained by reducing the carefully purified oxide in a current of hydrogen.

The reduction of the oxide to the granular form, rather than to a melted metal, is a virtual necessity. It is not practicable to produce a temperature high enough to melt tungsten (3370°C.); and besides, the metal becomes brittle when cast. The earlier metallurgists working with tungsten found it a very difficult problem to produce a workable mass of this metal. After long experimentation it was found that the most feasible method for compacting the granules was to work them mechanically while very hot. For this purpose, the finely divided metal is placed in steel dies and is pressed in a hydraulic press. The granules of the resulting bar are then caused to coalesce by placing the bar in an atmosphere of hydrogen and heating it by means of its resistance to the flow of an electric current. Toward the close of the process the temperature is raised to a point not far below the melting point of tungsten. As a result, the particles are joined and a definite crystalline structure is developed. By means of repeated heating and swaging or hammering, the sintered bar is worked into a slender rod. Although at first the bar is very brittle and weak, with repeated working, the strength and toughness increase so much that it may be drawn through dies to form wire. For very fine wire, such as required for lamp filaments, a series of as many as a hundred dies formed of diamonds, each with an aperture slightly smaller than the one preceding, are employed. If sheet or plate is desired, the bar is rough-forged under the hammer, and then is reduced to the specified gage by means of high-speed rolls.

Properties of Tungsten.—In the form of fine-drawn wire, tungsten possesses the highest tensile strength of any known material, 590,000 lb. per square inch.[1] With the exception of carbon, it has the highest melting point of all substances, 3370°C. (6098°F.). It retains its rigidity at higher temperatures than any other metal and exhibits the lowest vapor pressure.[2] At a yellow heat, tungsten may be welded. The metal is silvery white in color, and in the wrought form has a specific gravity of 19.3.

In air, tungsten oxidizes at a red heat. Melted sulfur attacks it slowly. It is affected very little by hot, dilute sulfuric acid, but the hot, concentrated acid attacks it slowly. Hot, concentrated hydrochloric acid also dissolves tungsten slowly, but the cold acid, both dilute and concentrated, is practically without action upon it. Concentrated nitric and hydrofluoric acids have

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[1] LATIMER and HILDEBRAND, "Reference Book of Inorganic Chemistry," p. 277.

[2] BALKE, "Metals of the Tungsten and Tantalum Groups," *Ind. Eng. Chem.*, **21**, 1002, September, 1929.

little affect on tungsten, but a mixture of the two attack it with moderate vigor.[1]

Economic Value of Tungsten.[2]—No other metal produced in such small quantity has so great an industrial importance as tungsten. Because of the convenience, comforts, and luxuries it provides to the present type of civilization, its importance is comparable to that of lead and zinc, and is exceeded only by that of iron and copper.

As has been indicated before, the two main uses for tungsten are in the manufacture of high-speed tools (pages 318 and 327), and filaments for lamps. It is estimated that the substitution of tungsten-bearing tools for carbon-steel tools and of tungsten-filament lamps for carbon-filament lamps saves the people of the United States not less than two and a half to three billions of dollars each year. Not counting an import duty of 200 per cent, which amounts to about one and a half million dollars, paid to the government, this saving is effected by an expenditure for tungsten, valued at the world's price, of approximately three-quarters of a million dollars.

The enormous saving that is brought about by the use of tungsten-alloy tools is made possible by the fact that one man is able to perform the work of several men in the turning, planing, and boring operations required in the fabrication of articles produced by the metal-working industries. Not only is less time and labor involved, but the mechanical equipment and the space needed to house it is less.

The economy in the use of tungsten filament lamps rests upon the fact that they require only 1.25 watts per candlepower, instead of the 3.25 watts consumed by the older type of lamp in furnishing the same illumination. It has been calculated that if the artificial light used in the United States in 1927 had been produced by carbon-filament lamps, an additional expenditure of two billion dollars would have been required. That tungsten is able to replace carbon in this efficient manner depends not only upon its high melting point, but upon its rigidity at

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[1] LIDDELL, "Handbook of Non-ferrous Metallurgy," vol. II, p. 1332.

[2] The facts and figures given under this topic are taken largely from the presentation of the subject by Frank L. Hess in "Mineral Resources of the United States," pt. I, p. 434, U. S. Geol. Survey, 1927.

high temperatures, its low vapor pressure, and its relatively high electrical resistance.

In addition to their admirable performance in the lighting field, tungsten filaments demonstrate their usefulness in radio tubes and *x*-ray tubes. When employed in the latter, such filaments make possible the generation of rays so penetrating that almost instantaneous *x*-ray photographs of the body can be taken. Moreover, by the use of these rays, a new science has been developed, that of the study of atomic and crystal structure, as well as the inspection of the interior of metals. In steel, for example, segregation, gas flaws, shrinkage flaws, slag and oxide inclusions and other faults may be detected without physical alteration of the specimen.

The one other purpose for which tungsten in the pure state finds extensive application is the making of the electrical contact points used in the ignition systems of internal-combustion engines. For this purpose it has almost completely replaced platinum and at a tremendous saving in cost.[1]

Important alloys of tungsten are discussed on pages 206, 326, and 327.

MOLYBDENUM

Occurrence.—The chief molybdenum ore is the sulfide, *molybdenite* (MoS_2). It is a soft, opaque, dark-gray, graphite-like or mica-like mineral. It occurs in flakes which cleave readily. *Molybdite* ($Fe_2O_3 \cdot 3MoO_3 \cdot 7\frac{1}{2}H_2O$) is a decomposition product produced by the weathering of molybdenite. *Wulfenite* ($PbMoO_4$) is also an important source of molybdenum.

Molybdenum ores are widely distributed in the United States, but the chief deposits occur in Colorado, New Mexico, and Arizona. At present the molybdenum output of the United States is much in excess of its consumption, and a large amount of concentrated ore is exported, particularly to Europe. Other countries that are important producers are Norway, Victoria (Australia), Chosen (Korea), and Austria.

Ferromolybdenum.—The chief use of molybdenum is in the manufacture of molybdenum steel. For this purpose the metal

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[1] BALKE, *loc. cit.*, p. 1005.

is supplied in the form of ferromolybdenum, an iron-molybdenum alloy, containing as much as 80 per cent of molybdenum. In preparing this alloy from molybdenite, the ore is concentrated by means of flotation (page 95) and the concentrate is reduced by carbon in the electric furnace in the presence of a lime-fluorspar flux. The lime is necessary for the removal of the sulfur as calcium sulfide, and the fluorspar is required to thin the slag. The reaction for the molybdenite is represented as follows:

$$2MoS_2 + 2CaO + 3C \rightarrow 2Mo + 2CaS + 2CO + CS_2$$

The iron in the alloy is derived from iron compounds mixed with the ore. Ferromolybdenum contains from 1½ to 3 per cent of carbon, which it absorbs from the reducing agent.

Metallic Molybdenum.—Almost pure molybdenum may be prepared by roasting molybdenite, and reducing the resulting oxide with aluminum in the thermit reaction. It may be secured also by reducing the oxide or chloride with pure, dry hydrogen.

Metallic molybdenum has a silvery-white luster. It is hard, but not hard enough to scratch glass. When hot it is malleable and ductile. It may be forged and welded, but it is difficult to form it into wire. Like iron it takes up carbon when hot and can be tempered. It has a specific gravity of 10.2, melts at 2620°C. (4748°F.), and boils at 3700°C.

Uses of Molybdenum.—The chief use of molybdenum is in the manufacture of alloy steels. It is employed in steel for the purpose of increasing the elastic limit without decreasing the ductility. It is rarely used for this purpose alone, but in conjunction with chromium or nickel or both. It may serve also as a partial replacement of tungsten in tool steels for high-speed lathes. Molybdenum is employed in cast iron with a beneficial effect that is said to be greater than that produced by its use in steel.[1]

Molybdenum finds application as hook wire to support the tungsten filaments in incandescent lamps, radio tubes, *x*-ray tubes, and the like. In radio tubes it is used also to form both the plate and the grid wire.

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[1] "Mineral Resources of the United States," pt. I, p. 401, U. S. Geol. Survey, 1927.

TITANIUM

Occurrence.—Titanium occurs in the earth more commonly than may be supposed. Among the elements it ranks tenth in order of abundance. The black, iron-bearing *ilmenite* ($FeTiO_3$) is the chief commercial source of titanium, but *rutile,* the dioxide TiO_2, also is frequently found. Other mineral forms of the dioxide are known as *brookite* and *anatase.* Workable deposits of both ilmenite and rutile, especially the former, occur in many parts of the world. The annual production of ilmenite in all countries combined is now probably in excess of 25,000 metric tons, with an estimated content of titanium dioxide ranging from 35 to 55 per cent. The chief contributors are the United States, Senegal, India, Norway, Brazil, and Canada. The domestic production is supplied chiefly by Virginia and Florida.

Metallic Titanium.—Because of the readiness with which titanium forms carbides, nitrides, and silicides at high temperature, it is difficult to prepare the metal in a free state. It is possible to reduce the oxide by means of aluminum, but a little of the aluminum enters into an alloy with the titanium. Like many other metals, titanium is steel-gray in color. It is comparatively hard, but is sufficiently malleable that it may be worked at a red heat. It has a density of 4.5 and melts *in vacuo* at 1800°C. (3272°F.).

When titanium is heated in the air it burns with a very brilliant incandescence; the dioxide is formed. It is one of the few metals that combine directly with nitrogen when heated in it. It decomposes boiling water with the evolution of hydrogen, and it dissolves in hydrochloric and sulfuric acids in the usual manner.

Industrial Applications.—When industrial applications of titanium were first made it was used in the form of ferrotitanium as a deoxidizing agent in the manufacture of steel but now attention is directed chiefly to its employment in the form of the dioxide as a white pigment (page 474). Because the pigment is chemically very inert, in addition to its use in paints, lacquers and enamels, it is employed in printing ink, rubber, oil cloth, linoleum, wall paper, window shades, etc.

VANADIUM

Occurrence and Ores.—The largest and richest vanadium deposit known occurs at Minasragra, Peru. The ore found there, called *patronite*, has a composition that may be represented approximately by V_2S_9. It occurs in conjunction with iron pyrite, free sulfur, and carbonaceous matter. The presence of the carbonaceous matter is interesting. It may be associated with the fact that the ashes of some Peruvian coals are almost half made up of vanadium pentoxide, and that about 1 per cent of the vanadium output of Peru is derived from the ash of a native asphaltite.

The countries next in order in the production of vanadium are Southwest Africa mandate, United States, and northern Rhodesia. Together their output is roughly equal to that of Peru. The chief African ores are *descloizite* [$Pb, Zn(VO_3)_2$], a lead-zinc vanadate, and *vanadinite* ($Pb_5(VO_4)Cl$), a lead-chlor vanadate. In the United States *roscoelite*, a vanadium mica of complex and somewhat indefinite composition, approximately represented by the formula $H_8K_2(MgFe)(AlV)_4(SiO_3)_{12}$, and *vanoxite*, a hydrous vanadium oxide, are found in Colorado, while *carnotite*, a potassium uranyl vanadate ($K_2O \cdot 2VO_3 \cdot V_2O_5 \cdot 3H_2O$) is mined in both Colorado and Utah. Commercially, roscoelite is second in importance to patronite as a source of vanadium.

The United States produces only a comparatively small amount of the vanadium consumed here; the remainder is imported mainly from Peru.

Ferrovanadium.—The chief use of vanadium is in the manufacture of vanadium steel. For this purpose an alloy, ferrovanadium, containing 30 to 40 per cent of vanadium, less than 0.5 per cent carbon, and small quantities of other elements, in addition to the iron, is used. Formerly, the ferrovanadium was almost entirely prepared by reducing the oxide in the presence of iron turnings by the use of aluminum or silicon, a modification of the thermit process, but recently a method has been developed for electric-furnace reduction with carbon. In the new process, the mixture of ore and flux is fed through a zone of extremely high temperature between closely spaced, graphite electrodes. The pentoxide is reduced directly to the metal and the use of the costly reducing agents, aluminum and silicon, is avoided.

Metallic Vanadium.—The preparation of pure vanadium is difficult, and very little is produced commercially. For obtaining the metal, acceptable methods are the reduction of the dichloride with hydrogen, and the electrolysis of vanadium trioxide in fused calcium vanadate.[1]

Vanadium is silvery white in color, is harder than quartz, but is sufficiently malleable and tough that, when heated to a suitable temperature, it may be rolled and hammered into rods, and drawn into wire. It has a density of 5.9, melts *in vacuo* at 1710°C. (3110°F.), and is non-magnetic. The metal is susceptible to a high polish and does not tarnish in air.

When heated rapidly in a stream of oxygen, vanadium burns brilliantly. When burning in air, it combines not only with oxygen but with nitrogen; a mononitride is formed.

Vanadium is insoluble in hydrochloric acid or in solutions of the alkalies. It is slowly attacked by concentrated sulfuric acid, but is readily soluble in nitric acid, both dilute and concentrated.

Uses of Vanadium.—As has been indicated before, the chief use of vanadium is in the manufacture of alloy steels (page 323). Non-ferrous alloys of vanadium are those of copper and aluminum, from which excellent castings may be made.

One of the new applications of vanadium is its use in the form of the pentoxide, instead of platinum, as a catalyst in the manufacture of sulfuric acid. Unlike platinum, vanadium pentoxide is not poisoned by arsenic and hydrochloric acid. The pentoxide serves to catalyze reactions other than the conversion of sulfur dioxide to the trioxide, and compounds of vanadium other than the pentoxide may be employed.

Vanadium resinate has proved to be a superior drier for paint and varnish oils (page 505).

BISMUTH

Occurrence.—The largest part of the world's supply of bismuth comes from Germany, Bohemia, Bolivia, United States, China, and Australia. Like antimony, it occurs in the metallic condition

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[1] LIDDELL, *loc. cit.*, p. 1321.

in nature, and deposits of the native metal contribute a noteworthy portion of the total output, but the oxide, *bismuth ocher* (Bi_2O_3), and the sulfide, *bismuth glance* or *bismuthite* (Bi_2S_3), are also of commercial importance. Bismuth ores are seldom found pure, but generally are associated with the ores of other metals. A considerable part of the bismuth on the market, in fact, is obtained as a by-product in the refining of other metals, such as lead, copper, and tin.

Production of Bismuth.—Native bismuth is separated from the gangue by heating the ore in cast-iron pipes set in the fire in an inclined position. The melted metal is collected as it drains from the lower end of the pipe.

Oxide ores are reduced with carbon in crucibles, or in small reverberatory furnaces, in the presence of a flux that will convert the gangue into a readily fusible slag. Metallic iron is employed in the charge to transpose the relatively small amount of bismuth sulfide that may be present into metallic bismuth and sulfide of iron. Sulfide ores are first roasted to the oxide and are then reduced in the same manner as the native oxides.

The crude bismuth is sometimes refined by heating at a carefully controlled temperature on a sloping iron hearth. The bismuth, having a low melting point, drains away. Melting in the presence of fluxes gives better results. A purer product is prepared by dissolving the crude bismuth in nitric acid, and then precipitating the basic nitrate with water, thus:

$$Bi(NO_3)_3 + 2H_2O \rightarrow Bi(OH)_2NO_3 + 2HNO_3$$

The insoluble basic nitrate is collected, dried, calcined to the oxide, and then is reduced with carbon.

Physical Properties.—Bismuth, like antimony is hard, highly crystalline, and brittle. It may be distinguished from antimony by the fact that the crystals of bismuth have a reddish sheen. It melts at 271°C. (520°F.), and volatilizes at about 1700°C. The specific gravity of solid bismuth is given as 9.82, and that of the melted metal as 10.055. On solidification, therefore, it expands a little over 2 per cent.

Chemical Properties.—By dry air at ordinary temperatures bismuth is practically unaffected, but in moist air it oxidizes slightly and becomes iridescent. When heated in air, it burns to the trioxide Bi_2O_3. At a red heat it decomposes steam with the liberation of hydrogen. It unites directly with the halogens. It dissolves tardily in hot hydrochloric acid, but hot sulfuric acid converts it readily into the sulfate $Bi_2(SO_4)_3$ with the evolution of sulfur dioxide. In nitric acid and in aqua regia it dissolves readily; the former produces the nitrate $Bi(NO_3)_3$, and the latter the trichloride $BiCl_3$.

Uses.—Bismuth is employed chiefly in the preparation of low-melting point alloys, of which there are in the main two varieties: those that contain bismuth, lead, and tin; and those that contain cadmium in addition to the preceding. The lowest-melting alloy has the following composition: bismuth 50 per cent, lead 25 per cent, and tin and cadmium each 12.5 per cent. It melts at 55.5°C. By varying the composition, almost any desired melting point may be obtained. Fusible alloys of this sort are employed in making electric fuses, safety plugs in boilers, sprinkler heads in automatic sprinkling devices, connecting links to hold in place automatic fire doors, etc.

Because of its expansion when solidifying, bismuth is useful in cast alloys that are required to take sharply the impressions of the mold. It is less employed than antimony for this purpose, however, because bismuth is more costly.

ANTIMONY

Ores and Occurrence.—Occasionally, in small quantities, antimony is found free in nature, but the chief ore is *stibnite*, the black trisulfide (Sb_2S_3), of which a plentiful supply is found in China, and notable quantities in Bolivia, Mexico, Algeria, and Czechoslovakia. China contributes approximately 90 per cent of the world's total output of antimony, and about 95 per cent of its production comes from the province of Hu-nan, where the largest known deposits of the world occur. Because of low labor charges and its large deposits of ore, China easily dominates the world's antimony market. The world's total production of antimony is roughly 30,000 short tons annually, and about 50 per cent of it is consumed in the United States.

Metallurgy.—There are several methods for extracting antimony from its ores, but in China the usual process consists of roasting the stibnite to the oxide, and then reducing the oxide with carbon. In other countries the trisulfide is heated with scrap iron which precipitates metallic antimony, as follows:

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS$$

To a small extent, antimony is obtained as a by-product in the refining of other metals, such as lead, copper, zinc, and silver.

Properties.—Antimony is silvery white, hard, highly crystalline, and so brittle that it may be readily powdered under the hammer. It has a specific gravity of 6.62, melts at 630°C. (1166°F.), and volatilizes at about 1600°C.

At ordinary temperatures antimony is chemically stable and does not tarnish in air, but when heated it burns with a bluish flame, forming the white, powdery antimony trioxide (Sb_2O_3).

In cold, dilute sulfuric acid, antimony is unaffected, but it dissolves in the hot concentrated acid. If finely divided, it is attacked by hydrochloric acid. Concentrated nitric acid converts it into the trioxide. In aqua regia it dissolves readily with the formation of the pentachloride.

Uses.—Antimony readily forms alloys with most of the heavy metals and in its metallic form it has few other uses. Hardness is its chief contribution to such alloys in most cases, but because it considerably increases the fluidity, advantage is taken of this property in preparing alloys to be cast with sharp detail, especially in type alloys. The metals with which antimony is most commonly alloyed are lead, tin, and copper.

About 90 per cent of the antimony consumed in the United States is employed for the following uses, which are named in the order of decreasing magnitude of consumption: babbitt alloy (page 209), storage-battery plates (page 642), soft metal alloys and solder, hard lead (for pipes, traps, etc.), type alloys, for vulcanizing rubber (in the form of the pentasulfide), bearing alloys, as oxide and sulfide in enamels for metalware, and in cable coverings. The antimony employed in storage-battery plates serves to make them more rigid and less likely to buckle. About 90 per cent of the antimony employed for this purpose is recovered.

Antimony is an important war metal. It is employed for hardening shrapnel bullets, in primers, and to produce white smoke for range finding.

Antimony is a component of many low-melting-point alloys, such as fuse blocks for indicating heated bearings.

MERCURY

Occurrence.—The largest mercury mine in the world is in Spain, the government-owned Almadén mine in the province of Ciudad Real. In Italy are several important mines, government owned in one district, the combined output of which in some years exceeds that of the Almadén, but regardless of which surpasses the other, these two countries together supply approximately 90 per cent of the world's total annual production of 3,500 to 4,000 metric tons of the metal.[1] In mercury output, the United States ranks third and Mexico fourth. California and Oregon are the chief producers in the United States, but in this country the imports of mercury are about twice as great as the domestic production.

Occasionally mercury is found free, and in amalgams of gold and silver, but most of the world's supply is obtained from *cinnabar*, the red sulfide HgS.

Production.—Mercury is extracted from cinnabar by roasting the ore in the presence of air, usually in some type of shaft furnace. The fuel, charcoal or coke, is charged with the ore. The sulfur is oxidized and the mercury is set free in accordance with the following equation:

$$HgS + O_2 \rightarrow Hg + SO_2$$

At the temperature of the reaction zone, any mercuric oxide produced would instantly be decomposed. The free mercury, vaporizing, passes from the furnace with the products of combustion and is recovered in a condensing system made up of brick chambers and long strings of tile pipe. Periodically the condensers are cleaned and the mercury is separated from the dust and soot by pressing it through linen or chamois skin. The metal may be purified by washing with nitric acid or by redistillation in the presence of air, which causes the vapors of volatile base metals, such as zinc and cadmium, to be converted into their oxides.

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[1] It is the custom to market mercury in iron flasks of 75-lb. capacity tightly closed with a threaded cover.

Properties.—Mercury is the only metal liquid at ordinary temperatures. Cæsium approaches it with a melting point of 26°C. Mercury melts at −38.9°C. (−38.0°F.) and boils at 357°C. Even at ordinary temperatures it has a noticeable vapor pressure. When gold leaf is suspended above the metal, its surface becomes coated with mercury in time. In the liquid and solid forms, mercury is an excellent conductor of electricity. The vapor is not conductive in the cold, but once an arc is struck, the current flows readily, producing the characteristic mercury spectrum, rich in green and ultraviolet rays. Mercury-vapor arc lights, among other uses, are employed in photographic work, in sterilizing water, and in connection with neon lights in illuminated-sign construction. The specific gravity of mercury is 13.59 at 0°C.; in the solid form at its freezing point, it is 14.19.

Except in the presence of hydrogen sulfide, mercury is not affected by exposure to air at ordinary temperatures. When heated in air to about 300°C., it combines slowly with oxygen to form the red oxide HgO, but when heated to a still higher temperature the oxide that has been formed decomposes.

In hydrochloric and cold sulfuric acids mercury is practically unaffected, but it dissolves in hot concentrated sulfuric and cold nitric acids. The alkaline hydroxides are without action upon it.

The alloys of mercury are known as *amalgams*. All metals except iron and platinum form amalgams, and even platinum will amalgamate under certain conditions. The zinc electrodes of primary batteries are amalgamated on the surface to prevent "local action" (page 627).

Uses.—Most of the mercury consumed in this country finds outlet in the form of mercury compounds. One of the largest uses is for the manufacture of mercuric fulminate [$Hg(OCN)_2$], employed for blasting caps and other detonators because under percussion it explodes. In the form of the artificial sulfide, mercury is used in coloring red rubber products. Anti-fouling paints for ship bottoms are made with the aid of the red oxide of mercury, which the salt of the sea slowly converts into mercuric chloride, an active posion. Only a comparatively small amount of the metal is needed for thermometers, barometers, air pumps, and other laboratory apparatus and scientific instruments.

Recently in the electric light plant of Hartford, Conn., mercury vapor, generated in a mercury boiler, has been employed effectively to operate the turbine of a prime mover for developing electric power. The original installation, generating 5,000 hp., required 2,800 lb. of mercury, but after about 4 years of operation an order was placed for additional equipment including a 10,000-kilowatt, mercury-vapor turbine requiring about 13 lb. of mercury per kilowatt capacity.[1] The mercury, of course, is employed in a closed system. Steam for an auxiliary unit is generated by the heat still resident in the mercury vapor after it passes the turbines.[2]

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[1] FURNESS, "Mineral Resources of the United States," pt. I, p. 52, U. S. Geol. Survey, 1927.

[2] For advantages of the mercury-vapor turbine over the steam turbine, see *Chem. Age* (*N. Y.*) p. 183, Feb. 19, 1927.

CHAPTER V

NON-FERROUS ALLOYS

Definition and Types of Alloys.—An alloy may be defined as a coherent, metallic mass produced by the intimate association of two or more metals or metal-like substances.

Although other methods may be employed, alloys are usually produced by mixing the constituents while in the melted state and then allowing the mixture to solidify. The components are generally more or less soluble in the melted state, and in some cases remain soluble in the solid state, but more frequently during solidification they separate either wholly or in part and form distinct crystals of the constituents. Alloys, like metals, are crystalline bodies; and it is with the composition and the relation of their crystals that we shall first have to deal. On this basis alloys may be divided into three classes: (1) intermetallic compounds, (2) solid solutions, and (3) mechanical mixtures.

Intermetallic Compounds.—In some cases the compound may be formed with elements of distinctly metallic characteristics, such as copper with tin, or tin with antimony; in other cases one element may be a metalloid, as silicon or carbon. The compounds may crystallize separately and produce mechanical mixtures, or may dissolve in one another or in elementary components and form a solid solution.

The following are examples of compounds formed by the interaction of metals and metalloids: Cu_2Sb, Cu_3Sb, Cu_3Sn, Cu_2Zn_3, $CuAl$, $CuAl_2$, Cu_3Al, Mn_2Sb, $PbMg_2$, $SnMg_2$, $ZnMg$, Mg_3Al, $FeZn$, $SbSn$, $NiAl$, $NiSi$, $FeSi$, Fe_3P, Fe_3P_2, and Fe_3C.

Solid Solutions.—A study of crystal forms reveals the fact that there are several definite systems according to which chemical elements and compounds crystallize. In each system there may be several forms, such as the cube, octahedron, and others in the so-called "regular system," the hexagonal prism in the hexagonal system, etc. For each metal or compound there is a definite shape that its crystals assume; it will take this form even though very powerful influences may tend to prevent it. If two metals crystallize alike, they are said to be isomorphous and may crystallize together, *i.e.*, the individual crystals may contain both metals.[1] The two metals are not merely mixed in the crystals; their association is much more intimate. They are completely merged and their individualities are not apparent. The crystal appears like a simple, uniform body; the merged components are said to be in solid solution. The crystal structure of an alloy consisting of a simple solid solution is shown in Fig. 5.

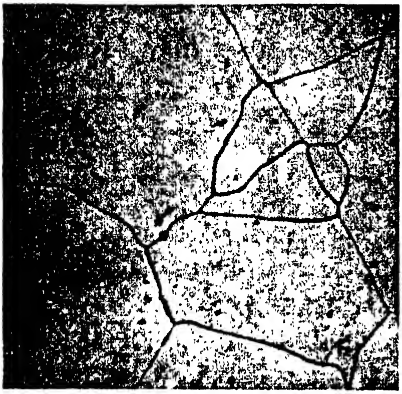

FIG. 5.—Copper-nickel alloy, containing 30 per cent of nickel, annealed, etched with acid ferric chloride. Uniform solid solution. Magnified 60 diameters. (*Kurnakow and Zemczuzny.*)[2]

The properties of the solution are not intermediate between those of the constituents; an entirely new set of characteristics has been gained. In this sense it is like a chemical compound. For example, although copper is present in copper sulfate, the compound exhibits none of the properties of that element as an element. On the other hand, the solid solution is not like a chemical compound in that the proportions are not fixed, but may vary through a rather wide range.

In solid solutions the primary, or initial, crystals tend to form in the same manner as they do in pure metals. A central trunk develops, and parallel branches grow out from the sides of the trunk as illustrated in Fig. 6. Because of its tree-like character, a crystal of this kind is called a *dendrite*, from the Greek *dendron*, a tree. Unless the crystallization has been sufficiently slow, the

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[1] Two metals, or other substances that are not isomorphous, reject material of the other kind when crystallizing. For example, two salts that do not crystallize alike, even though they may be present in the same aqueous solution, will form pure crystals; each salt will be excluded from the crystals of the other.

[2] Reproduced by permission from Gulliver's "Metallic Alloys."

proportions of the constituents of a solid solution will not be the same in all parts of the crystal. When the main trunk and branches of the dendrite first form, they will be richer in the higher-melting constituent than the liquid from which they separate. A cored crystal is produced, which grows by adding layers increasingly rich in the lower-melting constituent. If annealed so that diffusion is complete, all traces of the original dendrites may disappear.

Fig. 6.—Dendrites in antimony. (*Howe.*)

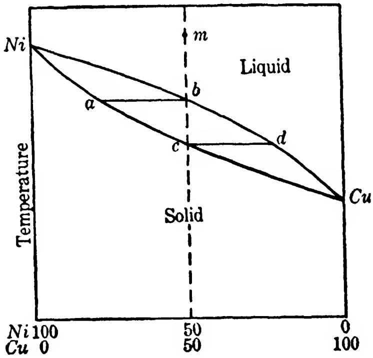

Fig. 7.—Solidification curves of the copper-nickel system of alloys.

The thermal diagram of a solid solution is illustrated in Fig. 7, which shows the freezing-point curve of the alloys of copper and nickel, two metals that are soluble in each other in all proportions in the solid state. For this series of alloys, the curve *NibdCu*, called the *liquidus* curve, indicates the temperature at which freezing begins, and *NiacCu*, called the *solidus* curve, marks the temperature at which freezing ends. Conversely, with a rising temperature, *NiacCu* marks the beginning of melting, and *NibdCu* the completion of melting. As an illustration, let us consider an alloy consisting of half nickel and half copper in the melted condition as indicated by *m* in the figure. As this alloy cools, it will begin to solidify at *b* on the *liquidus* curve, but the first dendrites that appear will have the composition represented by *a* on the *solidus* curve. As crystallization continues, due to the relatively more rapid removal of nickel from the melt, the percentage of copper in the fluid alloy increases. In other words, the composition of the remaining liquid follows the curve *bd*. Due to accretions from the melt and to diffusion, the composition of the solid aggregate that has formed moves along the *solidus* curve from *a* to *c*. At *c* the solidification of alloy *m* is completed, the last portion of the melt to solidify having the composition represented by *d*. Thus the crystals have cores that are richer in nickel and exteriors that are richer in copper, but if time is allowed, diffusion corrects this non-uniformity, and the crystals become homogeneous throughout. In normal cooling, however, diffusion lags behind solidification, and annealing is necessary to produce complete homogeneity. The completely homogeneous character of an annealed copper-nickel alloy is shown in Fig. 5.

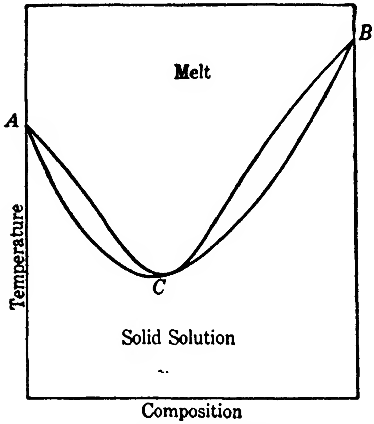

FIG. 8.—A solid-solution system with minimum freezing point.

Some of the other metals that form solid solutions in the manner just described are gold-silver, platinum-gold, antimony-bismuth, nickel-cobalt, iron-manganese, and tungsten-molybdenum.

A variation in the type of curve for a continuous series of solid solutions is shown in Fig. 8. In this case the melting point of the alloy is lowered both by the addition of metal *A* to metal *B*, and by metal *B* to metal *A*, with the *liquidus* and *solidus* curves meeting at *C*. All alloys in this series solidify after the manner of the copper-nickel series, except the alloy with the composition *C*. Alloy *C* freezes and melts at a fixed temperature just as if it were a pure metal. The solid and the liquid have the same composition, and there is no heterogeneity in the crystals.

The following list of systems of this type with the composition and freezing point of the alloy with the minimum freezing temperature is given by Campbell:[1]

FePt	30 per cent Pt	1500°C.	CrNi	39 per cent Ni	1290°C.
FeCo	65 per cent Co	1450	MnCo	30 per cent Co	1160
FeV	35 per cent V	1440	MnNi	45 per cent Ni	1000
FeNi	65 per cent Ni	1425	AuCu	18 per cent Cu	885
CrCo	53 per cent Co	1310	MnCu	68 per cent Cu	870

Mechanical Mixtures.—With alloys that solidify as mechanical mixtures, the constituents may be completely soluble in, or miscible with, each other in the melted state, and completely insoluble, or at most only partly soluble, in the solid state, so that during solidification (freezing) a complete separation must occur. With such alloys, certain components crystallize out first as the temperature gradually falls, and a low-melting constituent is left that freezes at a fixed and definite temperature after the manner of a pure substance. Because this manner of crystallization plays an important part in the explanation of the properties of some of the common alloys, especially of the iron-carbon alloys studied in a later chapter, the mechanism of the process will be discussed. Two cases will be considered: first, a liquid solution with the constituents completely insoluble in the solid state (solid solubility nil), and second, a liquid solution with its constituents partially soluble in the solid state (solid solubility partial).

Solid Solubility Nil.—As an illustration of this case, we shall consider the freezing of an aqueous solution of common salt, or sodium chloride, which although not an alloy, freezes in the same manner as alloys of this class, and besides is a more familiar occurrence.

When pure water is cooled, the temperature falls regularly until the freezing point, 0°C., is reached, where the temperature remains constant until all the water is frozen. When a certain amount of salt is dissolved in the water, the freezing is deferred until a lower temperature is reached. This is shown graphically

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[1] CAMPBELL, WILLIAM, in Liddell's "Handbook of Non-ferrous Metallurgy," vol. I, p. 14.

in Fig. 9, where the line *AB* indicates the temperatures at which salt solutions of various concentrations begin to freeze. Unlike pure water, a salt solution does not freeze at a fixed temperature, but spreads through a rather extended range. In the earlier stages, crystals of nearly pure ice separate out, and since this

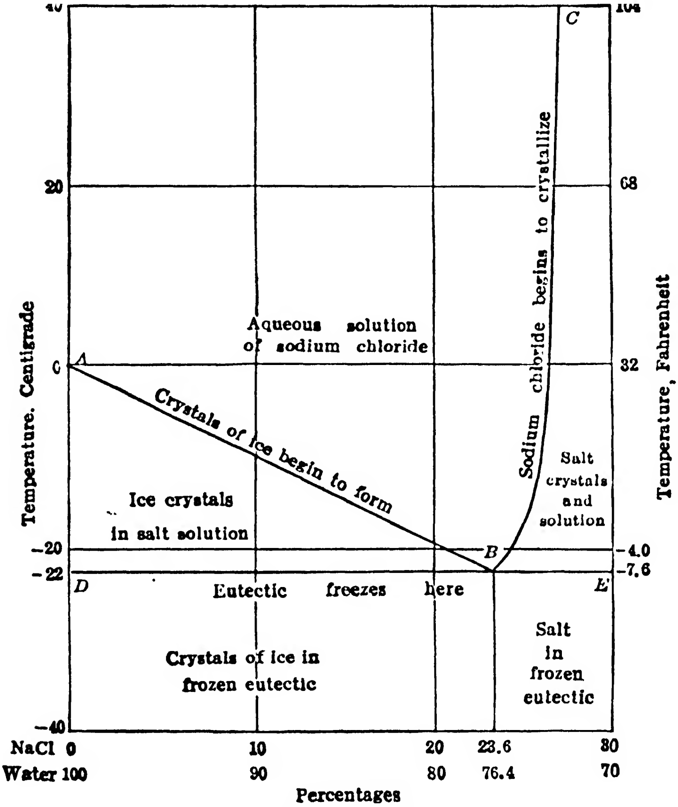

FIG. 9.—Formation and solidification of the eutectic in aqueous solutions of sodium chloride.

amounts to the removal of water, the remaining solution becomes richer in salt. Because it is richer in salt, its freezing point is lower as the line *AB* shows, and before more ice crystals form, the solution must be further cooled. With a constantly falling temperature, the formation of ice crystals continues until a certain quantity of concentrated solution (which will be small in amount if the percentage of salt in the original solution was small) is produced that will contain 23.6 per cent of salt, as shown at *B*. When this concentration has been reached, the temperature will have fallen to −22°C. (−7.6°F.); it will remain at this temperature until the concentrated residual solution is completely frozen. A solution containing 23.6 per cent of salt has the lowest freezing point of all the aqueous solutions of sodium chloride that can be made. Because it has the lowest freezing point, it has also the lowest melting point, since the freezing and melting of any substance take place at the same temperature. That portion of the solution, therefore, that was the last to freeze with a falling temperature will be the first to melt with a rising temperature; on this account it is called the *eutectic*. The term is derived from the Greek and means "easy-melting." With any aqueous solution of sodium chloride containing less than 23.6 per cent of the salt, the freezing will take place in the manner described.

If more than 23.6 per cent of sodium chloride is originally present, then, instead of crystals of ice, crystals of salt will be the first to separate out. Thus the solution will grow less concentrated, the percentage of salt moving to the left with a falling temperature as the line *CB* shows, until in this case also the final solution will contain 23.6 per cent of salt, and will freeze at −22°C. Consequently, a certain amount of solution of eutectic composition will be present in every aqueous solution of sodium chloride before final solidification has occurred. The solidification begins at the ice line or the salt line as the case may be, but it is completed at the eutectic line in all cases, as shown by the line *DE*.

When the temperature has fallen to the eutectic line but has not gone below it, so that the excess constituent has crystallized but the eutectic is still unfrozen, the mass will be only semisolid. With a solution that contained but little salt, or conversely a large excess of water, at a point just above the eutectic line, the structure may be compared to that of the confection known as an "ice" or sherbet. It will consist of a mass of crystals with liquid between them.

As the temperature falls below the eutectic line, −22°C., the eutectic solidifies; it crystallizes about the first-formed or primary crystals as they are called, and binds them together in the manner of a cement. Thus, the plastic mass becomes completely solid. When the eutectic freezes, it separates completely into its constituents, salt and ice. It was pointed out in the previous discussion that when the temperature crossed the line *AB*, ice crystals were formed, and when it crossed the line *CB*, salt crystals separated out. With the eutectic composition, in crossing the point *B*, both lines are crossed; consequently, in freezing, the components, ice and salt, separate completely. The crystals of the eutectic are smaller than the primary crystals, because the eutectic does not have an extended freezing range, but solidifies rather sharply. Rapid formation has a tendency always to lessen the size of the crystals. The primary crystals that separate in passing through the freezing range have a chance to grow by accretions from the melt in which they are carried.

If the original solution contains exactly 23.6 per cent of salt, no crystallization will occur until the solution has been cooled to −22°C. At this temperature the entire solution will freeze. With the percentage stated, the whole solution has the eutectic composition.

Solid Solubility Partial.—This case is illustrated by the alloys of lead and tin. In the melted state, lead and tin are soluble in each other in all proportions, and although they crystallize separately to a large extent on freezing, a certain amount of each will remain dissolved in the crystals of the other. In the solid state, lead can retain in solid solution as much as 4 per cent of tin, and tin can retain as much as 2 per cent of lead; consequently, the alloys at the ends of the series, containing not over the amount of each metal as stated, do not form eutectics.[1]

The freezing-point diagram for the lead-tin alloys is shown in Fig. 10. We shall first consider an alloy containing 3 per cent of tin and 97 per cent of lead, at a temperature of 320°C. This will be at the point *e* in the diagram. As this alloy cools through the range between the lines *AB* and *AD*, it will solidify, and the crystals that separate will contain both lead and tin; that is to

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[1] Although each metal forms a solid solution with the other as stated, the solution does not readily become saturated. Lead, for example, becomes saturated with tin (a 4 per cent solution) only after annealing for 3 weeks at 175°C., 5° below the eutectic temperature.

say, crystals of a solid solution will be formed. In like manner an alloy containing, for example, 99 per cent of tin and 1 per cent of lead as shown at *f*, will solidify as a solid solution in cooling through the range between the lines *CB* and *CE*.

If we now start with a melted alloy containing 60 per cent of lead and 40 per cent of tin at a temperature of 275°C. (the point *m* in the diagram) it will cool without change until a temperature of about 235°C. is reached, which will be a point on the line *AB*. This is the lowest temperature to which the solution can cool and contain 60 per cent of lead in solution. When cooled further, lead crystals begin to form in the alloy, *i.e.*, the lead begins to freeze. The alloy now consists of lead crystals in a rather thinly fluid, melted medium; its structure is comparable to that of a paint, which consists of solid mineral particles in a fluid medium. The lead crystals spoken of here are not in reality pure lead; they contain a little tin in solid solution.

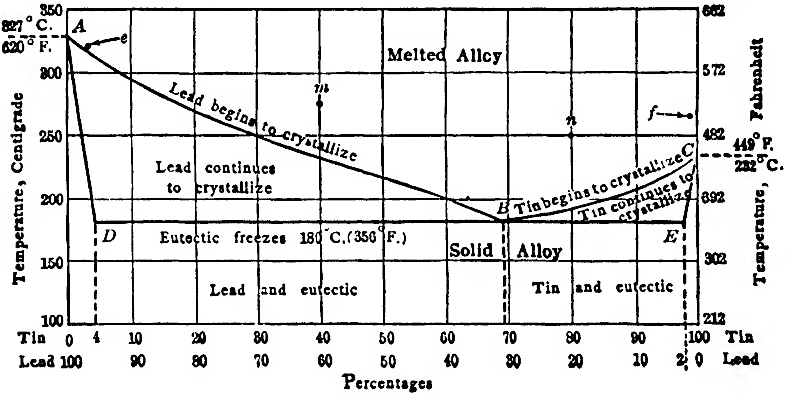

FIG. 10.—Formation and solidification of the eutectic in the lead-tin alloys.

As the cooling continues, the solubility of the lead in the residual melt becomes still less, and more lead crystals separate out. With a continuance of the formation of lead crystals, the composition of the remainder of the alloy moves to the right until the point *B* is reached, when the relatively small amount that still remains molten—the eutectic—will contain 69 per cent of tin and 31 per cent of lead. Thus, for the eutectic-forming alloys of the lead-tin series that contain more than the eutectic amount of lead, the freezing range lies between the lines *AB* and *DB*. The freezing will begin at the line *AB* and the eutectic will have been formed by the time the line *DB*, a temperature of 180°C., has been reached.

If, on the other hand, we should consider an alloy containing more than the eutectic amount of tin, say 80 per cent of tin, at a temperature of 250°C. (the point *n* in the diagram), it will cool without change until the line *BC* is reached. In cooling through the range between *BC* and *BE* a sufficient amount of tin crystals, each containing a little lead in solid solution, will form and thus cause the composition of the residual melt to move to the left. When the temperature represented by the line *BE* has been reached, that part of the alloy that still remains melted will have the eutectic composition.

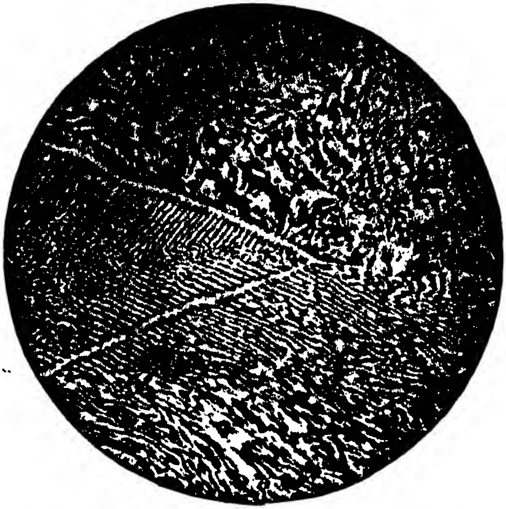

FIG. 11.—Eutectic alloy of bismuth and tin. Magnified 200 diameters. (*Desch.*)[1]

As the temperature falls to below the line *DBE* the eutectic will freeze, and as was the case with the salt solution, its constituents will separate. In this instance, the solidified eutectic will consist of mixed crystals of two solid solutions, one consisting chiefly of lead with a little tin dissolved, and the other consisting chiefly of tin with a little lead dissolved. These crystals of the

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

eutectic will be of relatively small size, when compared to the first-formed, or so-called "primary crystals," as was explained on page 168. The crystallized eutectic occupies a position between the primary crystals, and, in a sense, acts as a matrix in which the primary crystals are set. The structure of an alloy of this sort, highly magnified, is shown in Fig. 26, page 209. In this figure, the eutectic is represented by the dark areas; it appears dark only because it is photographed in shadow. In preparing a metal specimen for making a photomicrograph, the section is highly polished and then is etched by some reagent that has a selective action on the constituents. In this instance the eutectic has been dissolved away more rapidly; its surface is, therefore, at a lower level, and receives less light than the primary crystals. The detail of the structure of a eutectic alloy is shown in Fig. 11. Although the separate grains are frequently composed of laminations as shown in this figure, so that such structure may be considered to be typical, the eutectic is not always laminated in this manner.

Physical Properties of Intermetallic Compounds, Solid Solutions, and Eutectics.[1]—The various types of structural constituents have characteristic properties that they confer to a degree upon the alloys of which they are a part; therefore, a brief statement of their general effect is here given.

Compounds are harder than the elements from which they are formed, but are rather brittle, and lessen the shock resistance of the alloy. On the other hand, they increase the compression strength, an effect which is frequently advantageous, for example, in bearing alloys. They improve the working qualities with respect to turning, filing, etc. Examples of non-ferrous alloys containing intermetallic compounds are bronze with more than 8 per cent of tin, babbitt's alloy, and alloys of aluminum containing copper, nickel, or tin.

Solid solutions are relatively soft, malleable, and ductile, and tend to confer these properties upon the alloys in which they occur. Practically all of the non-ferrous alloys that are regularly cold rolled, cold drawn or spun consist of a single solid solution. Brass containing less than 36 per cent of zinc, cast bronze containing less than 8 per cent of tin, aluminum bronze containing

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[1] Derived from Law's "Alloys and Their Industrial Applications."

less than 7.5 per cent of aluminum and nickel silver are examples of malleable and ductile alloys consisting of a single solid solution.

Eutectics have low melting points, as has been explained, and in the non-ferrous alloys are brittle. Because the eutectic forms a matrix in which the primary crystals are embedded, the ultimate strength and ductility of the alloy are practically determined by the eutectic. Among the non-ferrous alloys, those that form eutectics are not used much for constructional purposes, but chiefly for solders and bearing alloys. The characteristics of the eutectic in ferrous alloys will be discussed in a later chapter.

Reasons for Making Alloys.—By forming alloys of metals, undesirable properties may be lessened and desirable properties increased. For example, alloys are always harder than their pure constituents, and will therefore wear better, but they are usually less malleable. Alloys are generally poorer conductors of heat and electricity than their components, and, as a rule are more fusible.

By making an alloy, the cost of production of an article may be lessened. Aside from the introduction of cheaper metals, the alloy may be rendered less expensive to work. For example, some metals, such as copper and aluminum, can only with difficulty be made to produce sound castings, and they can be machined and filed only with difficulty as well, but their alloys are much more conveniently manipulated. The effect of the formation of alloys on the physical properties of the metals is stated more in detail in the following paragraphs.

In only a few cases does the *specific gravity* correspond to that which would result from the calculation of the mean of the constituents. In most cases it is greater than the calculated mean; contraction takes place upon alloying. Specific gravity, which is in all cases dependent upon the density, or upon the closeness of the contact between the molecules, seems to be increased in most cases by the solution of one metal in another. Although the specific gravity of metals is increased by wire-drawing, hammering, and pressure which closes the pores, the increased density is not permanent; annealing removes it.

As has been indicated, *hardness* is always increased by making an alloy. Frequently, the increased hardness may be the only reason for forming the alloy. Pure copper is harder than pure tin, but an alloy of copper and tin containing only 5 per cent of tin is almost twice as hard as pure copper.[1] The hardness of copper and copper-tin alloys is also much increased by small amounts of iron and manganese. Although zinc hardens copper, its action is much less pronounced. The greatest hardness is produced by about equal parts of copper and zinc, when it is about twice that of pure copper.[2] Lead-tin alloys are harder than pure lead.

For the effect on *ductility* produced by alloying copper with zinc, see Fig. 23, page 187. With proportions suitably chosen, the ductility of the alloy is far greater than that of either constituent alone.

The *tensile strength* is generally improved. For example, the tensile strength of copper is considerably increased by adding to it a small quantity of tin, although tin by itself has a lower tensile strength than copper. The effect on tenacity produced by alloying zinc with copper is illustrated by the curves shown in Fig. 22, page 186. The tensile strength of copper as cast ranges from 25,000 to 30,000 lb. per square inch, while that of zinc is only about 5,400 lb. per square inch, but the tensile strength of a cast brass, containing 45 per cent of zinc and the remainder copper, is in excess of 68,000 lb. per square inch. The tenacity, ductility, hardness, and other properties of metals and alloys are greatly influenced by the mechanical treatment they receive, such as rolling, wire drawing, etc. For the effect on the tenacity of brass, produced by working and annealing, compare the curves in Fig. 22.

Alloys are not as good *conductors of heat* as their components, and the *electrical conductivity* also is usually less than that of either constituent. Good conductors of heat are also usually good conductors of electricity and *vice versa.*

Casting Qualities.—Metals that soften only gradually when heated and assume an intermediate pasty state, as copper and wrought iron, are more thickly fluid when molten than those that melt suddenly, as bronze and cast iron. Alloys pass more sharply into the fluid state than pure metals, and are as a rule more thinly fluid when molten. On this account, they are more

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[1] BRANT, "Metallic Alloys," p. 102.

[2] BRANT, *loc. cit.*, p. 102.

easily cast, both because they fill the mold more readily and because they allow the gases to escape from them more quickly. Copper and bronze that contain cuprous oxide are rendered more thickly fluid by it, just as is iron by ferrous sulfide.

Liquation.—Many alloys, either when solidifying from the molten state, or when being heated while in the solid state, allow constituents having low melting points to separate from the remainder of the alloy. This separation is termed liquation; sometimes if not pronounced, it may be termed segregation. The material that separates out in this manner may be either the eutectic or at times almost a pure metal; a good example of the latter is the almost complete separation of lead from zinc or copper.

The desirable qualities of an alloy increase as the liquation becomes less. Slow cooling tends to increase, and rapid cooling tends to lessen it, hence the separation is more pronounced the thicker the casting. In some cases after the exterior has solidified, its contraction brings such a pressure to bear on the interior of the casting that the more fusible constituents are forced into the pores of the solidified exterior; occasionally, they pass entirely through and form globular masses on the surface of the casting.

Gases in Metals.—Gases that separate out from molten metals are very objectionable because they produce flaws in the casting. The gases may separate because of a lessened solubility as the metal solidifies, or because they are being generated by a reaction that proceeds in the melted metal.

The first case is illustrated by hydrogen in copper. The hydrogen may be formed by a reaction between the hot metal and water vapor, thus:

$$H_2O + 2Cu \rightarrow H_2 + Cu_2O$$

If the liquid metal dissolves more hydrogen than the solid metal can retain at the moment of solidification, gas bubbles will be formed.

The second case also may be illustrated by copper. Commercial copper usually contains small quantities of cuprous oxide (Cu_2O) and cuprous sulfide (Cu_2S). Since they are present only in small quantities they may be considered as being in very dilute solution in copper. These compounds react with each other, as:

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

Being in dilute solution, the reaction is very slow and quite continuous. Hence, as the molten copper remains in the mold, gases are formed, which make it very difficult to produce sound copper castings. A similar action may occur between carbon and metallic oxides, which produces carbon monoxide gas. This difficulty is eliminated by introducing some element, as phosphorus, silicon, manganese, aluminum, or other metals that use up the oxygen with the formation of difficultly reducible oxides.

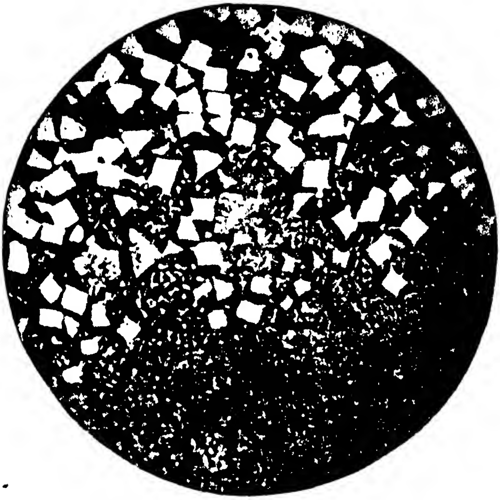

Fig. 12.—Alloy containing 79.7 per cent of lead, 14.5 per cent of antimony and 5.8 per cent of tin slowly cooled, etched with nitric acid. The white crystals of antimony-tin solution have floated to the top of the ingot. Magnified 100 diameters. (*Gulliver.*)

The Effect of Crystal Size in Metals and Alloys.—The rate of solidification and cooling of metals and their alloys is the chief factor in determining the size of crystals in castings. The more slowly the crystals are formed the larger they become, as shown in Figs. 12 and 13. Slow cooling allows a larger crystal growth, as is shown in Fig. 12, where the cooling has been sufficiently prolonged to allow the crystals that were first formed to float in that which was still melted. Large crystals are not usually desirable because they produce a weaker alloy. Rapid cooling produces fine crystals, and makes a harder, stronger, and more uniform alloy, although one that is much more brittle and less ductile. The center of a mass of alloy, cooling more slowly, will consist of coarser crystals than the outside. It should be noted also that crystal growth does not cease with the solidification of the alloy. While it is still hot, the molecules still have considerable freedom and can redistribute themselves. Then the larger crystals grow by absorbing the smaller ones.

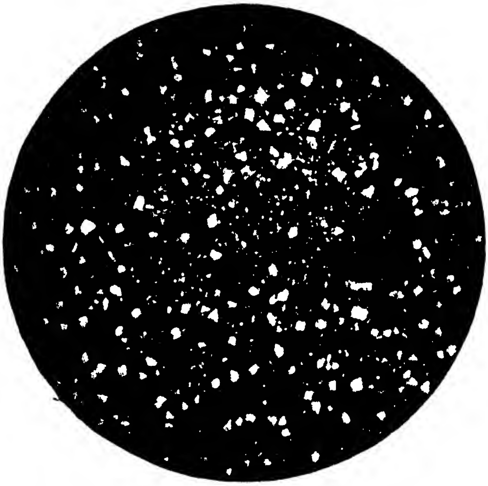

Fig. 13.—Same alloy as that of Fig. 12. Quickly cooled, etched with nitric acid. The crystals are much smaller and are distributed with fair uniformity. Magnified 100 diameters. (*Gulliver.*)

The temperature at which the metal is poured has an effect on crystal size. With higher pouring temperatures, the mold becomes more thoroughly heated. As a result, the cooling of the casting to the point below which crystal growth ceases is deferred.

Cold Working of Metals.—When metals are worked cold, they gain in hardness and strength but lose in ductility and shock resistance. In cold rolling and cold drawing, the crystals of the metal assume more or less the form of elongated platelets. If a suitably prepared specimen of metal that has been distorted in this manner is examined under the microscope, it will be found that the crystals show parallel lines running through them, changing direction from grain to grain. These lines are caused by a mass movement of crystal parts such as might appear when a stack of cards is pushed sidewise. The planes where the movement occurs are called slip planes. Wire drawing is possible, then, because of the extension of crystals along slip planes. The slipping occurs through the crystals, not between them. If distortion of the metal is carried beyond that which can be accommodated by the slip planes, rupture occurs.

Cause of Hardening by Cold Work.—In his discussion of this topic Campbell[1] calls attention to the well-known fact that a piece of soft wire, such as annealed copper or low-carbon steel, may easily be bent with the fingers into the form of a hair-pin, but that it is comparatively hard work to straighten it out again. Evidently the bending has produced some structural change in the metal that has increased its rigidity, an effect that is typical of all cold-working processes. Under the previous topic it has been explained that the permanent deformation produced by cold work is due to a block movement or shearing of crystals at planes of easy slip, called slip planes. Any factor that interferes with this slip will harden and strengthen the metal. Several explanations based on the theory of slip interference have been offered to account for the hardening of metals by cold working, but it seems that the hypothesis that fits the facts best is that the slip is stopped by end resistance. The increase in the resisttance at the end of the slip planes by cold work is probably due partly to both of two causes: first, to the production of more amorphous metal at the grain boundaries and, second, to the disregistry of the slip planes.

Amorphous Metal at Grain Boundaries.—With suitably chosen conditions, it can be shown that metals behave as they would if their granular components were held together by an envelope of amorphous metal. When pure metals at ordinary temperatures are broken, the path of the fracture for the most part runs through the grains, rather than between them. The strength of the joints between the crystals seems to be greater than the strength of the crystals themselves. On the other hand, when metals are ruptured at temperatures just below their melting points, the conditions are reversed; the parting occurs between the boundaries

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[1] LIDDELL, "Handbook of Non-ferrous Metallurgy," vol. I, p. 8.

of the grains. These observations are explained by the assumption that between the grains there is a layer of amorphous metal which at high temperatures is weak, but which at low temperatures is stronger than the crystalline metal. Facts other than these have been observed that tend to confirm the existence of this amorphous material. During cold work, each slip that cuts through a grain boundary produces an overlapping fragment, the surface atoms of which may be used to form more amorphous metal at the boundary of the grain.[1] In this way the successive slips caused by continued deformation of the metal will increase the thickness of the boundary layer. With increasing thickness, the amorphous envelope becomes more difficult to penetrate and the resistance of the metal to further deformation increases. In other words, it is harder and less amenable to cold working. When annealed, the amorphous material that has been developed recrystallizes, and the metal becomes soft and plastic again.

Disregistry of Slip Planes.—The motion of the crystal fragments is also impeded by the disregistry of the slip planes. When slip occurs in any one grain, it cannot, as a rule, extend into the next grain without change in direction because usually the potential slip planes of adjacent grains do not register or coincide. The effect of cold work is in some respects similar to a grain refinement. Because the number of the grains must increase with their fineness, cold work increases the number of points of disregistry, which, in turn, increases the interference with progressive slipping. The hardening of both pure metals and alloys may be accounted for by the theory of slip interference.

Slip Interference Due to Hard Particles.—Jeffries and Archer[2] have shown also that if hard, strong particles, such as those of a metallic compound, were interspersed in the crystals of a metal, its strength and hardness, even when unworked, is increased. The hard particles act as "keys" and interfere with the movement of the crystal fragments along the slip planes. This is shown diagrammatically in Fig. 14. The figure represents an idealized section through a crystal, and it will be noted that with the arrangement shown, every plane of potential slip

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[1] JEFFRIES and ARCHER, "The Science of Metals," p. 82.

[2] "Science of Metals," p. 395.

encounters at least one of the particles. The motion of all of the planes, therefore, is mechanically obstructed.

The size of the particles is important. If all of the particles shown in Fig. 14 were gathered together in a single large particle as shown in Fig. 15, although the strength of the single "key" would be increased, many planes would not be intercepted by it. They would, therefore, be free to move. On the other hand, if the particles were too small, they would become less effective. There is obviously, a certain size of the particles that hinders to the greatest degree the movement of the planes, and this is known as the critical size, or the diameter at critical dispersion.

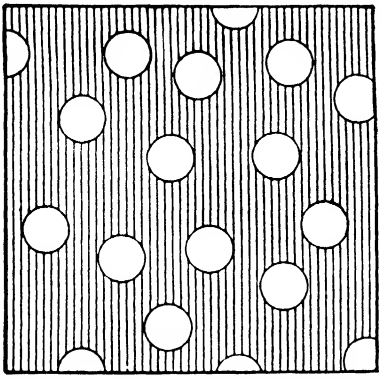

Fig. 14.—Slip planes keyed by hard particles. (*Jeffries and Archer.*)

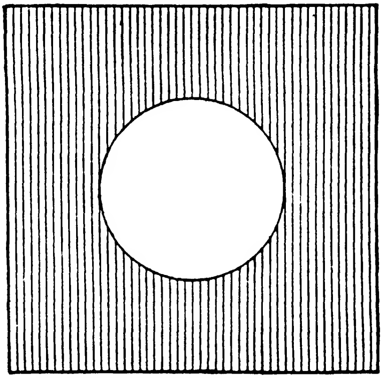

Fig. 15.—Hard constituent gathered into a single particle leaving many planes unkeyed. (*Jeffries and Archer.*)

It is estimated by Archer and Jeffries that the average diameter of the particles at critical dispersion is of the order of 10^{-7} cm. The hardening of duralumin (page 199) by heat treatment is accounted for by the precipitation of hard particles of the compound $CuAl_2$.

Annealing.—After cold working, as long as the temperature remains below a given point, which is different with different metals, the grains or crystals remain deformed, but when heated to a suitable temperature, known as the annealing temperature, they regain their symmetry and become equiaxed, as it is called. (*Cf.* Figs. 20 and 21, page 184.) The readjustment is possible at the higher temperature because of the greater molecular

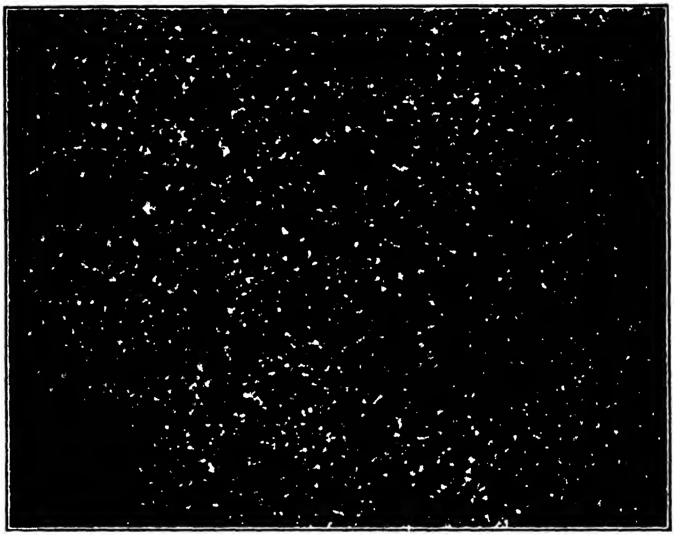

FIG. 16.—Rolled aluminum bronze containing 7.5 per cent of aluminum. Magnified 10 diameters. (*Law.*)

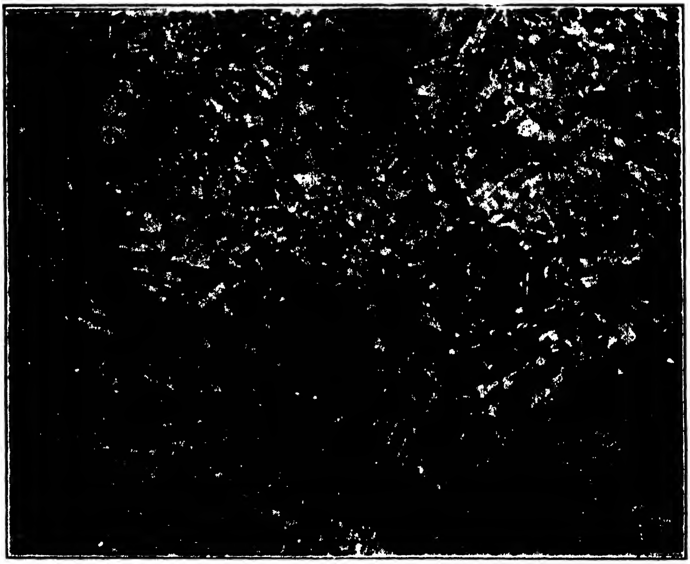

FIG. 17.—Same alloy as shown in Fig. 12, after repeated annealing. Magnified 10 diameters. (*Law.*)

activity. Upon annealing, the hardness and strength of the strained metal are decreased, but it regains its plasticity and workability.

In annealing, the temperature must not be held too long at the point at which grain *growth* occurs, because abnormally large grains may be formed by some crystals extending their boundaries and absorbing neighboring crystals. The temperature at which this occurs varies with different metals, and other factors being equal it will occur at lower temperatures if the metal is pure. An excessive enlargement of crystals may also be produced by holding the metal for an extended period at the proper annealing temperature. The coarsening of structure that results from this cause is illustrated by Figs. 16 and 17.

Hot Working.—In effect, hot working is a combination of cold work and annealing. The grain size is decreased by hot working, but if the process is not continued until a temperature that is too low is reached, the crystals regain their symmetry, and the strained condition that would have been produced by the distortion is not apparent. The effect, then, is to harden and to some degree to strengthen the metal without seriously affecting the ductility.

"Season" Cracking.—The brasses, bronzes, and some other alloys are subject to a type of failure known as "season" cracking. It is particularly likely to occur in brasses containing from 20 to 40 per cent of zinc, and it is practically always confined to alloys that have been forged or worked, especially cold worked, in some form such as rivets, rods, tubes, and sheets. The cracks are found in articles that appear to be made of sound material and according to approved design. They develop sometime after the piece has passed inspection, either in service under load, or even before being put into actual service. They may vary in size from those of microscopic dimensions to those causing complete rupture.

The primary cause of season cracking is initial internal stresses introduced during manufacturing by processes designed to yield a "work hardness" to meet specifications for high tenacity, etc. Corrosion is a contributory cause due to the fact that localized stresses are brought into play at the bottom of the little corrosion pits and corrugations formed on the surface of the metal.

Because the cracking develops so frequently in conjunction with corrosion, this type of failure is often spoken of as "corrosion" cracking. The cracking is augmented also by temperature changes.

In combating season cracking, the first step is to relieve the initial internal stresses by suitable heat treatment. Stress-free material may be obtained by annealing for 1 hr. at 400 to 550°C.,[1] but in some cases this leaves the metal too weak. The method of "springing," which consists of bending the bar backward and forward radially until all the outer fibers have been permanently lengthened, has been used with success.[2] If the surface of the metal is kept highly polished, the failures are inhibited because localized stresses are eliminated to some extent.

The Preparation of Alloys.—When preparing an alloy, if the metals being alloyed have much tendency to be destroyed by oxidation, they should be protected by a covering of small lumps of charcoal (no dust),[3] borax, or ground glass as soon as they are put into the crucible. When melted, the alloy should be thoroughly stirred, preferably with a stick of green wood, because such a stick burns less readily than a dry one.

If a large amount of one metal is being alloyed with a small amount of another, greater uniformity may be obtained by first preparing an alloy containing approximately equal parts of the two metals and then adding the remainder of the excess metal to this alloy in a second melting.

If the constituent metals have widely separated melting points, the one with the higher melting point is melted first, being covered well to prevent oxidation, and the lower-melting-point metal is then added. If the lower-melting-point metal were melted first, a great deal of it would be lost through oxidation while the temperature was being raised sufficiently to melt the other metal. If the lower-melting-point metal is much in excess, however, and is not very volatile, time and heat energy may be saved by melting it first, and then adding the higher-melting-point metal in small pieces. The molten metal usually dissolves the added

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[1] *U. S. Bur. Standards Tech. Paper* 82, p. 68.

[2] JOHNSON, "Materials of Construction," p. 749.

[3] The charcoal should be free from dust because the small particles remain entangled with the melted metal.

metal at a temperature much below the melting point of the latter.

When three or more metals with widely differing melting points are being alloyed, less loss will occur if the constituents are first formed into two independent alloys with melting points lying not far apart. With nickel, copper, and zinc, for example, a nickel-copper and a zinc-copper alloy may be first prepared; and the final alloy may then be made by combining the two intermediate alloys.

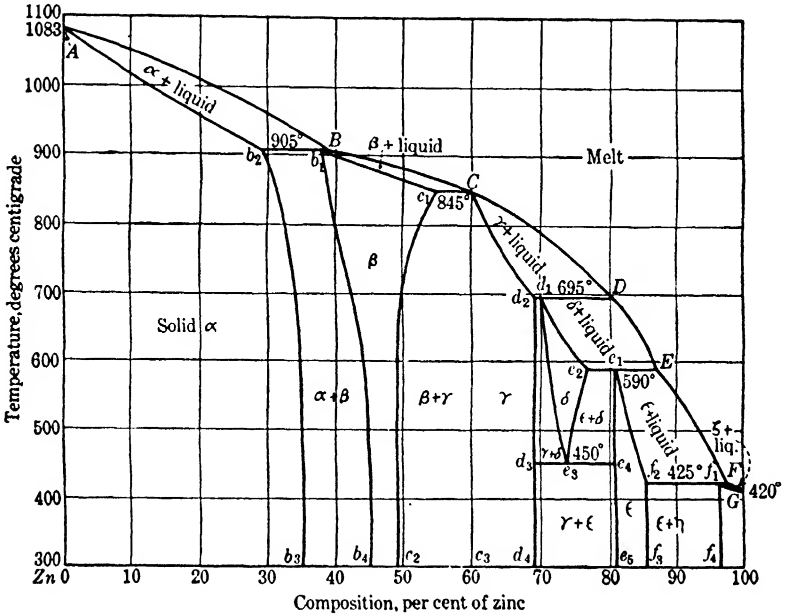

FIG. 18.—Thermal diagram of the copper-zinc system of alloys. (*After Mathewson.*)

BRASS

The Thermal Diagram and Structure of Brass.—Brass is an alloy of copper and zinc. These two metals form alloys in all proportions, but those containing above 60 per cent of zinc, being brittle, are of only minor industrial importance. As shown in Fig. 18, there are six solid solutions, which in accordance with the usual practice in naming a series of this kind, are called *alpha, beta, gamma, delta, epsilon,* and *zeta.* No eutectics are

FIG. 19.—Brass containing 35 per cent of zinc as cast. Magnified 50 diameters. (*Bassett.*)

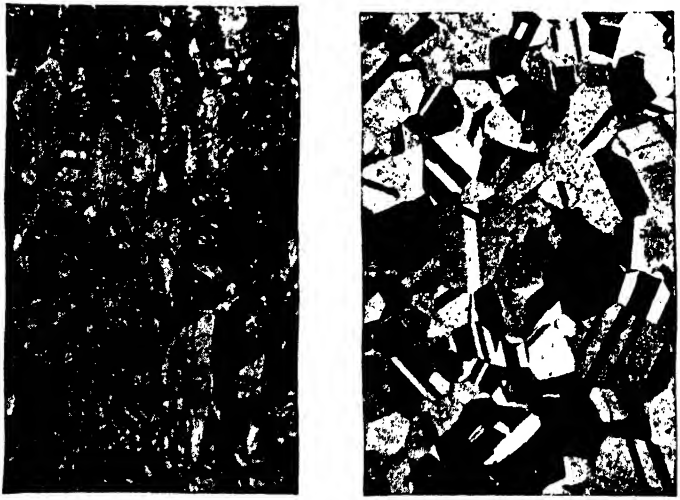

FIG. 20. FIG. 21.

FIG. 20.—Deformed grains in brass reduced 50.9 per cent in thickness by cold rolling. Zinc content 32 per cent. Magnified 75 diameters. (*Bassett and Davis.*)

FIG. 21.—Equiaxed grains in brass of same composition as in Fig. 20. Reduction in thickness by cold rolling 50.9 per cent followed by heating at 650°C. Magnified 75 diameters. (*Bassett and Davis.*)

formed in this series. The *liquidus* curve for the solid solutions is represented by *ABCDEF*.[1] With a falling temperature the solubility of the beta in the alpha constituent increases from approximately 29 to approximately 36 per cent, as shown by the curve b_2b_3. In a similar manner, with a falling temperature, curve b_1b_4 represents the change in the solubility of alpha in beta from 37 to 46 per cent, and curve c_1c_2 the solubility of gamma in beta changing from 55 to 49 per cent.[2] The *alpha* constituent is relatively soft and malleable; the beta constituent is much harder. Alloys containing 36 per cent of zinc or less are frequently spoken of as alpha brass because only the alpha constituent is present.

Alpha brass when cast exhibits the usual tendency of solid solutions to form dendrites or cored crystals (page 163). The appearance of grains of this kind is shown in Fig. 19. The structure of the alloy when cold rolled is shown in Fig. 20. Here the elongated form of the grains that is typical of cold-worked brass is clearly marked. Figure 21 illustrates the equiaxed, polyhedral grains typical of cold-worked brass after annealing.

Effect of Composition on Physical Properties.—If a brass were wanted for tensile strength only, it should contain about 45 per cent of zinc. As shown by the curves in Fig. 22, the tenacity reaches a maximum with about this amount and then falls off sharply. It should be noted, too, that the strength varies greatly with the mechanical and heat treatment that the alloy receives. Brass so proportioned, however, that the tensile strength is at the maximum, is very brittle as is shown by the low ductility with this composition in Fig. 23. Ductility reaches a maximum with about 30 per cent of zinc, but when the beta constituent appears, it rapidly decreases. Since a brittle alloy has very little value as a constructional material, some of the tensile strength must be sacrificed in order to gain ductility and toughness. Consequently, the most generally serviceable brasses are those that contain not above about 40 per cent of zinc. Law says[3] that brasses containing only the alpha

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[1] For a discussion of the solidification of alloys of the solid solution type, see p. 163.

[2] CAMPBELL in Liddell's "Handbook of Non-ferrous Metallurgy," vol. I, p. 26.

[3] "Alloys and Their Industrial Applications," p. 176.

constitutent may be rolled cold (although in practice they are more often rolled hot) while those containing the beta and alpha constituents are rolled hot. There is no sharply defined limit, of course, between those that can be rolled hot and those that can be rolled cold, but they may be classified in a general way in this manner. In a similar manner, it may be said that brasses that are to be subjected to working, either hot or cold, contain less zinc than those that are merely cast.

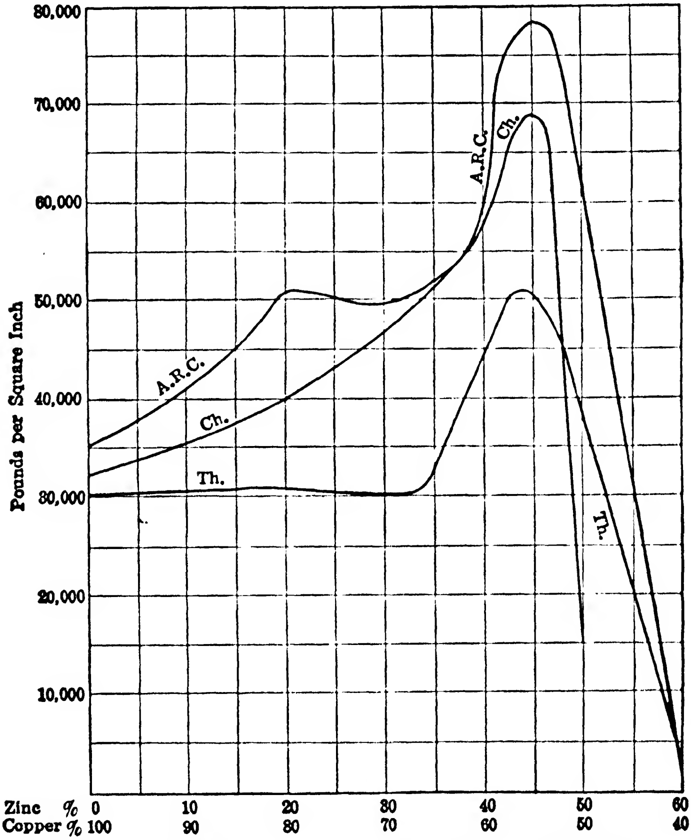

FIG. 22.—Tensile strength of copper-zinc alloys. (*After Sexton.*)
A.R.C.—Alloys Research Committee (worked rods).
Th.—Thurston (castings).
Ch.—Charpy (annealed brass).

High zinc alloys, containing 50 per cent or more of zinc, are used in brazing operations. They are too brittle for general use, but are suitable for brazing solder because of their lower melting points.

In 1832, Muntz patented in England an alloy containing 60 per cent of copper and 40 per cent of zinc; alloys of approximately this composition are still known as *Muntz metal.* They are harder and stronger, but more brittle than those containing less than 36 per cent of zinc.

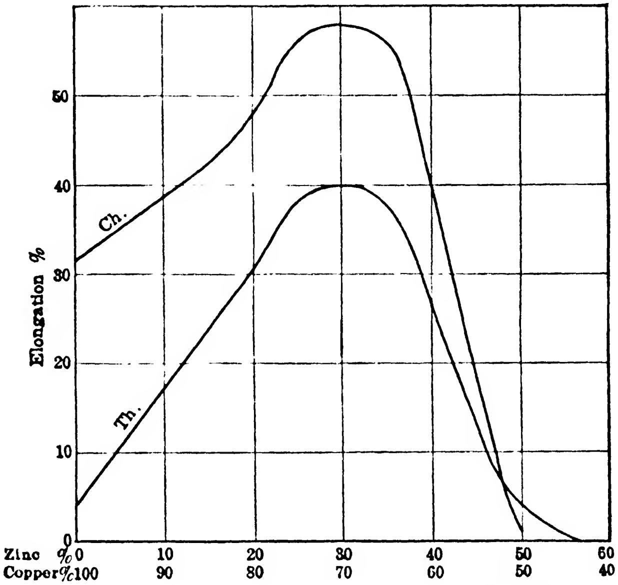

FIG. 23.—Ductility of copper-zinc alloys. (*After Sexton.*) Th.—Thurston. Ch.—Charpy.

Perhaps the most widely used brass is that containing 2 parts copper and 1 of zinc. This alloy is often spoken of as "common" brass. With about 25 to 30 per cent of zinc, brass is used for cartridge cases, in spinning operations and for similar uses requiring considerable strength and malleability.

The color of the brasses ranges from silvery white for those rich in zinc, through yellow for those containing a medium amount, to a reddish color for those that contain little zinc.

MODIFIED BRASSES

The hardness, tenacity, malleability, ductility, or other properties of the brasses are in some cases greatly improved by the introduction of relatively small quantities of one or more other metals. Some of the more common of these additions will be noted.

Aluminum Brass.—The amount of aluminum added to brass does not usually exceed 3 per cent. It raises the tensile strength but decreases the ductility. The product has a deep golden color, and resists corrosion better than ordinary brass. It casts well and may be forged or rolled.

Tin Brass.—Tin is one of the most usual metals added to brass. It increases the hardness and tensile strength but the amount employed should not exceed about 2 per cent, because with higher amounts the ductility begins to decrease. Tin renders brass less liable to corrosion in sea water, and since on this account it is used in naval construction, the alloy is sometimes called *Naval brass*. An alloy of similar composition, consisting of approximately 38 per cent of zinc, 2 per cent of tin, a little iron, and the remainder copper is known by the name of *Tobin bronze*. This also is a very useful alloy of high tenacity, good working qualities, and excellent corrosion resistance.

Manganese Brass.—The alloy referred to under this head is generally spoken of as *manganese bronze*, but it is in reality a brass since the main constituents are copper and zinc. The composition varies considerably, but the following percentages may be regarded as typical: copper, 60 to 62 per cent; zinc, 38 to 42 per cent; tin, 0.5 to 1.5 per cent; iron, 0.5 to 1.5 per cent; manganese, 0 to 0.5 per cent; and sometimes a little aluminum. The manganese is generally added in the form of ferromanganese; this accounts for the presence of iron, which in itself has important effects. Manganese is very active in reducing the oxides of other metals, an action that is highly beneficial. In some instances, no manganese is shown on analysis because it has all been eliminated by the reactions of deoxidation. In addition to its action as a deoxidizer, manganese hardens and strengthens the alloy.

In cast form, the tensile strength of the manganese brass lies in the neighborhood of 70,000 lb. per square inch and this is somewhat improved by working, as by rolling and forging. It is exceedingly tough and has a high resistance to corrosion even in sea water. It is used for pump rods, valves and cylinders, hydraulic rams, tubes, propellers, nuts, bolts, etc.

Iron Brass.—When iron is added to ordinary brass, it produces a harder, stronger, and tougher alloy and is easily cast. One of the most widely used alloys of this type is known as *delta metal,* which was brought out as a proprietary alloy. Under the original specifications, an iron-zinc alloy was first made containing about 8 to 10 per cent of iron, which in turn was combined in the proper ratio with copper; the combined metals were then deoxidized with phosphorus. The alloy as usually prepared contains 55 to 60 per cent of copper, 40 to 43 per cent of zinc, 1 to 3 per cent of iron and fractional percentages of manganese and tin. Its tensile strength is about two-fifths greater than a brass of similar composition with the iron omitted.

Lead Brass.—In brass that is intended for filing or turning, 1 to 2 per cent of lead is employed to prevent fouling of the tools and to cause the turnings to break more readily which prevents clogging of automatic machines. Lead increases the softness of brass. It is sometimes added to brass that is to be worked, but care should be taken to add but a small amount, because it reduces the ductility and strength. Only about 3 per cent will alloy with the brass; if more than this is added, it has a strong tendency to liquate. On this account "leaded" brasses should be chilled quickly when cast. Usually, lead in small amount is introduced accidentally from the spelter.

Arsenic, antimony, and **bismuth** may occur in brass, but when found, their presence is accidental. They are all objectionable because they are very active in producing brittleness.

Preparation of Brass.[1]—According to the general principles already given for making alloys, the copper, having the higher melting point and being in excess, is melted first, preferably under granular charcoal. Then the zinc, previously warmed, is added to the melt in pieces small enough that they do not chill the copper and cause it to solidify. If this should happen, zinc will be lost while awaiting the remelting of the copper. On the other hand, the temperature of the melted copper must not be too great, or the volatilization of zinc will be excessive. In some cases the crucible containing the melted copper is removed

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[1] For further information see Sexton, "Alloys," p. 248.

from the furnace and the zinc in the melted state is slowly poured in with stirring. When all the zinc has been added, the melt should be stirred thoroughly.

Since the melting point of copper is above the boiling point of zinc, a considerable amount of the latter will be lost through vaporization and oxidation in any case; the amount varies from about 5 to 10 per cent of that added, depending upon the care exercised. This loss must be taken into account in making brass to conform to given specifications.

In remelting brass, zinc is also lost. As a result, remelted brass is always richer in copper than before remelting.

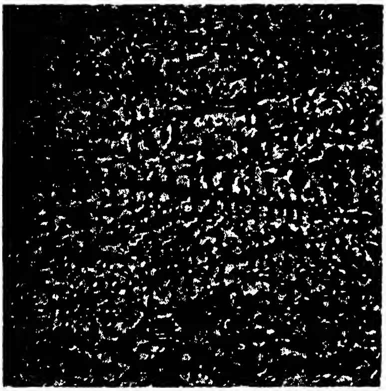

Fig. 24.—Gear bronze, rapidly cooled, showing dendrites of alpha solid solution of tin in copper. Magnified 50 diameters. (*Jeffries and Archer.*)

BRONZE

Structure.—Bronze is an alloy of copper and tin. Copper is capable of holding about 14 per cent of tin in solid solution, and this alloy is designated as the *alpha solution* or *alpha bronze.* Only in the annealed alloy, however, is 14 per cent of tin retained in solid solution at room temperature. Even when only 9 per cent of tin is present, the alloy, as cast, will not consist entirely of the alpha solution. Bronze, like brass, produces dendrites (Fig. 24) during solidification that are richer in copper than the liquid alloy from which they are formed. As a result, tin is concentrated in the melt between the alpha dendrites, and a second, or beta constituent, richer in tin, which is also a solid solution, is formed. The beta constituent is relatively unstable, and as the alloy cools slowly past 525°C. the beta constituent decomposes with the formation of the alpha solution and a hard, brittle substance, which is believed to be an intermetallic compound having the formula Cu_4Sn. At room temperature the cast alloy consists, then, of the alpha constituent, and angular masses of the compound. The presence of the compound increases the hardness and elasticity of the alloy but decreases its malleability and ductility. If the bronze is reheated to about 700°C. the compound dissolves and the beta constituent reappears. If held at this temperature, diffusion takes place, and finally a homogeneous alpha solution is obtained.[1] When cooled to room temperature after heat treating, it is found that the alloy is stronger and that its toughness is greatly increased.

The Effect of Composition on Physical Properties.—The tensile strength of bronze increases gradually with the amount of tin, reaching a maximum with about 20 per cent of tin, but as the tin increases beyond this amount the tensile strength very rapidly diminishes. Bronze is most ductile when it contains about 5 per cent of tin. With this amount it may be rolled satisfactorily at a red heat. Bronze is used chiefly for casting, however. As the amount of tin is increased above 5 per cent, the ductility gradually lessens and practically disappears with about 20 per cent of tin; since ductility is coordinate with toughness, these alloys are very brittle. They are also very hard. The most useful of the bronzes are those that contain from 8 to 11 per cent of tin, since the maximum *combined* strength and toughness is secured with about these amounts. Bronze containing tin within these limits was formerly known as *gun metal,* since because of its strength it was used for making guns, but now steel has entirely replaced it for this purpose. At the present time, the term gun metal is very loosely used, so that it cannot be said to have any definite significance. As cast, the alloy containing 9 per cent of tin has a tensile strength of about 30,000 lb. per square inch.

The copper-tin series of alloys containing between 15 and 25 per cent of tin is known as *bell metal.* Such alloys are very hard and brittle, but are sonorous, and are employed, therefore, in making bells and gongs.

By alloying 2 parts of copper with 1 of tin, a very hard, brittle, white alloy is produced called *speculum metal.* When highly polished, it serves excellently for mirrors and reflectors.

MODIFIED BRONZES

The properties of the bronzes, like those of the brasses, may be considerably modified by the introduction of a relatively

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[1] JEFFRIES and ARCHER, "The Science of Metals," p. 354.

small quantity of a third constituent; in some cases several additional elements may be employed. Perhaps one of the best examples of this class is zinc bronze.

Zinc Bronzes.—The zinc bronzes usually contain 88 per cent of copper, 8 to 10 per cent of tin, and 4 to 2 per cent of zinc. The presence of the zinc in the bronze increases the fluidity of the melted metal and in this way tends to prevent gas flaws in the casting. It also increases the tenacity and ductility. As reported by Karr and Rawdon,[1] the tensile strength of the 88-10-2 alloy when cast in sand was found to be about 38,000 lb. per square inch; when annealed by heating to 700°C. for 30 min. and cooling in the furnace for 24 hr. the tenacity was not lessened and the ductility was greatly increased. The specific gravity when cast in sand is about 8.58; the melting point is about 980°C.

Phosphor Bronze.—It is a well-known fact that the desirable properties of metals and alloys are greatly benefited by thorough deoxidation. In the report of zinc bronze just mentioned, Karr and Rawdon point out[2] that a microscopic examination of the fractured test specimens showed that the most common source of weakness was entrained or occluded oxides in the metal. Such oxides frequently occur as thin films in otherwise sound castings. The films produce brittleness and low ductility. By the reduction of these oxides with a suitable agent, the desirable properties of the alloy are much increased. Because of the great readiness with which it combines with oxygen, phosphorous has been found to produce excellent results when used for this purpose.

Since phosphorous may be added to a bronze of any composition the significance of the term *phosphor bronze* is quite indefinite. It is certain, however, that whatever good qualities the bronze might have, they are greatly increased by the addition of phosphorus. The tensile strength, the elasticity, and the power to resist repeated stresses—pulls, twists, and bendings—is enormously increased, so much so that it may almost be considered as an entirely new alloy.

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[1] "Standard Test Specimens of Zinc Bronze," *U. S. Bur. Standards Tech. Paper* 59, p. 41, 1916.

[2] *Loc. cit.*, p. 63.

Phosphorus is best added to the bronze in the form of phosphor copper, a hard, brittle substance of white fracture, containing about 16 per cent of phosphorus; or as phosphor tin, a white, brittle, crystalline material containing about 6 per cent of phosphorus. Upon being added to molten bronze nearly all of the phosphorus oxidizes and escapes, so that most phosphor bronzes contain no more than a few tenths of 1 per cent. The crystalline structure of two bronzes, one with, and the other without phosphorus, as shown by the microscope, seems to be the same in both cases. Phosphor bronze is then essentially a deoxidized bronze.

Although phosphorus produces very beneficial results through its activity as a deoxidizing agent, if there is much of it left in the alloy, it may be a decided detriment. This residual phosphorus increases the hardness and brittleness of the bronze; the amount left, therefore, must be kept within low limits. When special hardness is desired there may be 1 per cent, but as much as 4 per cent makes the alloy useless.

Phosphor bronze of proper composition can be forged, drawn cold, rolled, and cast. It seems to resist corrosion better than ordinary bronze, especially of sea water, so that it is much used for propeller blades. On account of its toughness, elasticity, and strength, it may serve as a substitute for steel, as in the manufacture of corrosion-resistance mine cables, ship sheathing, valve parts, etc.

Silicon Bronze.—Like phosphorus, silicon is active in the bronze as a deoxidizer; not infrequently the total amount added is nearly all eliminated through the reactions of deoxidation. Silicon bronze has many of the excellent properties of phosphor bronze, but to a somewhat less degree. It has a greater electrical conductivity than phosphor bronze, so that it is much used for telephone and other wires, particularly in those situations where high tensile strength is required. It possesses also a high corrosion resistance.

The following may be regarded as representative of the usual composition of silicon bronze: copper, 98.55 per cent; tin, 1.40 per cent; silicon, 0.05 per cent.

Other Metals in Bronze.—*Lead* in small quantities may find its way into the bronze as an impurity in the tin; it is sometimes intentionally added, but the introduction of as much as 2 per cent noticeably lessens the tensile strength and ductility of the alloy. If cooled quickly, the lead is distributed in fine grains, but if allowed to cool slowly it liquates. Leaded bronzes containing considerable lead are used for bearing metals and will be discussed later under that head. *Iron* in bronze confers great hardness, and for this reason it is sometimes added to bronze bearings. It whitens the bronze and lessens the fusibility. Although *ancient bronze* was hardened largely by hammering, it contained other elements beside the copper and tin that hardened it, as for example about 1 per cent of iron.

Preparation of Bronze.—In making bronze the copper is first melted, then the tin is introduced, and the mass is stirred at once in order that the tin may be quickly mixed and the oxidation lessened. The loss of tin by oxidation is likely to be very great; it is sometimes as much as 10 per cent. If the loss is no greater than 2 per cent, it is considered excellent.

Aluminum Alloys

General Considerations.—In the engineering field, great quantities of aluminum alloys are now employed. Some of the stronger ones, in the worked and heat-treated condition, may reach a tensile strength of as much as 63,000 lb. per square inch, or more. This is comparable with the strength of mild steel (page 287). When it is remembered that the tensile strength of cast commercial aluminum is approximately 12,000 to 14,000 lb. per square inch, the preparation of such alloys is in itself a noteworthy accomplishment, but when their lightness is taken into account, the achievement becomes even more important. The specific gravities of the aluminum alloys range from 2.69 to 2.82, which is approximately a third that of steel.[1] The growth of interest in aeronautics has given increased impetus to the development of light and strong aluminum alloys, but they are employed extensively in many other industries as well, for example, in the manufacture of automobiles. Briefly summarized, the properties that recommend these alloys for a wide variety of uses are their low specific gravities, high thermal and

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[1] Due to the fact that the yield point (incipient deformation) is lower in the strong aluminum alloys than in steel, in construction slightly larger sections of the aluminum alloys are employed. The saving in weight, then, as compared to steel, is about three-fifths.

electrical conductivities, pleasing appearance, and acceptable corrosion resistance. With regard to corrosion resistance, it should be noted that in the preparation of aluminum alloys, the elements commonly added to commercial aluminum usually lower its corrosion resistance. Manganese is an exception. An alloy containing 1.25 per cent of manganese has about the same corrosion resistance as commercial aluminum.

Aluminum-copper Casting Alloy.—Because of its marked shrinkage during solidification, and its tendency to develop gas flaws (page 87), it is not easy to make sound castings of pure aluminum. Besides, it is soft and difficult to machine. For these reasons, then, as well as for those given under the preceding topic, for making castings, an alloy is used. For a long time, practically all of the so-called aluminum castings were made of an alloy consisting of 92 per cent aluminum and 8 per cent copper, which is known as No. 12 alloy; but recently an alloy consisting of 90 per cent of aluminum, 7 of copper, 1 of iron, and 2 of zinc, as well as other complex alloys have been widely used. Due to impurities that exist in commercial aluminum, even the No. 12 alloy is not in reality a simple binary alloy, but may contain 0.5 per cent, or more, of both iron and silicon, and sometimes of manganese. Although the amounts of these elements present are comparatively small, they have a marked influence on the properties of the alloy. The ultimate strength in tension of the No. 12 alloy ranges from 18,000 to 23,000 lb. per square inch. The Brinell hardness of commercially pure aluminum is 22, but that of the alloy is 65. As would be expected from the greater hardness, the ductility of the alloy is lower than that of aluminum. With less than 8 per cent copper, the alloy is more ductile when cold. With more copper, it has greater strength at elevated temperatures, and is less likely to crack during casting. Upon solidifying from the molten state, the 8 per cent alloy shrinks about 0.156 in. per foot, which is only about three-fourths as much as commercially pure aluminum.

Constitution of Aluminum-copper Alloys.—The constitution of the aluminum-rich aluminum-copper alloys is shown in Fig. 25. The two metals unite chemically, and a hard, brittle compound, $CuAl_2$, containing 54 per cent of copper, is formed. In the diagram, C represents this compound at its melting point, 590°C. At 33 per cent of copper, a eutectic, melting at 545°C., appears. The eutectic consists of $CuAl_2$ and a solid solution of $CuAl_2$ in aluminum. The *liquidus* of this series is represented by ABC and the *solidus* by $ADBE$. At the eutectic temperature

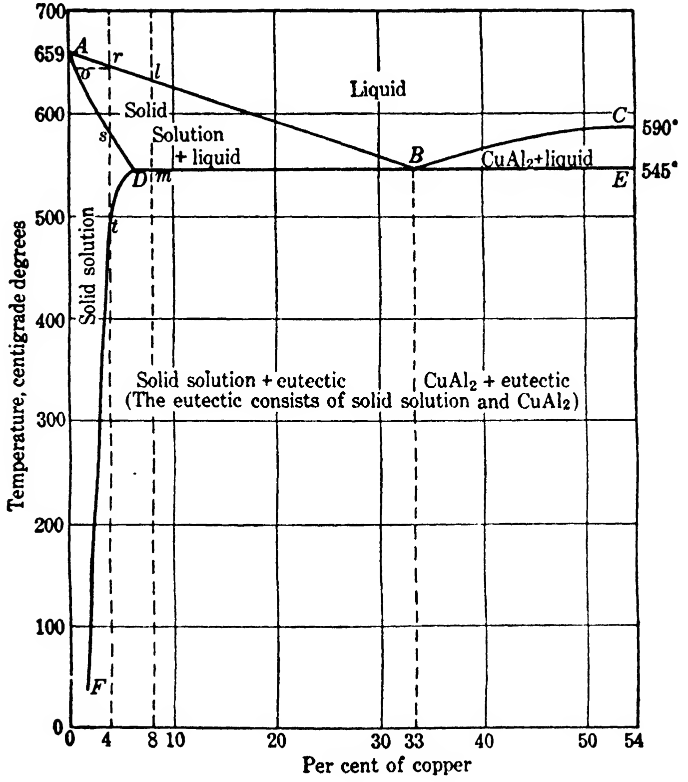

FIG. 25.—Thermal diagram of aluminum-copper alloys.

5.5 per cent of copper in the form of $CuAl_2$ is retained in solid solution, but the solubility decreases with a falling temperature, as shown by the solubility curve DF, and at room temperature approximately only 1 per cent remains dissolved.

To illustrate the changes taking place during solidification, we shall first consider an alloy containing 4 per cent of copper. As the alloy cools to the *liquidus* AB, a solid solution of $CuAl_2$

in aluminum will begin to separate at *r*. This constituent will have the composition represented by *o* on the *solidus AD* (*cf.* page 163). As the separation of the solid solution continues, the composition of the melt grows richer in copper along *AB*. Likewise, the copper content of the solid phase formed at *r* increases along *AD* to *s*. At *s* the solidification of the alloy is complete. Since, as shown by *DF*, the solubility of $CuAl_2$ in the solid solution *decreases* at temperatures below the eutectic *solidus*, when the alloy has cooled to *t*, the compound $CuAl_2$ begins to separate. This compound continues to separate until at room temperature the amount of copper that remains in solution is only about 1 per cent.

In a similar manner, with an alloy containing 8 per cent of copper, the solid solution begins to appear at the temperature represented by *l* on *AB*. The separation of this phase continues through the solidifying range between *AB* and *DB*, as described in the preceding paragraph, until at *m* the alloy that remains molten has the eutectic composition; that is to say, it contains 33 per cent of copper. In cooling past *DB*, the eutectic solidifies as a mixture of $CuAl_2$ and solid solution containing 5.5 per cent of copper dissolved. Five and one half per cent represents the solubility of copper in aluminum at the eutectic temperature. In cooling to room temperature, $CuAl_2$ separates from solution as before described. With moderately slow cooling, then, at room temperature this alloy also will consist of $CuAl_2$ and solid solution containing approximately 1 per cent of copper.

Aluminum Bronze.—This term is applied to the series of copper-aluminum alloys that contain between about 5 and 10 per cent of aluminum.[1] Within this range there is a distinct difference between the alloys that contain less than 7.35 per cent and those that contain more. Up to 7.35 per cent, the cast alloys are composed of a single solid solution, known as the alpha solution, but when this amount is exceeded, in addition to the solid solution, there is a hard, brittle, dark-colored constituent that is unstable and much influenced by heat treatment.[2] With

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[1] It is interesting to note that, although copper and aluminum form alloys in all proportions, it is only those high in aluminum (the casting aluminum), and those high in copper (aluminum bronze) that are of commercial importance.

[2] JOHNSON, "Materials of Construction," 5th ed., p. 752.

the appearance of this second constituent, the tensile strength increases, and the ductility decreases. The ductility and toughness of the alloys with aluminum below the amount stated are high, and increase gradually to a maximum at this point; then they fall off rather sharply. Those alloys containing as much as 12 per cent of aluminum are very brittle. With less than 7.35 per cent of aluminum, the alloys may be readily forged, rolled, and drawn cold; with more than this percentage, the alloy may be hardened by quenching. The ultimate strength in tension increases constantly with increase of aluminum up to between 10 and 11 per cent. The Alloys Research Committee[1] found that the tensile strength of a 10.78 per cent alloy, cast in sand and slowly cooled, was 29.5 tons per square inch. When this same casting was quenched from 800°C., the strength was 50 tons. For a chilled casting containing 10 per cent aluminum, the strength was found to be 36.93 tons; when this same casting was annealed the strength was 27.7 tons per square inch.

The aluminum bronzes are very fluid in the melted state and the metal is easily poured, but it is not easy to secure castings that are free from defects. A dross of aluminum oxide develops and very careful manipulation is required to prevent it from becoming entangled with the melted metal. Besides, the bronze shrinks considerably on solidifying, and open, spongy "shrinkage flaws" (see page 247) may be produced. If the castings are large, so that they cool slowly, the structure becomes coarsely crystalline; it is then in the same condition as an overannealed alloy, as shown in Fig. 17 on page 180. In this condition, the alloy is, of course, weak and brittle. Vickers states[2] that the aluminum bronzes are much improved by the addition of a few per cent of iron, and points out that although copper does not readily form an alloy with iron containing carbon, nevertheless, when aluminum is present, the alloy forms easily. He recommends proportions within the following limits: aluminum, 7 to 12 per cent; iron, 3 to 5 per cent; and the remainder copper. The amount of the aluminum must be not more than 2½ times that of the iron. An important claim made for this ternary alloy is that, whereas large castings made of the usual composition must be chilled

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[1] SEXTON, "Alloys," p. 157.

[2] "Metals and Their Alloys," p. 259.

to avoid the overannealed effect and produce a strong casting, the introduction of iron favors rapid solidification, and the coarsely crystalline structure does not appear. The properties of aluminum bronze are improved also by the judicious use of zinc and manganese.

Aluminum bronze has an extremely wide range of usefulness, and would be used much more if it cost less. Because of its malleability and toughness, it has been found to be useful as a bearing alloy. It resists corrosion in sea water exceptionally well, and is in general suitable for locations where high strength, great toughness, and corrosion resistance are essential. When exposed to the air at a red heat for some time, it oxidizes very little. In the cast form, alloys containing approximately 10 per cent of aluminum have a fine yellow color, resembling gold. This color is permanent as long as the surface remains as cast, but in the worked condition, the metal tarnishes.[1]

Wrought Aluminum Alloys.—Several strong and tough aluminum alloys have been developed that are capable not only of both hot and cold working, but also of heat treatment. Duralumin, developed about 1910, and now designated by the Aluminum Company of America as alloy 17S, is probably the best known of this class.

Duralumin.—This alloy embodies essentially a combination of the tensile strength of mild steel with the lightness and corrosion resistance of aluminum. Its nominal composition is as follows:

	Per Cent
Copper	4.0
Manganese	0.5
Magnesium	0.5
Aluminum (commercial, by difference)	remainder

Because commercial aluminum contains silicon and iron as impurities, the alloy will contain also about 0.3 per cent of silicon and about 0.5 per cent of iron. In the development of duralumin, the presence of the silicon was fortunate; it unites with the magnesium to form the compound Mg_2Si, which has an important effect on the heat-treatment possibilities of the alloy.

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[1] Campbell, William, in Liddell's "Handbook of Non-ferrous Metallurgy," p. 29.

The mechanical properties of duralumin are shown in the following table:[1]

MECHANICAL PROPERTIES OF DURALUMIN

Condition of alloy	Tensile strength, lb. per sq. in.	Yield point, lb. per sq. in.	Elongation, per cent in 2 in.	Brinell hardness, 500 kg. load, 10 mm. ball
Annealed	25,000–35,000	7,000–10,000	14–22	45–55
Heat treated.	55,000–63,000	30,000–40,000	18–25	90–105

The first line of the table shows the properties of the duralumin when it has been annealed after cold working. If the annealed alloy is heated to 500°C., is quenched in water, and is tested immediately after quenching, it will be found that the tensile strength has risen from the figure shown in the table to about 45,000 lb. per square inch without any decrease in the elongation; in fact, with this treatment, the elongation generally increases. If the quenched alloy is allowed to stand at room temperature for a time, a structural change occurs spontaneously that brings about a further marked improvement in the alloy. The process is known as *aging*. The change is rapid immediately after quenching, proceeds at a gradually diminishing rate as time goes on, and is substantially completed in about 4 days.[2] The same effect as that produced by aging may be secured in a much shorter time by heat treating the quenched alloy. The heat treatment consists merely of reheating the alloy to a temperature predetermined by experience and then allowing it to cool slowly. The mechanical properties of the heat-treated alloy are shown in the second line of the preceding table. That a non-ferrous alloy is capable of such decided improvement in hardness and strength by heat treatment is surprising, and merits further study.

Theory of Heat Treatment of Duralumin.—An examination of the thermal diagram of the aluminum-copper alloys on page 196

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[1] "Strong Aluminum Alloys," p. 15, publ. by Aluminum Company of America.

[2] "Strong Aluminum Alloys," p. 10, publ. by Aluminum Company of America.

will show that whereas 4 per cent of copper is soluble in aluminum at 500°C., the solubility at room temperature is only about 1 per cent (solubility curve *DF*). Further, as has been shown previously in explaining this diagram (page 197), the copper thrown out of solution as the temperature falls is believed to take the form of free particles of the compound $CuAl_2$. It is upon these assumptions that Merica[1] and his associates have based their theory of the heat treatment of duralumin. Although visual confirmation of the structural changes assumed is partially lacking, no contradictory evidence is known, and the theory accounts for the facts that have been observed.

Assuming, in accordance with the theory, that an aluminum-copper alloy, containing 4 per cent of the latter metal, in the annealed condition contains 3 per cent of the copper in the form of free particles of $CuAl_2$, when the alloy is heated to a little above 500°C. and is held at that temperature for a time, the copper compound will all dissolve in the aluminum to form a solid solution. It is assumed, also, that all of the copper will remain dissolved and form a 4 per cent solid solution when the alloy is quenched from 500°C. In practice, this process of heating and quenching is spoken of as *solution heat treatment.*

Judging from the tensile-strength and hardness values obtained in testing, it appears that the 4 per cent solid solution is harder and stronger than the 1 per cent solid solution containing an additional 3 per cent of copper in the form of free particles of $CuAl_2$ dispersed in the alloy, which is believed to represent the annealed condition. The existence of the free particles has not been confirmed by the microscope, but the fact that they have not, would be accounted for if the particles were submicroscopic in size. In support of the assumption that the particles are formed, we may mention the analogous case of supersaturated, aqueous solutions of salts obtained by cooling hot, saturated solutions to room temperature. These supersaturated solutions are unstable. It seems logical to assume that the supersaturated solid solution obtained by quenching the alloy is also unstable, and that on standing, or aging, the excess $CuAl_2$ precipitates in the form of very fine particles.

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[1] MERICA, WALTENBERG, and SCOTT, "Heat Treatment of Duralumin," *Chem. Met. Eng.*, **21**, 551.

The size of the precipitated particles is important; they must be neither too large nor too small. Particles of a certain intermediate size, known as the "critical" size, have been found to improve the alloy more than those of any other size.

In explaining the slip-interference theory of hardening (page 178), it was shown that when the dispersed particles were unduly large, many slip planes were left "unkeyed." With the increased rate of diffusion that is possible at the higher temperature, it is possible that during annealing, the particles of $CuAl_2$ grow until they have exceeded the critical size. The movement of the crystal fragments at many of the slip planes, under this condition, would be unimpeded. The alloy, therefore, would be softer and weaker than it would be if the planes were more perfectly "keyed."

In the highly dispersed condition of the particles, in the solid solution retained by quenching, the particles are evidently "subcritical" in size, a condition that allows the particles to be retained in part within the crystal fragments themselves. As a result, maximum interference with slipping is not secured. Consequently, in the quenched condition also, the alloy does not possess its maximum hardness and strength. Higher values for these two properties may be developed by aging, or by reheating, because then the free particles of $CuAl_2$ assume the critical size, that is to say, the size that causes the greatest number of potential slip planes to be keyed.

In this connection, the effect of the magnesium and silicon in duralumin must not be overlooked. These two elements combine chemically to form Mg_2Si, a compound the solubility of which in aluminum is affected by temperature changes in the same manner as that described for $CuAl_2$. Due to the presence of silicon as an impurity in commercial aluminum, Mg_2Si will exist in all alloys prepared by adding magnesium to aluminum of commercial quality. Such alloys, after quenching, show age hardening at room temperature. In fact, the presence of Mg_2Si is believed to be, at least partly, responsible for the precipitation of $CuAl_2$, or of some more complex compound, in duralumin, because when the Mg_2Si is absent, the age hardening of that alloy is greatly reduced.

Although pure binary alloys of copper and aluminum do not age harden materially at atmospheric temperature, they may be hardened by reheating after quenching, as has been explained. It has been found that reheating to temperatures between 100 and 175°C. produces very good results.[1] The process of hardening by reheating is known as artificial aging, or as *precipitation heat treatment.*

Although duralumin has a high resistance to all ordinary forms of corrosion, in the presence of salt water and air it is subject to a form of intercrystalline attack that causes the alloy to become brittle. The corrosion resistance of the alloy may be improved by a special form of heat treatment.[2]

Other Types of Aluminum Alloys, 25S and 51S.—Newer types of aluminum alloys, similar to duralumin in strength, lightness, and heat-treatment properties, but possessing much better working qualities than alloys of the duralumin type, are manufactured by the Aluminum Company of America under the designations 25S and 51S. Because the presence of copper and magnesium in conjunction, a combination that occurs in duralumin, seems to engender poor working qualities, these metals are not employed together in the two alloys now under consideration. Their composition is shown in the following table:

NOMINAL PERCENTAGE COMPOSITION OF 25S AND 51S[1]

Alloy	Copper	Manganese	Magnesium	Silicon	Aluminum, minimum
25S	4 5	0.8	...	0 8	92.0
51S	...	...	0.6	1.0	96.5

[1] "Strong Aluminum Alloys," p. 7, publ by Aluminum Company of America.

Although alloy 51S hardens to some extent when aged at room temperature after quenching from 500°C., alloy 25S does not, but both are very susceptible to precipitation hardening by artificial aging, *i.e.*, by heating for a suitable period of time within the temperature range between 100 and 175°C.

In the table of mechanical properties, which follows, the letters *O*, *W*, and *T* are employed after the serial number to

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[1] ARCHER and JEFFRIES, "New Developments in High-strength Aluminum Alloys," *Trans. Amer. Inst. Mining Met. Eng.*, **71**, 828, February, 1925.

[2] EDWARDS, FRARY, and JEFFRIES, "The Aluminum Industry," vol. II, p. 241.

designate the heat treatment used. The letter *O* indicates that the alloy has been annealed, and is in its softest and most ductile state; *W*, that it has been quenched, or, in other words, has been given the solution heat treatment; and *T*, that it has been artificially aged, that is to say, has been given the precipitation heat treatment.

MECHANICAL PROPERTIES OF STRONG, WORKABLE ALUMINUM ALLOYS[1]

Alloy	Tensile strength, lb. per sq. in.	Yield point, lb. per sq. in.	Elongation in 2 in., per cent	Brinell hardness, 500 kg. load, 10 mm. ball
25SO	23,000–35,000	7,000–12,000	12–20	45–55
25SW	45,000–53,000	15,000–30,000	15–22	68–85
25ST	55,000–63,000	30,000–40,000	16–25	90–105
51SO	14,000–19,000	4,000– 6,000	22–32	25–32
51SW	30,000–40,000	15,000–20,000	20–30	55–70
51ST	45,000–50,000	30,000–40,000	10–18	90–100

[1] "Strong Aluminum Alloys," p. 15, publ. by Aluminum Company of America

Applications.[1]—Alloys of the aluminum-copper type (25S) not only are suitable for the same applications as duralumin, but they have also distinctly better working qualities than that alloy. The aluminum-magnesium-silicon type (51S), in addition to considerable hardness and strength, has sufficient plasticity that it may be employed where cold forming of such nature is required that none of the other strong alloys will stand the operations.

Corrosion Resistance.—Some of the strong aluminum alloys are subject to a type of intergranular corrosion that causes a noteworthy loss in tensile strength and elongation. On the other hand, the product of the Hoopes cell (aluminum having a purity of 99.9 per cent), has a very high resistance to corrosion (page 90). By covering a strong alloy with a sprayed-on coating (page 358) of pure aluminum, a composite product is prepared in which strength and corrosion resistance are combined.[2] The coated alloy may be rolled, drawn, spun, or formed in other

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[1] ARCHER and JEFFRIES, *op. cit.*

[2] The Aluminum Company of America manufactures a coated alloy of this type under the name "Alclad."

ways. Tests have shown that coated sheet exposed to salt spray for 1 year was still bright at the end of that time. Because the coating has a higher solution tension than the base alloy, by means of electrolytic action (page 359) the pure metal will protect areas it does not cover, such as, for example, the edges of the coated sheet where it has been sheared.

NICKEL ALLOYS

Copper-nickel-zinc Alloys, Nickel Silver.[1]—This series of alloys may be described as brasses that by the addition of nickel have acquired a white color, much increased hardness, strength, and corrosion resistance. The alloy resists chemical action very well; many of its uses depend upon this fact.

Although the composition of the nickel silvers is not at all definite, it varies usually within the following limits: copper, 50 to 80 per cent; zinc, 10 to 35 per cent; and nickel, 5 to 30 per cent. It has been found that iron further whitens and hardens the alloy; practically all the commercial varieties contain some iron, generally from 1 to 3 per cent. Disregarding the iron, and also manganese, that the alloy frequently contains, the following may be regarded as typical: copper, 55 per cent; zinc, 25 per cent; and nickel, 20 per cent.

The alloy appears on the market in the usual commercial forms, sheet, strip, tubes, rods, and wire. The tensile strength in the annealed condition is about 70,000 lb. per square inch. It is used in the production of a large number of ornamental and other fittings where an attractive finish and high corrosion resistance are desired.

Monel Metal.—This is an alloy containing approximately 68 to 70 per cent nickel, 26 to 28 per cent of copper, and 2 to 3 per cent iron.[2] The alloy is not made by melting together the pure metals but is produced directly from a copper-nickel matte. Copper-nickel alloys exist as solid solutions in all proportions.

Monel metal melts at about 1360°C., and has a specific gravity (cast) of 8.87. Its tensile strength when cast is about 85,000

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[1] These alloys were formerly known as "German silver," but since the World War the trade has accustomed itself to the name *nickel silver*. "Nickel and Its Alloys," *U. S. Bur. Standards Circ.* 100, 1924.

[2] *Trans. Canad. Min.* Inst., vol. 16, p. 241, 1913.

lb. per square inch. The color of the metal very closely resembles that of nickel but it has a slightly darker tinge. It is susceptible to a high polish and does not tarnish readily. It is very resistant to corrosion. It is difficult to produced sound castings of monel metal because of its pronounced tendency to form blow holes. To correct this, ferromanganese and magnesium are sometimes added in small amounts. It may be rolled into sheets, drawn into wire, forged, and machined.

Because of its high resistance to corrosion, it has been found very useful in making piston rods, valves, window screens, roofing sheets, "pickling" tanks and crates for "pickling" steel, steam turbine blading in marine work, and in other situations where a combination of high strength, ductility, and resistance to corrosion is essential.

COBALT ALLOYS

Stellite.—The alloys known by this name constitute a group that consist essentially of cobalt and chromium, but generally contain other metals, such as tungsten, molybdenum, and iron. Their composition may be represented by the two examples that follow: (*a*) cobalt 60, chromium 15, tungsten 20, and molybdenum 5 per cent; (*b*) cobalt 30, iron 52, tungsten 14, and chromium 4 per cent.[1] Stellite alloys are grayish in color, are very strong, tough, hard, and resistant to abrasion and corrosion. They retain their hardness at a full red heat, and can, therefore, be used for cutting tools in high-speed lathes. They cannot be forged, but must be cast and ground to shape.

The stellite alloys are very serviceable also for surgical instruments, since they may be sterilized in a flame without injury to the edge or to the polish.[1]

CEMENTED TUNGSTEN CARBIDE

A new hard alloy, which exhibits a startling performance when used as a material for high-speed cutting tools, consists of grains of tungsten carbide cemented together with cobalt. The excessive hardness of tungsten carbide has long been known,

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[1] LATIMER and HILDEBRAND, "Reference Book of Inorganic Chemistry," p. 316.

but by itself it is too weak, porous, and brittle to serve for any industrial purpose. The new tool material is not the first instance, however, in which advantage has been taken of its almost diamond-like hardness in the production of alloys. The high-speed tool steels of the older type also contain tungsten carbide, but in order to secure the necessary strength, toughness, and other properties that were desired, a great deal of the inherent hardness of the carbide was sacrificed. In this recent development, an alloy has been prepared that is about half as strong as high-speed steel, with a hardness still above 9 on the scale in which the diamond is 10. The sapphire (page 84) ranks next to the diamond in hardness, and the sapphire is scratched by this alloy.

In preparing the cemented tungsten-carbide alloy,[1] a very fine powder of tungsten carbide is first produced. By milling the fine powder with cobalt in a ball mill, cobalt is caused to be smeared over the microscopic particles of the carbide. After milling, the mixture is pressed into the desired shape, and then is sintered together with heat. After dressing the surface, the sintered mass is firmly cemented together by heating in an electric furnace to a brilliant white heat in an atmosphere of hydrogen. The finished product, then, consists essentially of minute particles of tungsten carbide cemented with cobalt or with cobalt containing tungsten and carbon. There are several grades of the alloy. One grade, containing 87 per cent of the carbide and 13 per cent of cobalt, is tough, although not so hard as a grade containing 6 per cent of cobalt, for example. With the lower cobalt content, however, the alloy is more brittle. In the harder varieties of the alloy, the cobalt matrix is only just sufficient to cement the grains of carbide together. In the softer varieties, the carbide grains are more widely dispersed in the matrix.

Cemented tungsten carbide was first developed by the Krupp Steel Works at Essen in Germany, and was named by them *widia* (from *wie diamant*, meaning diamond-like). In the United States, the General Electric Company produces the alloy under the name *carboloy*. Other producers employ other names.

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[1] JEFFRIES, "The Present Status of Cemented Tungsten Carbide Tools and Dies," *Metals and Alloys*, **1**, 222, November, 1929.

Unlike high-speed steel, cemented tungsten carbide requires no heat treatment; it is fully hard after cooling to room temperature, and it is immaterial whether the cooling is fast or slow. It has no temper that can be injured by heat. Its red hardness exceeds that of any other substance employed in the manufacture of tools.

At a bright red heat, widia or carboloy will cut nickel steel without ill effect on the tool. It will cut a deep, narrow groove in an alundum grinding wheel without suffering much loss itself.[1] Screw threads in a glass rod may be cut by it, and hard porcelain and concrete may be readily cut and drilled. Molded compounds, such as bakelite and hard rubber, for which diamond-tipped tools were formerly used, may be cut at high speed with the new alloy. In cutting through the hard silicate scale on cast iron, no special precaution is necessary. This is an almost impossible accomplishment for an ordinary tool. For deep, tearing cuts in steel, however, the ordinary high-speed steels are still used. The cemented tungsten carbide has not sufficient strength for this work.

BEARING ALLOYS

The friction between two metals is directly proportional to the pressure applied. Of course, this is true only when both surfaces are sufficiently hard that one does not gouge or rub into the other. The amount of the load that can be borne before gouging begins is greater, the harder the metals. Arguing from this point, to reduce friction and avoid cutting, hard surfaces should be used for bearings. This is true, but only under perfect adjustment. In an ordinary bearing there are points of greater and lesser pressure, and therefore of friction; hence the bearing must be sufficiently soft to mold itself about the shaft. But it must be able to resist wear as much as possible also. The best fulfilment of these requirements has been obtained by the use of an alloy containing hard grains in a soft matrix. The soft matrix allows an adjustment, so that local pressures, which are generally responsible for trouble, are avoided; the hard grains on the surface resist the wear. This structure is found in

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[1] HOYT, "Carboloy—A New Tool Material," *Gen. Elec. Rev.*, **31**, **585**, November, 1928.

the so-called "white alloys," which consist of lead, tin, antimony, copper, etc.

The White Alloys. 1. *The Lead-antimony Alloys.*—These two metals alloy readily in all proportions; the hardness and brittleness of the product increase with the amount of antimony. The eutectic melts at 245°C., and contains 13 per cent of antimony. With less antimony than this, the structure of the alloy is made up of crystals of soft lead in a harder eutectic; with more than this amount, the alloy consists of hard crystals of antimony in a softer eutectic, as shown in Fig. 26. This latter structure fulfils the requirements of a good antifriction metal. As much as 15 to 20 per cent of antimony is advantageous in some cases, as for very heavy pressures.

Fig. 26.—Lead-antimony alloy, containing 40 per cent of lead, etched with picric acid. Bright crystals of antimony surrounded by eutectic. Magnified 100 diameters. (*Gulliver.*)

2. *The tin-antimony-copper alloys* are called "babbitt metal." They are more expensive than the preceding, because they contain a large amount of tin, but for the same reason they are considerably better. The tin becomes a constituent of the hard grains, diminishing their hardness it is true, but also their brittleness. The tin enters the matrix also and increases its compression strength.

The structure of the babbitt metal is made up of a mass of tin containing cubical crystals of tin-antimony alloys, and needle-like crystals of an antimony-copper alloy, as shown in Fig. 27.

An alloy having the same composition as babbitt's original alloy is made by first melting together the following: copper, 4 parts; tin, 12 parts; antimony, 8 parts, and then adding 12 parts of tin after fusion. The antimony and the first portion of the tin are melted together, then the copper is added, and finally the remainder of the tin. This is called the hardening alloy.

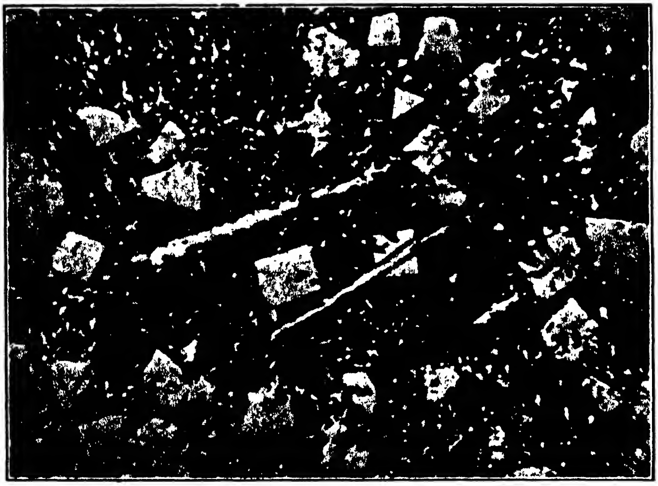

FIG. 27.—Tin-copper-antimony bearing metal. (*Law.*)

The bearing metal proper is made by melting 1 part of this alloy with twice its weight of tin, which makes a final alloy having the following composition: copper, 3.7 per cent; antimony, 7.4 per cent; and tin, 88.9 per cent.[1]

The Leaded Bronzes.—Bronzes to which a considerable amount of lead has been added are also used as bearing metals, but their structure is the reverse of the white alloys, since they consist of soft grains in a hard matrix. They are inferior to the white alloys as bearing metals, because they are less plastic and do not mold about the shaft so well. Although they are

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[1] For detailed directions for making babbitt alloy, see *Foundry*, data sheet 81, January, 1911.

stronger than the white alloys, this does not allow then to bear heavier loads, because they have a greater tendency to "cut."

A leaded bronze that is used to a considerable extent for bearings has the following composition: copper, 64 per cent; tin, 5 per cent; lead, 30 per cent; and nickel, 1 per cent. This is known as plastic bronze; although it is not so plastic as the white alloys, it is more plastic than an ordinary bronze.

The structure of the plastic bronze is largely determined by the fact that lead does not alloy much with copper nor with bronzes having a low tin content, and therefore remains to a large extent as an independent constituent in the bronze. The copper-tin alloy becomes the matrix in which the grains of lead are held. The small amount of nickel probably lessens the segregation of the lead by causing the alloy to solidify at a higher temperature. Aside from the fact that the presence of lead increases the plasticity of the bronze, the soft granules wear more rapidly than the harder matrix and form cavities in which the lubricant may be held.

SOLDER

Solder is a readily fusible alloy used to join the surfaces of metals. Its joining ability depends upon the fact that a surface alloy is formed between the solder and the parts soldered. Soldering may be accomplished by the means of various alloys, the composition of which depends upon the melting point desired and the metals to be joined. The most common solder, however, is an alloy of tin and lead, known as *soft*, or *tinner's, solder*. This is used for a great variety of purposes.

Physical Structure of Soft Solder.—The freezing-point curve for the lead-tin alloys is shown on page 169. As is indicated there, those alloys containing no more than 4 per cent of tin or no more than 2 per cent of lead solidify as solid solutions. All of the other alloys of these two metals solidify with the formation of eutectics as is shown in this figure; the eutectic contains approximately 31 per cent of lead.[1] The tin content of the commercial lead-tin alloys ranges from about 25 to 75 per cent, hence the structure of these alloys consists of more or

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[1] For a discussion of this figure see p. 168.

less pure crystals of either tin or lead, depending upon the proportions used, held in a matrix of smaller crystals of the eutectic.

Composition and Properties.—The tensile strength of solder is greatest with 72.5 per cent of lead, but this alloy is not sufficiently fusible to be used for general soldering. Any of the alloys that contain above 70 per cent of lead have a melting point too high to be used in ordinary soldering with a copper tool, although they may be used with a steel one. The chief use to which such alloys are put is for coating iron or steel sheets for roofing, for filling hollow castings, etc.

The alloy that contains about 67 per cent of lead is used for plumber's solder; it will be discussed later under that head. The alloys containing from 55 to 60 per cent of lead melt from about 215 to 230°C., and are sufficiently fusible and freely flowing for ordinary soldering. That which contains 58 per cent of lead is used to a considerable extent for soldering joints in electric wiring because it is considered an easily flowing solder.

But by far the favorite alloy with those who use solder is that which contains 50 per cent lead and 50 per cent tin; it is known commonly as "half and half." This alloy melts readily, flows freely, and presents a bright surface when the joint is finished. It can be used for every purpose to which soft solder is applicable, except "wiping joints," as it is technically called, in plumbing. But all kinds of work do not require a solder as high in tin as this, even though, because of its many good properties, it is much desired by the user. Its high price is a very great objection. Since the consumer desires to buy solder cheaply it happens that many grades of solder appear on the market designated as "half and half" that contain much less than 50 per cent of tin. Very often the upper limit of the amount of tin contained in the "half and half" solder is determined by the price the customer is willing to pay.

For some purposes, as for manufacturing gas meters, electrical instruments, etc., where a bright, freely flowing solder is desired, in order that all joints may be completely filled with the solder, greater amounts than 50 per cent of tin are used. As is shown by the freezing-point curve in Fig. 10, the melting point of the alloy falls gradually with increase of tin up to the amount of 69 per cent. This is the eutectic alloy and melts at 180°C., the lowest temperature at which any alloy of lead and tin will melt. A disadvantage in using a solder containing so much tin is that it forms an alloy with the copper of the soldering tool and etches it away; by this action the surface is pitted. When the soldering tool has been pitted, it is somewhat difficult to file smooth, because the surface alloy formed is rather hard. The difficulty may be avoided by using a steel tool.

In soldering work that has been galvanized, it is necessary to use solder containing an excess of tin. Galvanizing consists of a surface coating of zinc, and since lead does not alloy well with zinc, a good joint cannot be made if an excess of lead is present.

Schultz says[1] that solder that contains at least 50 per cent of tin may be known by the character of its surface when it is allowed to cool in an open mold. It will be uniformly bright. If any frosted lines appear, it may be known that it contains less than 50 per cent tin. Solder that contains more than 50 per cent tin will have the same bright surface, but when lead is in excess, the frosted surface appears and increases with the increase of lead until when the alloy contains 67 per cent of lead the surface will be frosted all over. Workmen make use of this fact in preparing solder containing a preponderance of lead, as for "wiping joints" in plumbing. Lead is added to the molten solder until the desired proportions are obtained as is shown by the surface when it cools.

Plumber's solder contains usually 67 per cent of lead and 33 per cent of tin. As this alloy cools through its solidification range, as shown in Fig. 10, it acquires a plastic condition, in which it has about the consistency of baker's dough, before it cools enough to grow hard. While in this plastic state it may be molded into shape in the so-called "wiping of joints." Solders may be used in this way that contain from 60 to 67 per cent of lead. The 60 per cent alloy begins to assume the plastic state at about 235°C., and the 67 per cent alloy at about 243°C. The final solidification of both takes place at 180°C., the eutectic point, so that there is a range of about 55 to 60°C. during which they are plastic. The plasticity is due to the presence of the lead crystals that separate out as the temperature falls. The portion

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[1] SCHULTZ, F. W., "Tin, Lead, and Solder," chap. XIII, 1908.

that still remains fluid serves as a vehicle in which the crystals are carried. The crystals increase the consistency of the fluid portion in much the same manner as additions of sand increase the consistency of a thin mortar. It is these lead crystals also that give to the wiped joint its frosted appearance; they are responsible also for the frosted appearance of the solder when poured in an open mold as was mentioned in the preceding paragraph.

Occasionally it is necessary to use block tin[1] for certain purposes, as for making receptacles and conductors for distilled water, and for syrups and liquid charged with carbon dioxide. Now since plumber's solder begins to assume the pasty state at a temperature somewhat above the melting point of tin, considerable care and skill are required if it is to be employed for joining articles made of this metal. An alloy consisting of 2 parts tin, 2 parts lead, and 1 part bismuth, melting at 145°C., may be used as a solder under these conditions.

Care of Solder.—When using solder it is highly essential that it be kept absolutely free from oxides and foreign material of every kind. It is bad practice to gather scraps and droppings from the floor and put them back into the melting pot, since foreign metals are then likely to be introduced. More than ordinary care must be exercised when soldering upon galvanized articles or brass, because the solder that has been brought into contact with these zinc-bearing alloys is almost certain to acquire a small quantity of zinc. And when lead is added to the solder by the consumer there is also a likelihood that foreign metals will be introduced. Lead is very likely to contain small quantities of such metals as arsenic, antimony, zinc, etc. In the manufacture of solder these impurities are removed, usually by a process of oxidation.

The Effect of Foreign Elements in Solder.—Arsenic, antimony, iron, copper, zinc, and sulfur, all have detrimental effects on solder.

Arsenic causes the solder to be hard and brittle. Fortunately it oxidizes very readily and but little of it remains for very long. The presence of arsenic may be detected by its garlicky odor as it oxidizes.

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[1] See p. 117.

Antimony has an effect similar to that of arsenic, but it is not so readily removable. When as much as 2 per cent is present, small, bright crystal faces appear on the surface of the solder when the alloy is poured in an open mold.[1]

Iron, even in amounts much less than 1 per cent, causes the solder to have a noticeably high melting point and to be sluggish when molten. When solder containing iron is poured in an open mold the surface will have readily perceptible dark streaks upon it.[1] Iron in solder is difficult to remove.

Copper finds its way into solder perhaps more frequently than any other foreign metal. This results from the practice of filing the copper tool to brighten it before tinning and then allowing the filings to find their way into the molten solder with solder scrap. When poured into an open mold the presence of copper in solder is indicated by a slight iridescence or pale-blue color where the solder comes into contact with the iron. It is difficult to remove copper from solder because it readily forms an alloy with tin, and oxidizes less readily than either lead or tin.

Zinc is usually found to be more objectionable to the users of solder than any of the other elements mentioned. Like copper and iron, it causes the solder to flow sluggishly; small lumps occur which cause the work to appear rough. Because of these objectionable features, an effort is usually made to remove the zinc.

Removal of Zinc.—Users of solder have been taught to employ sulfur as a medium for the removal of the real or fancied presence of zinc. It should be remembered, however, that when sulfur is brought into contact with any of the common metals in the molten state, it immediately combines with them with the formation of sulfides. By the introduction of sulfur into molten solder, a great amount of lead and tin are wasted, because their sulfides which are formed are skimmed off and thrown away. Still, small amounts of these sulfides remain occluded in the solder and are in themselves objectionable.

Zinc may be removed from solder by oxidation, which is one of the commonest methods of purifying metals. Moreover, the oxidation is promoted in this case by the relatively low boiling point of zinc. Zinc boils at 918°C., lead at about 1525°C., and tin at about 2275°C. If the solder is heated to about 1000 or

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[1] SCHULTZ, F. W., *loc. cit.*, chap. XX.

1100°C., the zinc will distill out. For securing this temperature, the ordinary solder-melting device is insufficient, but the necessary heat may be secured in any good blast type of gas-fired crucible furnace. The crucible employed should be of graphite or fire clay. The ordinary, cast-iron, solder-melting pot will not serve because the eutectic in cast iron melts at 1135°C. Besides, at this temperature, the tin of the solder would readily form an alloy with the iron of the pot. While hot the solder should be ladled thoroughly to promote the oxidation of the zinc. The ordinary solder ladle may be employed here if it is not used so continuously that it becomes unduly hot.

After the solder has cooled considerably, it should be fluxed with a small amount of ammonium chloride to remove the metallic oxides that have remained entangled in the melted metal. The chloride should be thoroughly stirred into the melt with a stick of green wood or a carbon rod such as the electrode employed in the ordinary arc light. The cast-iron ladle must not be used for this purpose because the ammonium chloride will cause the solder to form an alloy with the iron. If the oxides were not removed, they would cause the solder to be sluggish when melted and weak when solidified. Ammonium chloride is easily volatilized, so that a considerable amount of fume will be produced during the process.

Aluminum Solder.—For aluminum, the solders most generally used are the tin-zinc alloys. The tin may range from 50 to 75 per cent, with the remainder zinc. An alloy consisting of 8 to 15 per cent zinc, 5 to 12 per cent aluminum, and the remainder tin has also been found satisfactory. A cadmium-zinc alloy, containing 40 per cent cadmium and the remainder zinc, although more difficult to melt than the preceding alloys, has better corrosion resistance. With regard to corrosion resistance pure zinc is the best aluminum solder, but it is somewhat difficult to work.[1]

In using these solders, the edges to be joined are filed or are scraped clean, and if the article will allow it, it is heated with a torch or similar device to a temperature at which the solder will melt; then the edges are rubbed briskly with a stick of the solder.

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[1] Edwards, Frary, and Jeffries, "The Aluminum Industry," vol. II, p. 463.

If the object cannot be heated in the manner stated, then the edges are heated with a tinned copper tool and the solder is rubbed on as before described. No flux of any kind is used. When the melted solder has run well over the surfaces to be joined, they are held pressed firmly together until the solder has solidified.

In no case should much dependence be placed on a soldered aluminum joint. This is particularly true if the work is exposed to the weather or to a damp atmosphere. Aluminum solders are electropositive to aluminum, and, in the presence of moisture, an electrolytic action is developed that causes the joints to disintegrate. There is no solder for aluminum of which this is not true.[1]

The Use of Fluxes in Soldering.—The value of a flux depends upon its ability to gather up, by dissolving or otherwise, the oxide or other adherent matter on the surface of the metal. It must stay in place also and keep away the oxygen of the air so that further oxidation cannot take place before the solder can be caused to flow over the cleaned surface and alloy with it. If the metal were cleaned mechanically, as with a file, a film of oxide, imperceptible to the eye, would spread over the surface of the metal before the solder could be applied. Solder cannot alloy or combine with metallic oxides. In the method described for soldering aluminum, although the metal becomes oxidized after it is cleaned by filing or scraping, this relatively thin oxide layer is removed at the moment the melted solder is applied by rubbing with the stick of solder itself.

Kinds of Fluxes.—For use with the ordinary lead-tin solder, *zinc chloride* is a very serviceable flux for practically all the common metals and alloys. It does not serve for aluminum, however, because the oxide on aluminum forms so readily and adheres so tenaciously that some special method, such as that previously described, must be used. Zinc chloride may be employed in the form of a solution, as a paste made of the salt slightly moistened with water, or as a paste made by stirring the finely divided salt into *vaseline*. Instead of using vaseline, a mixture of fats such as *olive oil* and *tallow*, either with or without *rosin*, may be employed. The fats and the rosin are first melted

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[1] "Solders for Aluminum," *U. S. Bur. Standards Circ.* 78, March, 1923.

together and the zinc chloride is then stirred in. Sometimes *ammonium chloride* is used to replace a part of the zinc chloride in these mixtures.

If a solution of zinc chloride is to be used, it is prepared most cheaply by diluting commercial hydrochloric acid with water and then neutralizing it with zinc in excess. If the acid is not sufficiently diluted it will not all be neutralized, since after the zinc ions in solution reach a certain concentration, it becomes increasingly difficult for more zinc to dissolve. After action has ceased, the solution may be tested for complete neutralization of acid by taking a sample and diluting it with about half its volume of water and then inserting a piece of zinc. If effervescence occurs, the whole of the stock solution must be further diluted and allowed to stand longer with the zinc.

Although *hydrochloric acid*[1] by itself is often used as a flux, it is not recommended. It leaves the metal in an etched or pitted condition. The dissolved salts in these pits are then sealed in when the solder is applied; numerous minute electric cells are formed. The electrochemical action that is set up weakens the joint eventually, particularly when the work is exposed to the weather. A similar action, although less pronounced, may occur when the zinc ănd ammonium chlorides are used for work that is exposed to the weather. When used in the paste form with the vaseline or fats, the chance of this occurring is practically eliminated. Although it is a much less active fluxing agent than the chlorides that have been mentioned, for outside work, *rosin*, used alone, is often employed as a flux.

In the so-called "brazing process," borax, either with or without a little ammonium chloride, is used as a flux.

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[1] For a comparison of the values of hydrochloric acid and zinc and ammonium chlorides, see Lippmann, "The Chemistry of Soldering Agents," *Sci. Amer.*, **101**, 389, 1909.

CHAPTER VI

IRON AND STEEL

Occurrence of Iron.—Iron exists in almost every portion of the earth's surface, but only very rarely is it found in the free state, and nowhere is it obtained in commercial quantities in this condition. This scarcity is due to the marked instability of the metallic element in the presence of air and moisture.

IRON ORES

The ores of iron include the oxides, hydroxides, carbonates, and sulfides. Of these, the most important commercial forms are haematite, magnetite, limonite, and siderite. Pyrite is used to some extent.

Haematite (Fe_2O_3).—With respect to composition, this ore is equivalent to ordinary iron rust from which most of the combined water has been removed. Theoretically, it contains 70 per cent of iron, but because of impurities, especially of an earthy nature, the amount of iron present in the commercial variety usually does not exceed 55 to 58 per cent. The ore may vary in color from red to brown, or even black, but it always produces a red streak when drawn across a surface of unglazed porcelain; it may be identified by this test. In some deposits it occurs more or less in the form of hard lumps, while in others it is of a soft, earthy nature. In the open-pit mines of the Mesabi Range in the Lake Superior district, the ore is loaded on open cars by means of steam shovels.

Haematite is the chief ore of the United States and many other countries; in fact, it is found on all the continents and is the most important ore in the world for the production of iron.

Magnetite (Fe_3O_4).—This ore, the hardest and richest of all the ores, has the same composition as mill or forge scale. If pure, it would contain 72.42 per cent of iron. It shows a black streak on porcelain. It is highly magnetic, from which fact its name has been derived. Naturally magnetized specimens are known as lodestone.

Although not an important ore in the United States, some magnetite is mined in eastern New York and northern New Jersey, but it contains impurities, such as silica, phosphorus, and titanium oxide, in objectionable quantities. On the other hand, the magnetite ores of Sweden are of exceptionally high grade, and form one of the sources of Swedish iron and steel, so well known for their purity.

Limonite (Fe_2O_3, nH_2O) is a hydrated haematite, containing about 15 per cent of combined water. The commercial ore contains from 40 to 50 per cent of iron. It is found to a considerable extent in southern ore deposits of the United States and in Cuba.

Siderite ($FeCO_3$) called also "spathic ore," contains 48 per cent of iron when pure, but as mined, the iron content ranges usually from 30 to 40 per cent. Siderite was formerly an important ore in Pennsylvania, but now is of little consequence anywhere in the United States. The principal known deposits occur in Germany, England, and Wales.

Pyrite (FeS_2) in the pure form has an iron content of 47 per cent. It is of a golden-brown color and produces a greenish or brownish-black streak on porcelain. It is found very widely distributed, but because it must first be roasted to remove the sulfur and to convert the iron into its oxide, and because other much more desirable ores are relatively abundant, there is very little iron derived at present from the pyrite. It is possible that a time may come when this ore will be regarded with greater favor.

THE PRODUCTION OF IRON

Reduction of the Ore.—In the metallurgy of iron, the oxide of the ore is reduced to the metallic state by the use of carbon. Coke or charcoal have been found best for this purpose. The process is carried out in a tall, cylindrical type of furnace known as the blast furnace.

The Blast Furnace.—The general character of the furnace is shown in Fig. 28. It is a brick-lined, steel structure from 90 to 100 ft. high and 30 ft. in diameter at its widest part. That part of the base which has perpendicular walls is called the hearth or crucible of the furnace. The melted iron and slag collect here. At the bottom of the hearth is an opening, called the iron notch, for drawing off the iron. The location of the iron notch is indicated by *L* in Fig. 29. Another opening called the slag or cinder notch, about halfway up the hearth, is used for drawing off the slag. When not in use, both openings are closed by ramming in moistened fire clay.

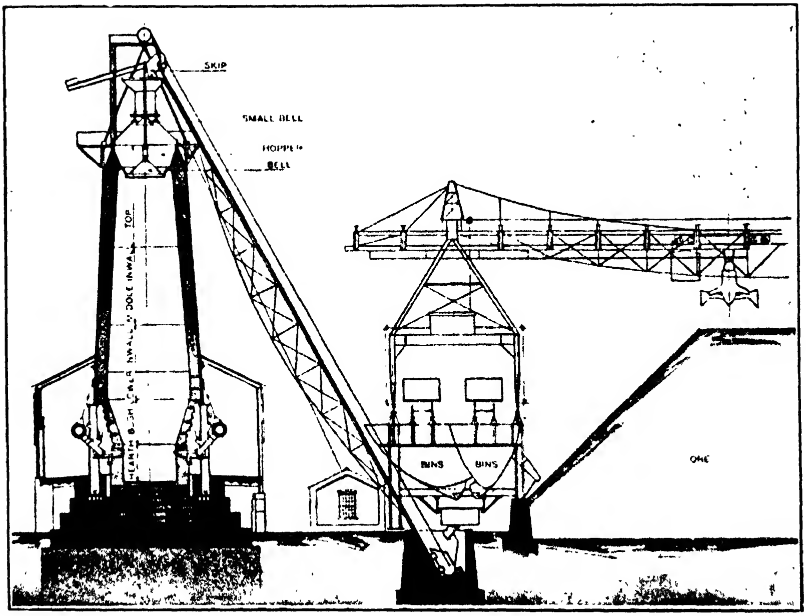

FIG. 28.—Section of blast furnace showing filling arrangement, bins and ore bridge.

Through the wall of the upper part of the hearth, previously heated air blast is introduced through 10 to 16 injectors known as tuyères, equally spaced about the furnace. The ends of the tuyères are surrounded by hollow bronze rings through which cold water is circulated to prevent them from fusing. The air blast from the blowing engines is supplied to the tuyères from a large, refractory-lined conduit about 4 ft. in diameter, known as a bustle pipe, which completely surrounds the furnace.

The inverted cone frustrum just above the hearth is known as the bosh. The descending inward slope of the walls of the bosh tends to promote arching of the charge and checks its downward movement at this point. The bosh is the fusion zone. To assist the walls in withstanding the high temperature, hollow castings known as "bosh plates," through which cold water is circulated, are set in the brick work. In the left wall of the bosh in Fig. 29 the increased abrasion resistance that results from the cooling has been illustrated.

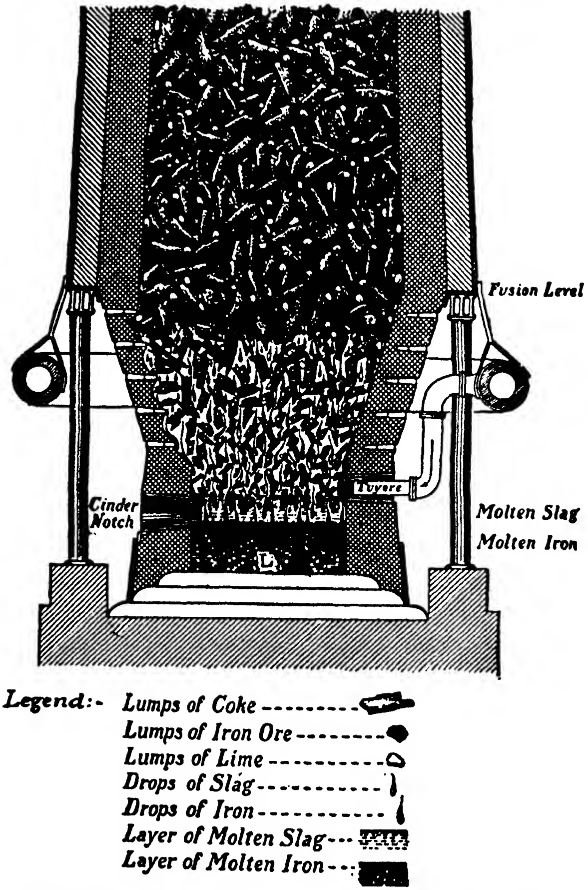

Fig. 29.—Lower part of blast furnace. The left wall of the bosh shows wear. (*Howe.*)

The upper part of the furnace, between the bosh and the bell, is known as the stack. It is lined with a refractory lining, which in thick-walled furnaces is 5 ft. thick. The stack rests upon an annular support known as the "mantle ring," which in turn is supported by 8 to 12 pillars, two of which are shown in the illustration. The stack widens downward to allow the charge to descend easily without sticking.

The top of the furnace is equipped with a hopper and double bell for introducing the materials of the charge. The materials are conveyed to the hopper by small cars known as "skips," which are operated over an inclined runway by means of cables. In Fig. 28, one of the skips is in a position to be discharged, while the other is in the loading pit beneath the bins.

The gases from the top of the furnace are conducted away through a large conduit known as a "downtake" or "downcomer." It leads off just below the lower bell and delivers into the dust catcher. The dust catcher is a circular, steel receptacle, somewhat funnel-shaped at the base, in which the fine particles of ore, coke, etc., that have been swept along by the blast, are deposited. The material collected is periodically dumped into hopper cars and taken away to the sintering plant, where it is heated to incipient fusion to cause it to mass together in small lumps so that it will not again be blown out when it is returned to the furnace. If more complete purification of the gases is desired, as when they are to be used in an internal combustion engine, they are conveyed to a scrubber or gas washer.

The Blowing Engines.—The blast for the furnace is developed by a battery of blowing engines. These are usually gas engines operating on the washed gases from the top of the furnace, and are capable of developing from 2,000 to 2,500 hp. each. The rated capacity of an engine of this kind is from 50,000 to 65,000 cu. ft. of air per minute at a pressure of 15 to 30 lb. per square inch, which about fulfills the requirements of one furnace.[1]

The Stoves.—Since the introduction of the great volume of air that is necessary would cool the furnace if it were injected at atmospheric temperature, the blast is preheated in stoves. The stoves are tall, cylindrical steel shells, approximately as high and as wide as the furnace, with a relatively small, tubular combus-

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[1] Stoughton, "Metallurgy of Iron and Steel," p. 20.

tion chamber in the center or at the side, and numerous small flues of fire brick for heat absorption. The gas mixed with air is blown in at the base of the combustion chamber, burns as it passes upward, and the hot products of combustion are discharged downward through the flues on their way to the stack. When the brick work is sufficiently hot, the air from the blowing engines is sent through the heated stove in the reverse direction. In this manner the blast is heated to 500 or 600°C. (approximately 1000°F.). With a furnace having four stoves, each stove will likely be on gas 3 hr. and on air 1 hr. Only about one-third of the top gases of the furnace is needed for heating the blast; the remainder is used for developing power for various purposes about the plant.

THE INPUT OF THE BLAST FURNACE

The Charge.—The total amount of material dumped into the top of a large, modern, American furnace frequently exceeds 2,000 tons in 24 hr. This consists usually of 1 part limestone, a little less than 2 parts fuel, and a little more than 3 parts ore. The material is dumped into the hopper and by alternately opening and closing the two bells, it is passed into the furnace without allowing the blast at any time a free exit. With the single bell of the earlier furnaces, as much as 15 per cent of the charge was blown away during charging. About 15 hr. are required for any given unit of the charge to pass through the furnace.

The Fuel.—Coke is the fuel generally used, because it is relatively cheap and because it best supports the weight of the charge; it has, however, a high ash content that must be fluxed. In some respects charcoal is more desirable than coke. It has a much lower ash content, and contains much less sulfur and phosphorus, both of which are undesirable in a metallurgical fuel. On the other hand, charcoal is expensive and is not strong and firm. For the use of charcoal, smaller furnaces must be built. If charcoal were used in the usual coke furnace, the fuel bed in the bosh would be crushed by the weight of the charge, and the blast could not easily ascend. Only about 1 per cent of the iron produced in the United States is charcoal iron, but because of its higher purity, it sells for 25 to 30 per cent more than the coke iron. In Sweden the largest part of the iron produced is charcoal iron.

The Flux.—The earthy material of the ore, called gangue, and the ash of the fuel are difficult to melt; consequently, some substance called a flux is required to react with them and produce a readily fusible slag. Otherwise, the furnace would soon be clogged. Since the gangue and ash are rich in silica (SiO_2) which is an acid anhydride, a basic anhydride is required as a flux. Limestone is generally employed for this purpose. As it descends through the furnace it is dissociated by the heat into lime and carbon dioxide. The lime reacts with the silica and also with the alumina of the clay, forming the corresponding silicates and aluminates which melt more easily than the anhydrides themselves. The lime is also concerned with reactions involving the sulfur, as will be later explained.

The Blast.—About 60 per cent of the weight of the total input of the furnace is air. Four or five tons of air are required for each ton of iron produced. Of this enormous amount, 77 per cent is nitrogen, which serves practically no purpose other than to absorb heat in the lower levels of the furnace and distribute it through the charge in the upper part. The oxygen, of course, is the active constituent of the blast. The reactions in which it eventually becomes involved are shown later on page 226. Before entering the furnace the blast is heated in stoves as previously described.[1]

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[1] The constituent of the blast that is third in amount is the moisture or water vapor. Depending upon the humidity of the atmosphere, this varies from $\frac{1}{3}$ to 2 gal. of water for each 10,000 cu. ft. of blast. It has been estimated that during the month of July, for example, the average quantity of water that enters a furnace using 40,000 cu. ft. of air per minute is approximately 224 gal. per hour. The water vapor reacts with the heated carbon, producing carbon monoxide and hydrogen; although they afterward burn, the reaction of formation is endothermic and heat is thus removed from the zone of fusion where it is most desired. On this account, at a few plants, the blast at one time was first dried by condensing the moisture in chambers chilled to a low temperature by refrigerating machinery. It was found that as much as 15 per cent of the fuel otherwise required could be saved in this way, but the cost of drying the blast and maintaining the drying equipment more than counterbalanced the saving in fuel.

REACTIONS IN THE FURNACE

Furnace Zones.—For convenience in studying the reactions, the furnace will be divided into three zones:

1. An upper zone, extending downward from the surface of the stock to about 30 ft. above the level of the tuyères, or between the temperatures of about 250 and 800°C.

2. A middle zone, extending from the lower limit of the upper zone to the top of the bosh, or between the temperatures of about 800 and 1250°C.

3. The smelting zone, extending from the top of the bosh to the surface of the melted iron, or between the temperatures of about 1250 and 2000°C.

1. The Upper Zone.—When the materials of the charge are introduced into the furnace, they come immediately into contact with a rapidly moving current of hot gases. One constituent of the gas stream is CO, which is present in sufficient quantity to produce strongly reducing conditions. Although the reactions are rather interwoven, there are three main occurrences that should receive attention in this zone.

a. The liberation of carbon: This begins at almost the very top of the stock; the carbon is deposited in a form similar to lampblack on the walls of the furnace and the constituents of the charge [Eq.(1)].

b. The gradual reduction of the ore: The ore passes from ferric oxide to magnetic oxide; to ferrous oxide; to metallic iron, not melted, but in the red-hot, spongy form [Eqs. (2) to (4)].

c. The gradual increase in the amount of carbon dioxide in the gas stream as it passes upward [Eqs. (1) to (4)].

The reactions taking place in the upper zone are represented by the following equations:

$$2Fe_2O_3 + 8CO \rightarrow 7CO_2 + 4Fe + C \qquad (1)$$

$$3Fe_2O_3 + \left\{\begin{matrix} C & & CO \\ & \rightarrow & \\ CO & & CO_2 \end{matrix}\right\} + 2Fe_3O_4 \qquad (2)$$

$$Fe_3O_4 + \left\{\begin{matrix} C & & CO \\ & \rightarrow & \\ CO & & CO_2 \end{matrix}\right\} + 3FeO \qquad (3)$$

$$FeO + \left\{\begin{matrix} C & & CO \\ & \rightarrow & \\ CO & & CO_2 \end{matrix}\right\} + Fe \qquad (4)$$

Opposing Reactions.—The carbon dioxide produced as shown in the preceding equations becomes involved in secondary reactions. In these reactions some of the reduced iron and carbon are reoxidized, as follows:

$$C + CO_2 \rightarrow 2CO \tag{5}$$
$$Fe + CO_2 \rightarrow FeO + CO \tag{6}$$

The ferrous oxide produced, as in Eq. (6), is again reduced by the time the temperature of 800°C. is reached.

2. The Middle Zone.—There are two important reactions occurring in this zone:

a. The decomposition of the calcium carbonate of the limestone into lime and carbon dioxide [Eq. (7)].

b. The reduction of carbon dioxide to carbon monoxide [Eq. (8)], as:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{7}$$
$$CO_2 + C \rightarrow 2CO \tag{8}$$

There is another occurrence in this zone that, although not of a chemical nature, is important; carbon is absorbed by the spongy iron that has been reduced. These two elements form, in a sense, an iron-carbon alloy which is easily melted when the zone of fusion is reached.

3. The Smelting Zone.—The material that enters this zone is mainly a mixture of gangue, quicklime, coke and spongy iron. The occurrences are:

a. The melting of the spongy iron, which becomes saturated with carbon as it trickles over the coke.

b. The formation and fusion of the calcium silicates and aluminates [Eq. (9)]. The silica and alumina enter the furnace in the ore and the ash of the coke.

c. The reduction of silica to silicon [Eq. (10)].

d. The conversion of iron sulfide into calcium sulfide [Eq. (11)]. The iron sulfide occurs both as ferrous sulfide and iron pyrite in the ore and fuel.

e. The reduction of the P_2O_5 of the phosphates [Eq. (12)]. The phosphates also are impurities in the ore and ash of the coke.

f. The reduction of the manganese oxide [Eq. (13)]. Apparently all iron ores contain small quantities of manganese ore, usually as the dioxide MnO_2.

The melted material collects in the hearth in two layers, the slag above the iron. As in all smelting operations, the reduced elements are dissolved by the metallic layer; those that are still in the oxidized form are dissolved by the slag.

The reactions of this zone may be represented as follows:

$$SiO_2 + CaO \rightarrow CaSiO_3 \tag{9}$$

$$SiO_2 + 2C \rightarrow Si + 2CO \tag{10}$$

$$FeS + CaO + C \rightarrow CaS + CO + Fe \tag{11}$$

$$P_2O_5 + 5C \rightarrow 2P + 5CO \tag{12}$$

$$MnO_2 + 2C \rightarrow Mn \rightarrow 2CO \tag{13}$$

Control of the Hearth Reactions.—The hearth reactions are very important because the extent to which they occur controls the characteristics of the iron. The greater portion of the silica will be converted into calcium silicate [Eq. (9)] and will enter the slag; but a part will be reduced to silicon [Eq. (10)] which will enter the iron. In a similar manner a part of the iron sulfide will be transposed to calcium sulfide [Eq. (11)] which will be taken up by the slag; the part that is not transposed will be dissolved by the iron. The reactions represented by Eqs. (9) and (11) are promoted by highly basic slags, so that excess of lime tends to lessen both the silicon and sulfur in the iron. Equations (10) and (11) are promoted by high temperatures. Thus, if the temperature of the furnace is above normal, the amount of silicon in the iron will be high and the sulfur will be low; but if the temperature is lower than normal, the iron will be high in sulfur and low in silicon. For this reason, the quantity of these two elements can be controlled by the furnace operator. On the other hand, the quantity of the phosphorus in the iron can be controlled only by the composition of the materials that are charged into the furnace. The operator can control it in no other way; practically all that enters the furnace, in whatever constituent of the charge, is reduced [Eq. (12)] and ultimately absorbed by the iron. The manganese is nearly all reduced [Eq. (13)] and absorbed by the iron.

Output of the Furnace

The Top Gases.—The composition of the gases issuing from the top of the furnace varies with the other variable factors in furnace operation, but the analysis shown on page 68 may be considered as typical. The thermal value of such a gas is about 90 B.t.u. per cubic foot, and the amount produced from one furnace is about 90,000 cu. ft. per minute.

The Slag.—Depending upon the composition of the materials charged, the quantity of slag may vary approximately from one-half to twice the weight of the iron produced. It consists essentially of the calcium compounds produced by the reaction between the lime and the silica, alumina and the iron oxide, in addition to a little calcium sulfide. The slag is tapped probably three times between each tapping of iron, and is disposed of in various ways. For example, it may be received in large ladles and carried away to the dump, or it may be granulated by running it into a water pit and used for road dressing or in the manufacture of Portland cement.

The Iron.—A large, modern blast furnace will produce from 400 to 600 tons of iron in 24 hr., and may be tapped four or five times in this period, from 100 to 150 tons at a heat. The iron is tapped immediately after a slag run. When ready to tap, the burned-clay plug in the iron notch is removed by drilling and ramming. The melted iron then pours through the runner in the sand at the base of the furnace. It is received in a large ladle and may be removed to the steel plant for direct conversion into steel without cooling, or it may be poured into small molds and allowed to solidify. These molds are generally semicircular or V-shaped in cross-section, are about 5 in. wide at the top, about 24 in. long, and yield a casting weighing from 100 to 125 lb. These castings are known as pigs, or *pig iron*, because formerly it was the custom to cast the iron in sand beds at the base of the furnace, when the open arrangement of channels and molds was said to resemble a sow with suckling pigs. At the present time, the pigs are formed in a mechanical pig-casting machine. This machine consists of an endless chain carrying open metallic molds into which the iron is poured from the ladle as the molds travel slowly past. The molds are coated with either a lime or clay wash to prevent the iron from sticking. Pigs made in this way are not coated with sand as are the sand-cast pigs. Even though, as has been said, the iron may be employed in the manufacture of steel without having been allowed to cool and solidify, it is nevertheless spoken of as pig iron or pig metal.[1]

Grading the Iron.—Since the iron is graded by chemical analysis, samples are taken for this purpose by collecting small ladlefuls at intervals from the iron pouring through the main channel at the base of the furnace during tapping. These samples may be granulated by pouring into water, or drillings may be taken from small castings made of the iron. In addition to the analysis, the fracture of castings made in sand or metal molds is carefully inspected. These tests are called "sand tests" or "chill tests." If the test piece has been properly prepared, the operator can form a close estimate of the quality of the iron by an examination of the surface of the fracture, but the most reliable method, of course, is to grade by chemical analysis.

The usually specified limits for the chief grades of pig iron are as follows:

Grade of iron	Per cent Si	S	P	Mn
Number 1 foundry	2.50–3.00	Under 0.035	0.50–1.00	Under 1.00
Number 2 foundry	2.00–2.50	Under 0.045	0.50–1.00	Under 1.00
Number 3 foundry	1.50–2.00	Under 0.055	0.50–1.00	Under 1.00
Malleable	0.75–1.50	Under 0.050	Under 0.20	Under 1.00
Bessemer	1.00–2.00	Under 0.050	Under 0.10	Under 1.00
Low phosphorus	Under 2.00	Under 0.030	Under 0.03	Under 1.00
Forge	Under 1.50	Under 0.100	Under 1.00	Under 1.00
Basic	Under 1.00	Under 0.050	Under 1.00	Under 1.00

The quantities of silicon and sulfur present are usually the most important considerations in grading the iron. The higher the silicon, within certain limits, and the lower the sulfur, the greater, in general, will be the soundness and softness of the casting.

In the table, the term "malleable" is used to denote iron suitable for making malleable cast iron; restricted silicon and sulfur are important. "Bessemer" denotes iron suitable for making Bessemer (or acid open-hearth) steel. For such iron, phosphorus must not be above the amount allowed in good steel. "Forge"

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[1] Over 38,000,000 tons of pig iron, valued at about two-thirds of a billion dollars, were shipped from the blast furnaces of the United States in 1928.

indicates a low grade of iron high in sulfur that may be used in making wrought iron. "Basic" signifies a high-phosphorus iron that may be converted into steel by the basic open-hearth process because by this method phosphorus may be removed from the metal.

CAST IRON

Cast Iron Distinguished from Other Commercial Forms.—There is no essential difference between cast iron and pig iron. The term pig iron is used to designate the iron in the molten state as it is obtained direct from the furnace as well as when it has been cast in the form of pigs. The term "cast iron" applies more properly when the iron has been cast in some form other than pigs.

From a scientific standpoint, cast iron may be considered as an alloy of iron and carbon. It differs from steel, which is also an alloy of iron and carbon, in its lack of malleability, in its lesser iron and greater carbon content, and in its impurities; the lack of malleability is due, in fact, to the large amount of carbon. Cast iron differs from wrought iron in much the same way as it does from steel, although wrought iron contains much entrained slag, whereas cast iron and steel contain but little.

Composition of Normal Cast Iron.—The following percentages will serve to illustrate the composition of cast iron that is known to the trade as medium iron:

	Per Cent
Carbon	3.50
Silicon	2.00
Sulfur	0.05
Phosphorus	0.75
Manganese	0.70
Iron (by difference)	93.00

Iron Compounds in Cast Iron.—Although commercial analyses of iron (and steel) are reported in the form given in the preceding table, the elements shown do not, as a rule, actually exist in the elementary form. With the exception of a part of the iron and a part of the carbon, they are present as binary iron compounds. In the harder varieties, less than half of the cast iron will consist of elementary iron. In such irons, the carbon is present in the form of an iron carbide Fe_3C. A calculation of the percentage composition will readily show that the weight of the compound is fifteen times as great as the weight of the carbon contained; hence, if the cast iron contained 4 per cent of carbon, all in the combined form, it would contain 60 per cent of iron carbide.

The silicon is present as iron silicide (FeSi); the phosphorus as iron phosphide (Fe_3P or Fe_3P_2); the sulfur as iron or manganese sulfide (FeS or MnS); and the manganese either as the sulfide just mentioned, or as manganese carbide (Mn_3C).

Importance of Impurities in Cast Iron.—As has been indicated in the definition and in the preceding table, the fundamental constituents of any cast iron are the iron and the carbon. The other elements are classed as impurities. It would be possible to have a pure cast iron consisting of iron and carbon only, but it would be only a laboratory curiosity. In the commercial irons, the impurities are always present to some extent; it would be practically impossible to get along without them, for it is chiefly by means of these impurities that the widely varying properties of cast iron are regulated.

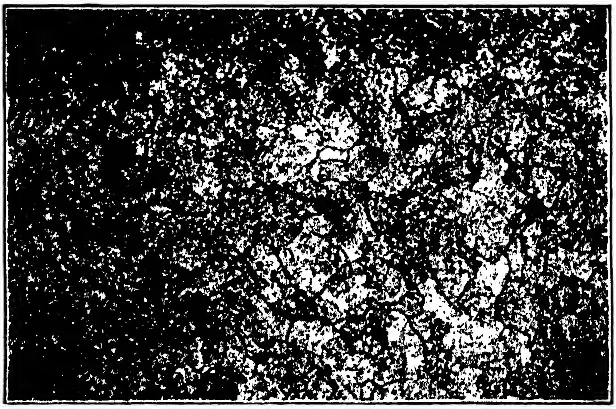

FIG. 30.—Grain structure of carbonless iron, practically 100 per cent ferrite. Magnified 100 diameters.

The Condition of the Carbon in the Iron.—The most important single factor in determining the characteristics of cast iron is the condition of the carbon, *i.e.*, whether it is present in the free state as graphite, or whether it is in the combined state as iron carbide (Fe_3C). In discussing the structure of any of the commercial products consisting essentially of iron, the free iron is designated as ferrite. Before proceeding further with the discussion of the cast irons, it will be advisable to describe the properties of its three major constituents, ferrite, graphite, and iron carbide. The last is known also as cementite.

Ferrite is very soft, but it is very tough, ductile, and malleable. It somewhat resembles copper in respect to these properties. It has very high magnetic permeability and fair electrical conductivity. Wrought iron serves best to illustrate the properties of ferrite, since, aside from the seams of slag which wrought iron carries, it resembles closely the composition of ferrite. The grain structure of ferrite is shown in Fig. 30.

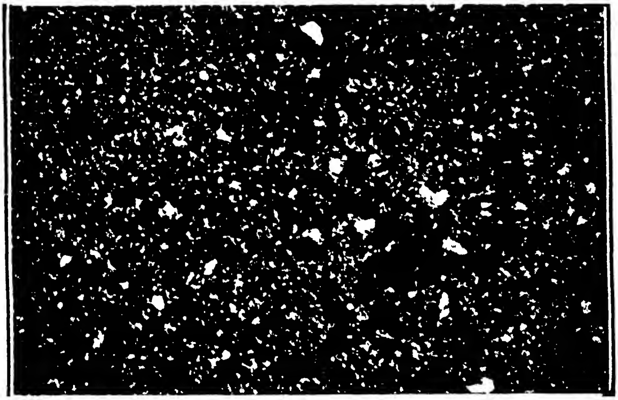

FIG. 31.—Graphite flakes in gray pig iron. Natural size.

Graphite is one of the forms of carbon. It occurs in cast iron in the form of soft, thin flakes, which may vary in size from particles just visible with the microscope to others one-eighth of an inch square, as illustrated in Fig. 31. Each flake is composed of other flakes, which have but little coherence between them. Graphite has a relatively low specific gravity, being only 2.25 as compared with pure iron, which has a specific gravity of 7.86. On this account, an iron that contains 3 per cent by weight, contains by volume about 12 per cent of graphite.

Cementite (Fe_3C) is an extremely hard substance—the hardest of all the constituents in iron or steel. It is harder than glass and almost as brittle. It has a very low resistance to shocks or any form of vibratory stress. By weight it is, as has been pointed out, roughly one-fifteenth carbon. It usually crystallizes in the form of relatively thin, flat plates. In Fig. 32 are shown crystals of cementite removed from an iron high in carbon while it was solidifying.

The manganese carbide Mn_3C is often found crystallized with the iron carbide. These combined crystals are known as *manganiferous cementite.*

Decomposition of Cementite.—When the melted cast iron has just solidified, the carbon is in the combined form as iron carbide.

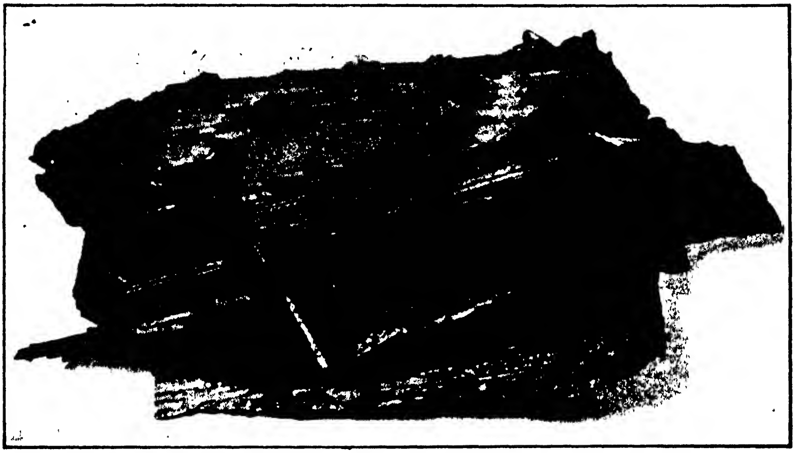

FIG. 32.—Primary cementite crystals. Slightly reduced.

Depending upon conditions, during the cooling of the iron to atmospheric temperature, the carbide may or may not decompose[1] into ferrite and graphite in accordance with the following equation:

$$Fe_3C \rightarrow 3Fe + C$$

Whether this decomposition will take place or not, is determined largely by two factors: the effect of the impurities, and the cooling rate. Of the impurities, silicon and sulfur are the most important; silicon tends to promote the reaction while sulfur opposes it. The predominating effect is determined by the

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[1] The manner in which the cementite is formed and the mechanism of its decomposition is explained later on pp. 311 to 313.

relative amounts of these impurities in the iron. The action of phosphorus and manganese cannot be stated so briefly; their effects will be explained later when these elements are discussed.

The effect of the cooling rate is easily understood. As in all chemical reactions, a certain amount of time is necessary for the decomposition reaction to run to completion. Hence, if the cast iron is quickly cooled, the amount of decomposition will be lessened. In fact, if the silicon is very low, the sulfur high, and the cooling rate very rapid, it is possible that practically no cementite will be dissociated. On the other hand, if the silicon is high, the sulfur low, and the cooling rate slow, most of the cementite will decompose; the iron will then contain its carbon largely in the graphitic condition.

Fig. 33.—Fractures of gray and white cast iron.

Kinds of Cast Iron.—Depending upon the condition in which the carbon exists, pig iron and cast iron may be divided into two major classes: (1) Pig and cast iron in the fracture of which the iron itself is nearly concealed by the graphite so that the fracture has the color of the graphite is called *gray pig* or *cast iron*. (2) Pig and cast iron in the fracture of which little or no graphite is visible so that the fracture is silvery white is called *white iron*. In this kind of iron the carbon is nearly all combined.

In the commercial cast irons, the carbon, which may amount to 3 or 4 per cent, is neither wholly combined in the white iron, nor wholly graphitic in the gray. The white iron will contain some graphite, although the flakes will be small and not readily visible on the face of the fracture. Gray-iron castings will contain usually from 0.25 to 1.50 per cent of combined carbon and the remainder in the graphitic state.

Cast irons which are a mixture of the gray and the white are sometimes produced. Such irons are called *mottled iron* because of the appearance of their fractures.

FIG. 34.—White cast iron containing about 3 per cent combined carbon. The light areas are cementite. Magnified 56 diameters.[1]

Physical Properties of Cast Iron.—If we assume that a *white cast iron* contains 3 per cent of combined carbon, then it will contain approximately 45 per cent of iron carbide (Fe_3C). It therefore partakes of the nature of this compound. Thus, white cast iron is very hard and brittle, and can be readily shattered by hammer blows. It is machined only with the greatest difficulty; on the other hand, it will withstand abrasion well during use. Its uses are few as compared to gray iron.

In *gray cast iron,* graphitic carbon predominates. This predominance implies a relatively small amount of combined

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

carbon and consequently the existence of much ferrite. Since both graphite and ferrite are soft, gray iron also is relatively soft. Because of its softness, gray iron is used for general foundry purposes, since most castings require some machining. Also, in the gray casting, the formation of the graphite crystals prevents the excessive shrinkage which is so characteristic of the white iron. Other properties that make the gray iron suitable for foundry purposes are: its low melting point, its fluidity, and the ease with which its properties may be varied.

FIG. 35.—Gray cast iron free from combined carbon. Magnified 100 diameters. Not etched. (*Langenberg.*)[1]

Its disadvantages are: its lack of strength, ductility, and malleability. The reason for the lack of these properties in gray iron is quite apparent, for, although the ferrite of which it is largely composed is very ductile and malleable, the flake-

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

like graphite crystals very effectually break up the continuity of the metallic mass, as is shown in Fig. 35, so that it becomes weak and brittle.

In order to summarize briefly those properties of cast iron that are dependent upon the condition of the carbon the following table is quoted from Howe.[1]

PROPER DISTRIBUTION OF CARBON BETWEEN THE STATES OF GRAPHITE AND CEMENTITE TO GIVE VARIOUS PROPERTIES

Properties sought	Example of use	Distribution of carbon		Color of iron
		Cementite	Graphite	
Resistance to shock	Machinery	Little	....	Open gray
Softness, easy machining	Machinery	Little	....	Open gray
Sharpness of detail, expansion in solidifying	Ornaments	....	Much	Open gray
Fluidity (phosphorus)	Pipes	Moderate	....	Close gray (No. 3)
Strength	Car-wheel centers	Moderate	....	Close gray
Imperviousness	Hydraulic cylinders, radiators	....	Very little	Very close gray
Hardness	Tread of car wheels	Much	....	Nearly white

Chilled Cast Iron.—For some purposes castings are desired that have one or more surfaces very hard, so that they may resist wear, without the casting at the same time being brittle. This combination of properties is secured by producing castings with an outside layer rich in cementite, and an interior of normal gray iron. In iron for castings of this sort, the silicon must be rather low, about 1.00 per cent, and the sulfur rather high, about 0.07 per cent. If such iron is cooled rather rapidly, the carbon will remain combined; if it is allowed to cool slowly, the cementite will decompose. Then, for the surfaces that are to be hard, the walls of the mold are formed of iron plates. When the casting is poured, the metal that lies against these plates is rapidly cooled, or chilled; the carbon remains largely in the combined form as cementite. The iron of the interior, and of the other surfaces of the casting that lie against the sand, cools much

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[1] "The Metallurgy of Steel and Cast Iron," p. 109.

more slowly, so that the cementite decomposes into ferrite and graphite.

EFFECT OF IMPURITIES IN CAST IRON

The effect of the impurities in cast iron is important. The properties of the iron depend almost entirely on the condition of the carbon; *i.e.*, whether it will be in the free or combined state. The condition of the carbon, in turn, depends very largely upon the amount of impurities present.

Silicon in Cast Iron.—The amount of silicon in cast iron may vary from 0.50 to 3.00 or 3.50 per cent. It is probable that it all combines with iron to form an iron silicide FeSi, which then dissolves in the remainder of the iron. The amount of this iron silicide is equal to exactly three times the weight of the silicon; consequently, if the iron contains, for example, 2.5 per cent of silicon, it will contain 7.5 per cent of iron silicide. Silicon is a very important element in cast iron because of its marked tendency to cause cementite to decompose into ferrite and graphite. It softens and makes easy to machine iron which would, without it, be very hard and brittle.

It has been noted before that slow cooling works in conjunction with silicon. For the conversion of cementite into ferrite and graphite, however, the use of an abundance of silicon, unaided by slow cooling, is preferred to an equivalent production of graphite brought about by less silicon and a prolonged cooling period, because under the latter conditions the graphite flakes will be broad and will introduce more extended planes of weakness into the casting than will the smaller flakes produced by silicon without the help of slow cooling.

When the iron is melted the silicon burns, thus increasing the temperature, and consequently decreasing the amount of sulfur the iron can take up, for it has been observed that a high temperature in a furnace or cupola causes the iron to take up less sulfur.

In remelting, silicon acts as a deoxidizer also. It helps to eliminate blowholes by lengthening the time of fluidity of the iron. This action is aided by the fact that it increases the solubility of the gases in the solidifying iron, which lessens the separation of gas bubbles. Its action in lessening the sulfur content also works toward the elimination of blowholes.

Silicon lessens the tendency of iron to "chill," and also tends to offset the hardening effect of manganese.

High-silicon Iron for Acid-proof Castings.—Although in ordinary cast iron, the amount of silicon does not, as a rule, exceed 3 per cent, nearly five times this amount of silicon is employed in castings of a special alloy prepared for its corrosion resistance. The approximate composition of the corrosion-resistant alloy is as follows:[1]

	Per Cent
Silicon	14.25 to 14.50
Carbon	0.75 to 0.85
Manganese	0.30 to 0.60

With these percentages, the product must be considered as an iron-silicon alloy instead of an iron-carbon alloy. Castings of the high-silicon alloy are not made for strength or general utility; in fact, the tensile strength of the alloy is low and its brittleness is high. It cannot be machined conveniently, but must be cast and ground to shape. The alloy shows a remarkably high resistance to hot concentrated sulfuric and nitric acids, but for hot concentrated hydrochloric acid it is generally considered unsuitable. Its resistance to hot dilute and to cold concentrated hydrochloric is fairly satisfactory. Acid-resistant castings of the iron-silicon alloy are sold under the trade names of "Duriron" and "Tantiron."[2]

Sulfur in Cast Iron.—Cast iron of good quality does not contain sulfur in an amount greater than 0.07 per cent, although for special purposes, such as the making of chilled castings, as much as 0.20 per cent may be allowed. It occurs in the iron both in the form of manganese sulfide (MnS), and ferrous sulfide (FeS), but usually in the form of the manganese compound. These metallic sulfides are in turn dissolved in the iron. Each part of sulfur produces approximately 2½ parts of either of the two sulfides. As long as there is sufficient excess of manganese present, practically all of the sulfur will be in compound with that metal, because manganese is able to transpose the ferrous sulfide

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[1] *Chem. Met. Eng.*, **36**, 541, September, 1929.

[2] *Jour. Ind. Eng. Chem.*, **8**, 879, 1916.

into the form of the manganous compound. Should there not be a sufficient excess of manganese present to cause all of the sulfur to combine with it, the remaining sulfur would then exist in the form of the ferrous compound.

The effect of the sulfur upon the condition of the carbon in cast iron is directly opposite to that of silicon. It has a tendency to keep the carbon in the combined form. It is usually considered that 0.01 per cent of sulfur will neutralize the effect of fifteen times (0.15 per cent) as much silicon in this effect upon carbon. Sulfur in the form of the manganese compound, however, is not so effective in this respect as when it is in combination with iron. Consequently, if sufficient manganese is present to combine with all the sulfur, its effect is not so pronounced. Since sulfur keeps carbon combined, white iron usually contains more sulfur than the gray. High sulfur and high silicon are not to be expected in the iron at the same time, since a furnace "working hot" decreases the amount of sulfur and increases the amount of silicon in the iron, while a furnace "working cold" produces an iron high in sulfur and low in silicon (page 228).

Additional effects of sulfur are that it makes the iron somewhat more easily fusible, but makes it more viscous or sluggish when melted. This increased viscosity causes the production of unsound castings because the gas bubbles cannot separate so readily from the more sluggish metal. It increases shrinkage because it prevents the formation of crystals of graphite, which would, if they formed, increase the bulk of the iron and so help to offset the contraction during cooling of the casting. It increases the hardness of the iron. It increases the depth of "chill," *i.e.*, the layer of surface metal of a casting free from graphitic carbon, produced by casting the metal against a metallic wall. It causes the iron to "check," *i.e.*, crack at a red heat; if put under strain at this time it exhibits the phenomenon of "red shortness," *i.e.*, brittleness when red hot. The weakness at a red heat is due to the fact that at this temperature the ferrous sulfide is in the semifluid condition.

Phosphorus in Cast Iron.—In ordinary foundry iron the amount of phosphorus does not usually exceed 1.00 per cent. It exists as definite phosphides (Fe_3P and Fe_3P_2). The effect of phosphorus on the condition of the carbon depends somewhat upon the amount of silicon present. Its direct effect is to keep the carbon in the combined condition; it will do this especially if the amount of silicon is small, for example under 0.75 per cent, and the phosphorus high, for example above 1.25 per cent. But if the amount of silicon is high enough that its effect is quite pronounced, for example between 1.50 and 2.50 per cent, the final effect of phosphorus is to cause carbon to take the graphitic form. The phosphorus does this under these conditions because it has a very marked effect upon the time of fluidity of the iron. It seems to cause the iron to remain fluid, or at least in a semifluid state until much lower temperatures are reached than would be the case if phosphorus were absent. The longer time of fluidity allows the silicon a much greater period, perhaps several minutes longer, through which its influence is effective. Consequently, more graphite is separated, and in larger crystals. High phosphorus causes the iron to be especially easily broken by impact or vibration. This condition is described as "cold shortness." When working in conjunction with silicon phosphorus lessens the amount of shrinkage.

Because of the fact that phosphorus allows the iron to remain fluid at lower temperatures, iron high in phosphorus is selected for making thin castings which naturally cool quickly. If phosphorus were absent, such castings might solidify before the iron had perfectly filled the mold. Being high in phosphorus, articles that are cast in thin section are, therefore, more brittle than they would be if they were cast in larger size of ordinary foundry iron, less rich in phosphorus, and then machined to an equally thin section. This will be further discussed under Composition and Size of Castings.

Manganese in Cast Iron.—Manganese is a metal that resembles iron in many of its properties. It alloys with iron in all proportions, but the amount in cast iron should not exceed 1 per cent as a rule. There is seldom more than 2 per cent, and it may be as low as 0.10 per cent.

Manganese increases the ability of iron to absorb carbon and thus increases the total amount in the iron. All of the manganese in ordinary cast iron exists in combination with either sulfur or carbon. Primarily it combines with sulfur; but if there is sufficient present so that there is an excess above that needed for the sulfur, the excess combines with the carbon and takes the form of manganese carbide, which becomes associated with the iron carbide to form manganiferous cementite.

Because manganese exists in two compound forms in iron, it has contradictory effects upon the condition of the carbon. Any manganese that exists as the carbide serves to keep carbon in the combined form, but that which is in the form of the sulfide is not active in this manner. In fact, its influence is in the opposite direction, because, were it not for the presence of the manganese, the sulfur would exist in the form of ferrous sulfide, which is extremely active in keeping carbon in the cementite form. Manganese transposes sulfur from the ferrous compound into the manganous compound and thus renders it relatively inactive. Besides, the manganous sulfide is to a greater extent removed by the slag; hence, it depends upon the amount of sulfur and manganese in the iron, whether the manganese aids finally in producing graphite or cementite.

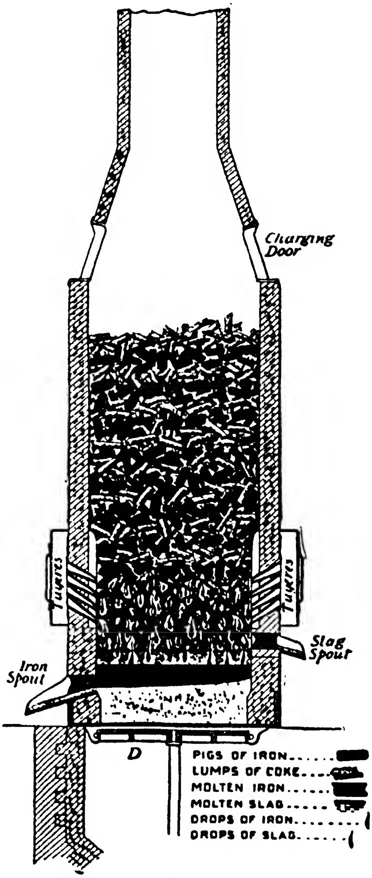

Fig. 36.—Cross-section of foundry cupola furnace. (*Howe.*)

Manganese has other noteworthy effects. It removes oxygen, *i.e.*, it transposes ferrous oxide into the form of manganous oxide which is taken up by the slag. It makes iron less fusible, but when molten, makes it more fluid. This it is able to do because of its decomposition of ferrous sulfide, which makes iron sluggish when molten. If present in a large amount, it hardens and toughens the iron and may make the castings noticeably more difficult to machine. By its removal of sulfur it tends to remove "red shortness." By its removal of oxygen it tends to prevent "boiling" during cooling and so aids in preventing blowholes.

Composition Affected by Remelting.—When the iron is remelted in the cupola, its composition is altered slightly, especially with reference to sulfur and silicon. As the drops of molten iron trickle down over the coke, sulfur is absorbed from the coke by the iron. The amount of this absorption depends upon the percentage of sulfur in the coke as well as on the proportions of coke and iron used in the charge. The sulfur absorbed will vary from 0.02 to 0.035 per cent of the iron; *i.e.*, if the sulfur in the pig iron charged was 0.08 per cent, there will be from 0.10 to 0.115 per cent in the castings.[1] Also, the sulfur in the first iron melted will be higher than that in the middle of the run, because of the extra amount of coke burned before any iron is tapped.

As the molten metal passes from the melting zone down through the blast from the tuyères, some silicon is oxidized and carried into the slag. The silicon lost in this way varies from 0.25 to 0.40 per cent, but according to Stoughton, with good practice it should be no more than 0.30 per cent. To illustrate, if the loss is just 0.30 per cent then, when the pig iron charged into the cupola contains 2.00 per cent silicon, the amount in the castings will be only 1.70 per cent.

Also, during the melting, a small amount of manganese will be lost through oxidation, and a small amount of phosphorus may be gained from the coke, but these alterations are of comparatively minor importance.

Composition and Size of Castings.—The size of the casting largely controls its rate of cooling; therefore the composition of the iron should vary with the size of the casting. Since a thin casting cools rapidly, it should be made of iron that is very fluid, and has no pronounced tendency to retain its carbon in the combined form. On the other hand, a large mass of iron, which would cool slowly, should not have a composition that would allow it to form large crystals of graphite in its interior. It may be said in general that small castings should be high in silicon and phosphorus, and large ones should be high in manganese

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[1] Stoughton, "Metallurgy of Iron and Steel," p. 258.

and sulfur. The following limits of composition, based on size of castings, have been suggested:[1]

Thickness of section	Si	P	Mn	S
Under ¼ in. thick	3.25	1.00	0.40	0.020
¼ to ½ in. thick	2.75	0.80	0.40	0.040
½ to ¾ in. thick	2.50	0.75	0.50	0.050
¾ to 1 in. thick	2.00	0.70	0.60	0.060
1 to 1½ in. thick	1.75	0.65	0.70	0.070
1½ to 2 in. thick	1.50	0.60	0.80	0.080
2 to 2½ in. thick	1.25	0.55	0.90	0.090
2½ to 3 in. thick	1.00	0.50	1.00	0.100

Composition and Use.—The composition of the iron that is suitable for certain uses may be illustrated by the composition of the samples used by the Committee on Standardizing the Testing of Cast Iron.[2]

Uses	Si	P	S
Novelties	4.19	1.236	0.080
Stove plate	3.19	1.160	0.084
Cylinders	2.49	0.839	0.084
Light machinery	2.04	0.578	0.044
Heavy machinery	1.96	0.522	0.081
Dynamo frames	1.95	0.405	0.042
Ingot molds	1.67	0.095	0.032
Car wheels	0.97	0.301	0.060
Chilled rolls	0.98	0.482	0.070
Sand rolls	0.72	0.454	0.070

Composition and Hardness.—In order to illustrate the kind of iron that is suited for the making of castings of different degrees of hardness, the specifications of the Case Threshing Machine Company are given:[3]

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[1] Forsythe, "The Blast Furnace and Manufacture of Pig Iron," p. 312.

[2] *Jour. Amer. Foundry Assoc.*, **10**, pt. II, p. 25.

[3] *Iron Age*, pp. 4 and 5, Sept. 29, 1898.

Constituents and Mechanical Properties	Soft castings, pulleys, or small castings	Medium castings, cylinders, gears, pinions, etc.	Hard castings, valves, and high-pressure cylinders
Si, per cent	2.20–2.80	1.40–2.00	1.20–1.60
S	Below 0.085	Below 0.085	Below 0.095
P	Below 0.700	Below 0.700	Below 0.700
Mn	Below 0.700	Below 0.700	Below 0.700
Tensile strength per square inch	18,000 lb.	20,000 lb.	22,000 lb.
Transverse strength per square inch	2,000 lb.	2,200 lb.	2,400 lb.
Deflection not less than	0.10 in.	0.09 in.	0.08 in.
Shrinkage, per foot, not over	0.127 in.	0.136 in.	0.148 in.
Chill, not over	0.05 in.	0.15 in.	0.25 in.

Shrinkage of Cast Iron.—White cast iron begins to shrink almost immediately after solidifying, and shrinks rather uniformly and continuously. Gray cast iron does not shrink at all immediately after solidifying, but undergoes a noticeable *temporary expansion,* which is due, of course, to the separation of the graphite. When the iron is high in both silicon and phosphorus, the expansion is very long continued. The metal has cooled almost to a black heat before the contraction of the metal due to cooling overcomes the expansion, and the piece has shrunk again to the size it was when just cast. By prolonging the fluidity, the phosphorus allows a more perfect separation of graphite. This is also an explanation of why the phosphorus-bearing irons fill the mold so perfectly; by the long-continued expansion, the pasty metal is forced into all the crevices.

As the shrinkage generally increases with the hardness of the cast iron, or in other words, with the decrease of graphitic carbon, it becomes a valuable indication to the quality of the iron.[1] It may be measured with comparatively little trouble. Shrinkage is usually considered to be about 1/8 in. to the foot. It is variable, however, and depends upon the silicon content and the area of the cross-section, as is indicated in the following table,

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[1] FORSYTHE, *loc. cit.*, p. 311.

in which the amount of shrinkage is stated in the decimals of an inch.

The perpendicular readings show decrease of shrinkage due to increase of silicon, and the horizontal readings show decrease of shrinkage due to increase of size.[1]

Per cent of silicon	½-in. square	1 in. square	2 in. by 1 in.	2 in. square	3 in. square	4 in. square
1.00	0.183	0.158	0.146	0.130	0.133	0.102
1.50	0.171	0.145	0.133	0.117	0.098	0.087
2.00	0.159	0.133	0.121	0.104	0.085	0.074
2.50	0.147	0.121	0.108	0.092	0.073	0.060
3.00	0.135	0.108	0.095	0.077	0.059	0.045
3.50	0.123	0.095	0.082	0.065	0.046	0.032

Although silicon in conjunction with phosphorus has perhaps the most important effect in reference to shrinkage, the effect of sulfur is also noteworthy. Because it is very effective in keeping the carbon in the combined form, sulfur helps to increase shrinkage. Manganese tends to increase the amount of graphite by increasing the total carbon; therefore it helps to lessen shrinkage. It has the same effect because it combines with sulfur and causes it to become inactive.

Since the last metal to solidify is the interior of the larger portion of the casting, it not infrequently happens that the interior has a spongy texture or contains open flaws with rough and crystalline surfaces, as illustrated in Fig. 37. As the exterior cools and solidifies, the shrinkage of the underlying portion is compensated for by metal from the interior, until when solidification is complete, there is a lack of metal in this portion of the casting. These open or spongy spots are known as *shrinkage flaws* or cracks. They can be readily distinguished from the unsound spots due to gas bubbles by the character of the surfaces of the openings, as will be apparent from a comparison of Figs. 37 and 38. Shrinkage flaws can be prevented by the judicious use of risers, *i.e.*, reservoirs of melted metal above the casting.

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[1] Stoughton, *loc. cit.*, p. 328.

Cracking or "Checking" of Castings.—Occasionally parts of castings, especially thin sections, that are so located that they contract against cores or other portions of the mold, crack during cooling. This usually occurs when the casting is just above a black heat, for at this time the metal is in a very weak and loosely coherent state. Sulfur has a very important bearing upon this tendency to "check," because both the sulfide of manganese and of iron have relatively low melting points and, at the temperature mentioned, are in a pasty condition so that they can offer very little resistance to breaking. Stoughton says that the sulfide of iron is much worse because it is spread out in thin plates or in network form, and thus offers more extended planes of weakness than the sulfide of manganese, which is more likely to exist in a globular state.

FIG. 37.—Shrinkage flaws in white and gray cast iron.

Phosphorus helps to increase the liability of checking because it has a tendency to produce large-sized crystals. Manganese tends to decrease crystal size and so, in a measure at least, offsets the effect of phosphorus.

Segregation of Impurities.—When iron is molten, carbon and the impurities are dissolved in it. The impurities are not so soluble in the solid metal and consequently tend to separate out as the iron freezes. It is quite apparent, therefore, that each layer of metal as it solidifies, beginning at the outside, rejects some of its impurities to be taken up by the iron which remains molten in the interior. This action is aided by the fact that the compounds in which the impurities exist have much lower melting points than the ferrite matrix. Then the portion of the casting that solidifies last will be richest in impurities, especially in sulfur and phosphorus. The result of this action is known as *segregation*, and may be defined as the collection of the impurities in spots. Because the material last to solidify is usually in the larger sections of the casting, it is in these larger portions that the shrinkage flaws or cracks occur. In these cracks, or spongy areas, the metal collects which is rich in impurities, has a low melting point, and consequently remains fluid while the other portions solidify. Such areas, when very bad, are sometimes known as "hot spots," probably because of their deferred solidification. If rich in ferrous sulfide, they may be so extremely hard that no tool can cut them.

This segregation may be obviated to a large extent by the use of large risers or headers, which, because they are large, solidify last and prevent the formation of shrinkage spots by feeding the rest of the metal well under pressure. Then, too, because they solidify last, the segregation occurs in them and is thus temporarily removed. Because the risers find their way back into the cupola as scrap and thus increase the quantity of impurities in subsequent castings, this method is not advisable as a continuous practice.

Blow Holes in Castings.—Blow holes are unsound spots in castings, produced by gas bubbles. The gas is absorbed by the liquid metal, but cannot be retained in the same proportion in the solid metal, hence it separates as the metal solidifies. In cast iron, and in cast steel as well, these gases are found to be chiefly hydrogen, with smaller quantities of nitrogen and the oxides of carbon. The hydrogen is produced from moisture decomposed by the heat, probably in the case of cast iron from moisture in the cupola blast. The carbon monoxide and dioxide are produced by the reaction between the carbon of the iron and some oxidized constituent of the metal. There is no difficulty in distinguishing between the irregular sponginess of shrinkage flaws and the smooth surfaces of blow holes. In iron castings, an oxidized surface indicates trapped steam or air; a bright surface is produced by gases set free during solidification, because these gases are, almost without exception, either reducing in their effect, or entirely inactive.

Manganese and silicon are very effective in preventing blow holes. They act in two ways: by combining with the oxygen in the metal so that the gaseous oxides of carbon are not formed, and by increasing the dissolving power of the solid metal for gases so that less gas separates. Aluminum and titanium are also sometimes added for the same purpose, although the latter element has an additional effect in that it combines with nitrogen.

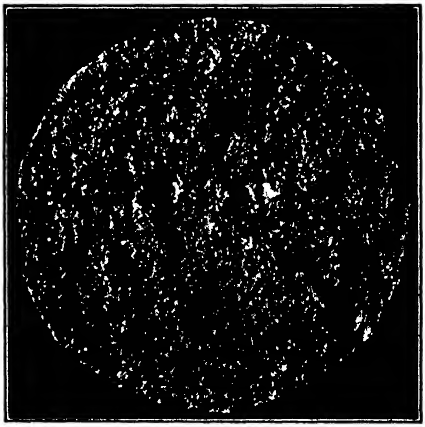

Fig. 38.—Gas flaws (blow holes) in cast iron.

General Rules.—In a general way it may be stated that for the average foundry irons these rules hold good:[1]

To Increase the Strength of Castings.—Decrease phosphorus and lessen graphite by decreasing silicon, thereby allowing more combined carbon. The manganese may also be increased and the casting cooled more rapidly.

To Decrease the Hardness and Shrinkage of the Casting.—Decrease the quantity of combined carbon and increase the graphite by decreasing sulfur or by increasing silicon and cooling more slowly.

To Prevent "Chilling" of the Casting.—Decrease sulfur, increase silicon and cool more slowly.

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[1] Forsythe, *loc. cit.*, p. 310.

To Prevent Blow Holes in the Casting.—Decrease sulfur and increase manganese and silicon.

To Prevent Kish, or Accumulations of Floating Graphite.—Decrease the percentage of carbon by adding scrap to the cupola.

The addition of small quantities of ground ferromanganese or 50 per cent ferrosilicon gives generally beneficial results. It deoxidizes the metal, thereby softening and strengthening it. It aids in lessening shrinkage and helps to make clean castings without materially altering the composition of the metal.

MALLEABLE CAST IRON

Definition of "Malleable Cast Iron."—Malleable cast iron is iron in which the combined carbon has been slowly set free in an amorphous condition without melting the iron. Although called "malleable," it is not malleable in the true sense, since it cannot be rolled or forged. It is, however, more malleable than gray cast iron, because the natural malleability of the ferrite has not been destroyed by flakes of carbon.

Outline of Process of Manufacture.—Malleable cast iron is a product obtained by two operations. The casting is first made of white cast iron of special composition. This hard, brittle casting is then cleaned and subsequently made malleable by annealing, or heat treatment. Malleable cast iron of the kind here described cannot be made from gray cast iron.[1] During the annealing process, the cementite of the white cast iron is decomposed, and the combined carbon is set free, not, however, in the form of flakes. It is liberated in a very finely divided amorphous condition, which, unlike graphitic carbon, is readily oxidizable. The name of "temper carbon" has been given to it. Malleable cast iron consists, then, almost entirely of ferrite and "temper carbon." Its characteristic microstructure is shown in Fig. 39.

Composition of the White Casting.—The composition of the iron for the original white casting must be kept within rather well-defined limits. Since it is absolutely necessary that the castings be white, it might be supposed that the total absence of silicon would be advantageous. This is not so, however, because the temper carbon will not separate out in the anneal-

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[1] For the annealing of gray cast iron, see p. 314.

ing process unless a certain amount of silicon is present. Still, too much silicon must not be allowed because it will prevent the original casting from being white. In brief, then, the composition of the metal poured must be such that the carbon is just on the line between being separated out as graphite and being held as cementite.

FIG. 39.—Typical malleable cast iron, showing structure of ferrite, and temper carbon. Magnified 100 diameters. Etched.

The composition of the pig iron ordinarily used for making the casting is about as follows: Si (according to the weight of the casting) 0.75 to 1.25 per cent; Mn not over 0.6 per cent; P not over 0.225 per cent; S not over 0.05 per cent. In normal American practice this will result in a white casting of about the following composition: Si 0.45 to 1.00 per cent, Mn 0.3 per cent; P up to 0.225 per cent; and S up to 0.07 per cent. The charge, however, is not usually made up of pig iron alone. It more commonly consists of part steel scrap, "return scrap" from the malleable foundry itself, and pig iron.

Melting.—The iron for the original white castings may be melted in the cupola, open-hearth furnace, or air furnace. Each has its advantages and disadvantages, but it seems that in view of all considerations the air furnace is generally recognized as being the best.

The air furnace is a reverberatory furnace. A reverberatory furnace consists essentially of an enclosed fireplace where the fuel is burnt, and from which the products of combustion are conducted across the adjacent, basin-like hearth. It may or may not be supplied with forced draft. In some cases an air blast (top blast) is applied above the hearth. The hearth is covered with an arched or sloping roof set in such a way that the heat is caused to reverberate or reflect upon the hearth.

In melting for malleable cast iron, the hearth is lined with silica sand, and soft coal or gas is generally employed for fuel. The furnace is charged through a large side door or by removing the roof which may be constructed of a series of units, each bound with an iron frame. The purpose of the air furnace is to melt the iron and bring it to the proper temperature without materially affecting the composition of the charge. The composition may be modified by burning out some of the silicon and carbon, but a better product is obtained when the desired composition is obtained initially by mixing pig iron, malleable cast-iron scrap, and steel scrap. After the charge is melted, it is stirred or "rabbled" by the operator, and at intervals slag is skimmed off. When the desired composition and temperature have been obtained, the castings are poured.

Contraction and Shrinkage in Casting.—The hard castings contract in the mold to a degree almost equal to that of steel. The contraction is due to the lack of graphite formation. A fault that occurs frequently in malleable castings is due to this same contraction. The exterior of the casting solidifies to a continuous shell while the interior lessens in bulk, and thus becomes full of cracks and planes of separation known as "shrinkage flaws" (see page 248).

Annealing.—After cooling, the castings are cleaned and packed in annealing boxes in some material, such as iron ore, mill scale, lime, or sand.[1] Then they are placed in the annealing ovens and heated to about 730°C., which is about 450° below their melting point. After having reached this temperature, they are kept at this point for about 60 hr. During the heat treatment, the separation of the carbon, which was prevented by rapid cooling and other influences when the casting was formed, occurs.

When the carbon separates during annealing, an expansion takes place that is about equal to that which would have occurred if the carbon had been allowed to separate in the original casting as graphite and produce gray cast iron.

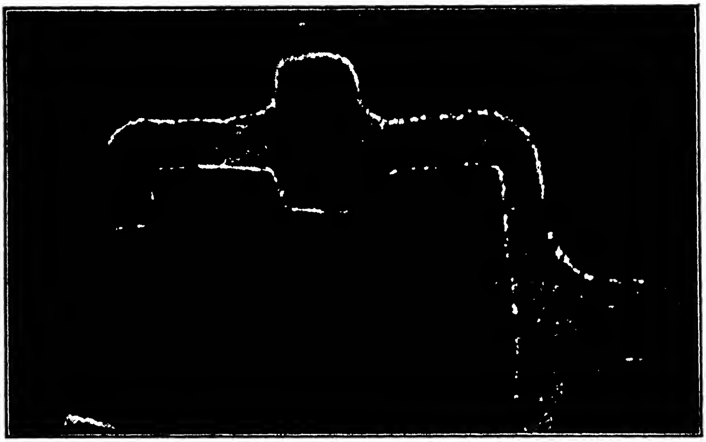

Fig. 40.—Typical fracture of "black heart" malleable cast iron.

If the annealing is carried out at a temperature that is too high, or too long continued, the separated carbon will combine again to form iron carbide (Fe_3C) and the casting will have a steely fracture.

The "Black-heart" Malleable.—When the annealing is conducted with iron oxide as the packing material, the annealed product will have a fracture such as is shown in Fig. 40. Due to the oxidizing effect of a packing of this sort, the carbon is entirely removed as CO from the outer layer of the casting, and

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[1] The object of this packing material is to support the castings equally at all points, and thus prevent them from warping while they are hot. In some cases, however, by carefully arranging the castings in the oven, the packing material and boxes may be omitted altogether.

practically iron only is left. Because of the resultant white skin and dark interior this product is called "black-heart" malleable. It is malleable castings of this kind that are usually produced in American practice. Some castings, however, are annealed in lime or sand so that the fracture is totally black with no white exterior. The presence of the white outer layer has been quite generally considered to add much to the strength of the casting and is still so considered by some, but Touceda[1] seems to have shown that this belief is not supported by the facts.

All-white Malleable Cast Iron.—If during the annealing process, the castings are packed in an iron-oxide packing, as described, and held at a temperature of about 800 to 875°C. for 4 or 5 days after reaching the full heat (about twice the usual annealing period), the carbon will be entirely removed. The condition that exists in the white exterior of the "black-heart" casting will then have extended entirely through it. The carbon probably diffuses to the surface and is there oxidized to carbon monoxide. For this process it is necessary to make the castings quite thin, ½ in. or less in thickness. In the original method of making malleable cast iron, the castings were all annealed in this manner; it is still the present practice on the continent of Europe.

Properties of Malleable Cast Iron.—The specifications of the American Society for Testing Materials require that malleable cast-iron castings shall have a minimum tensile strength of 50,000 lb. Such castings, however, very often have a strength of 60,000 lb. and more. Malleable cast iron can be twisted and bent to a slight degree, but its greatest advantage is its resistance to shock. It is especially able to resist blows that flatten the face of the metal without extending their influence very deeply. Steel castings cannot stand constant battering because their structure is made up of distinct crystals of ferrite closely packed between other crystals of iron carbide, and, between these components, planes of cleavage are developed. The malleable casting is made up of iron crystals between which are scattered particles of free, amorphous carbon, which have a cushioning effect and so increase the shock resistance.

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[1] Remarks on the "Strength and Ductility of Malleable Castings after the Skin Has Been Removed," *Trans. Amer. Foundry Assoc.*, **23**, 440, 1914.

Uses.—Malleable cast iron is especially useful for all purposes where the casting is required to withstand any form of vibratory stress. For example, trolley-car parts are made of it. It is used very largely for railroad work, although it has been superseded by steel for couplers and bumpers. On the other hand, it has replaced gray iron for journal boxes. Agricultural machinery and pipe fittings are made of it.

It is especially suitable for the making of small castings. Small castings that are made of ordinary cast iron are brittle and cannot withstand impact. It is difficult to make steel castings of small size, owing to the difficulty in obtaining a temperature sufficiently high to cast them properly. Consequently, small castings that are required to possess considerable strength are made of malleable cast iron. Window fastenings and harness fittings may be considered to be typical of small castings of this sort.

Sometimes tools, such as carpenter's chisels, hammers, etc., are made of malleable cast iron; and occasionally they are improperly sold as cast steel. There is a zone or layer just beneath the white exterior of the "black-heart" malleable casting of the nature of tool steel, and use is made of this to form the cutting edge of the tool. The existence of this steel-like layer is no doubt the result of its position. It lies midway between two layers, one rich in carbon and the other practically carbon free, and has a composition midway between the two. Consequently, under heat treatment it acts as steel; it is capable of hardening and tempering. The malleable casting may be given a steel-like fracture throughout, if the annealing is carried out at a temperature that is higher than normal, or if it is continued for a longer period than usual, and then cooled rapidly. Sometimes the mere heating and quenching of a properly annealed casting will cause the carbon to assume the cementite form.

WROUGHT IRON

Definition.—Wrought iron is defined as slag-bearing, malleable iron[1] that does not harden materially when suddenly cooled. It

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[1] The term "malleable iron" as used here, must not be construed to refer in any way to the malleable cast iron just discussed. Wrought iron is actually malleable; *i.e.*, can be rolled or forged, whereas malleable cast iron cannot.

consists essentially of ferrite; therefore, it is quite soft, but very tough, malleable, and ductile.

Manufacture of Wrought Iron by the Puddling Process.—Wrought iron produced by the hand-puddling process is made by melting pig iron and exposing it to the flame of a reverberatory furnace (page 253), called in this instance, a "puddling furnace," the hearth of which is lined with iron oxide. The iron oxide employed may be a high-grade ore, mill scale, or roasted cinder from a previous heat. Although gas is sometimes employed, the fuel is generally bituminous coal.

In addition to its use for the furnace lining, iron oxide is employed to form the slag, so that the charge is substantially enclosed in an envelope of oxidizing material. In this way, the impurities in the metal are very largely removed in the oxide form. The manganese and silicon are removed first; their oxidation is nearly completed in the melting-down stage. The iron oxide, acting as a basic anhydride, unites with the phosphorus pentoxide that was formed by the oxidation of the phosphorus, and forms an iron phosphate which becomes a part of the slag. The carbon is eliminated in the form of carbon monoxide as,

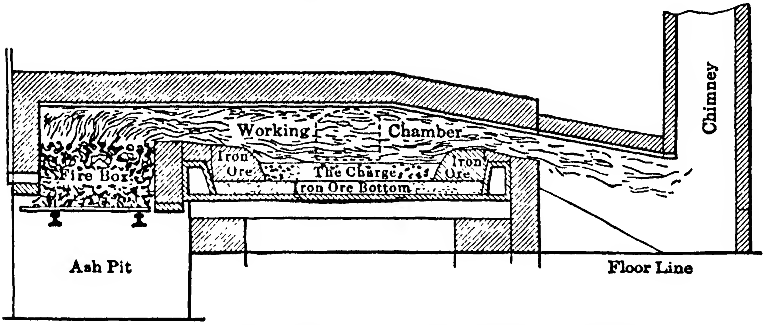

FIG. 41.—Cross-section of a puddling furnace. (*Howe.*)

$$Fe_3O_4 + 4C \rightarrow 3Fe + 4CO$$

Of all the impurities, sulfur is removed to the least extent.

During the oxidizing or purifying process the iron is stirred or "puddled," in order that air and the iron oxide of the slag may gain access to all parts of the charge. The period during which the carbon is removed is known as "the boil." The formation of carbon monoxide causes the charge to swell to such an extent that approximately half the slag flows out through a slag hole provided for this purpose. Toward the end of the boil the iron "comes to nature" as it is called. This means that it has assumed a pasty state. The pastiness is due to the fact that the melting point of the iron rises as it approaches purity. Hence, even though the temperature of the furnace may have increased considerably during the working of the heat, the melting point of the purified charge eventually surpasses the temperature of the furnace, and the iron begins to solidify.

Fig. 42.—Bar of wrought iron hammered cold, showing its stranded character.

The furnace operator or "puddler" now breaks up the charge with a bar and roughly forms it into balls which may weigh 125 to 180 lb. These balls consist of innumerable, loosely coherent globules of iron, which are almost pure in themselves, but between which is a great quantity of slag. The mass of iron and slag is taken from the furnace and compressed in a squeezing apparatus, or under the hammer, to force out the slag and weld the globules of iron together. The slag, however, is never completely removed by this process. When the ball is brought to the squeezer or press, the slag, in more or less globular masses, is held in pockets in the iron. As the ball is worked into a bar, the slag that is not squeezed out by the compression, is drawn out into elongated patches or lines. After rolling, the product is known as "muck bar." To further eliminate slag, and to interweave the strands of the iron, the muck bar is cut and piled in accordance with a specified arrangement, sometimes at right angles. It is then wired together, is reheated to a welding heat, and is rolled again. This treatment makes the merchant iron of commerce. In the merchant iron, the amount of the slag will vary from 0.5 to 1 or 2 per cent. It produces planes of separation between the strands of iron, as exhibited by the cold-worked specimen in Fig. 42.

Manufacture of Wrought Iron by the Aston Process.—Because of the arduous labor involved in carrying out the hand-puddling process, a great many attempts have been made to produce wrought iron by mechanical methods. Some of these attempts have been attended with a measure of commercial success, but none of them has shown the essentials of a sound manufacturing method, namely, high quality of product, low cost of production, and adaptability to large tonnage output, to the degree that these factors are combined in the newly developed Aston process.

The new method differs sharply from the puddling process in that the final result is brought about by distinct, separate steps, instead of in a single furnace operation as in the old method. If available, Bessemer-grade pig iron (page 230) in the melted condition is taken directly from the blast furnace. In the absence of this source of supply, the iron is melted in a cupola. Because of the increment of sulfur gained by the iron from the coke during cupola melting (page 244), about 21 lb. of soda ash per ton of iron are placed in the ladle into which the metal is tapped. By the reaction that ensues, a portion of the sulfur content is removed from the iron as a sodium sulfide and is taken up by the slag, which is then raked off. After having been treated with soda ash, the iron is refined in side-blown, acid-lined Bessemer converters (page 266) until the analysis of the metal is about as follows:[1] carbon, 0.06; manganese, 0.03; phosphorus, 0.10; silicon, 0.02; and sulfur, 0.05 per cent. Unlike the practice in the Bessemer process for steel, no manganese, silicon, aluminum, or other deoxidizing or degasifying agents are added at the end of the blow. Degasification occurs in a unique manner later.

While the metal is being refined, a typical wrought-iron slag, essentially a ferrous silicate high in iron oxide, is prepared sepa-

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[1] Aston, James, "Byers' New Process for Wrought Iron," *Iron Age*, **124**, 341, Aug. 8, 1929.

rately in a basic-lined, open-hearth furnace. Unlined, stationary, cup-like receptacles, placed on the floor, are filled about two-thirds full of the slag. In order to produce a slag-bearing metal of the puddled-iron type, the converter product is poured slowly into the slag. Because the temperature of the slag is about 1300°C. (2350°F.), and the temperature of the metal poured is about 1510°C. (2750°F.), the slag chills the iron. Each cup receives about 2,500 lb. of metal. During pouring a marked churning or "boiling," caused by gases escaping from the solidifying metal, takes place. This gas evolution aids very materially in breaking up the metal particles to produce a spongy mass, and on this account facilitates the incorporation of the slag with the iron. Being heavier than the slag, the iron particles settle to the bottom of the cup; and being at a welding temperature, they cohere. It is claimed that the slag, which is oxidizing and basic, further reduces the metalloidal content of the metal. This is evidently true, because it is upon just this set of reactions that

FIG. 43.—Wrought iron. Longitudinal section showing slag lines. Magnified 100 diameters. (*Boynton.*)[1]

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[1] Reproduced by permission from Sauveur's "Metallography and Heat Treatment of Iron and Steel."

the making of puddled iron depends. After the process of incorporating the slag is finished, the cup is picked up by a crane, and the excess slag is poured into a neighboring cup, where the process is repeated. In the bottom of the cup the solidified, but pasty, spongy mass of metal remains. From this point in the process, the metal is squeezed, rolled, and in general is treated in the same manner as the product of the puddling furnace.

Wrought iron made by the Aston process has been shown to possess essentially the same microstructure and mechanical properties as puddled wrought iron, and it meets the consumer's specifications for that metal. Besides, it can be produced on the tonnage basis of steel, a factor of great importance in lowering the cost.

Comparison of Wrought Iron with Low-carbon Steel.—Wrought iron can be distinguished from low-carbon steel by the slag content of the iron. Stoughton states[1] that there is usually more than 0.5 per cent of slag in wrought iron, and less than 0.3 per cent in steel. With suitably polished samples, one may be distinguished from the other by the aid of the microscope, but the section examined must be cut from the specimen on an axis parallel to the direction of rolling. If cut transversely, the cross-sections of slag lines could not always with certainty be distinguished from intercepted slag nodules sometimes found in steel of poor quality.

The results of chemical analyses cannot be relied upon for the purpose of making a distinction between wrought iron and steel, because the percentages of carbon, silicon, sulfur, phosphorus, and manganese in the two may fall within the same limits. Still, normal wrought iron is usually almost free from manganese, while normal Bessemer and open-hearth steel will contain 0.4 per cent, or more. Wrought iron, moreover, generally contains more than 0.1 per cent of phosphorus, while steel, as a rule, does not.

Although wrought iron has a distinctly lower tensile strength, for some purposes many users of these materials prefer it to steel. When overloaded, steel may break without warning, while wrought iron will yield more gradually, and will give notice that rupture is imminent. On this account, wrought iron is

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[1] "Metallurgy of Iron and Steel," p. 65.

often specified for chains. The yielding links of a wrought-iron chain may compress so sharply upon the interlooping ends of the adjacent links, that the whole chain may become rigid before the breaking point has been reached.

The American Society for Testing Materials specifies the following minimum requirements for refined bar wrought iron: tensile strength, 48,000, and yield point, 25,000 lb. per square inch; with 22 per cent elongation in 8 in. These figures should be compared with those in the table for steel on page 287.

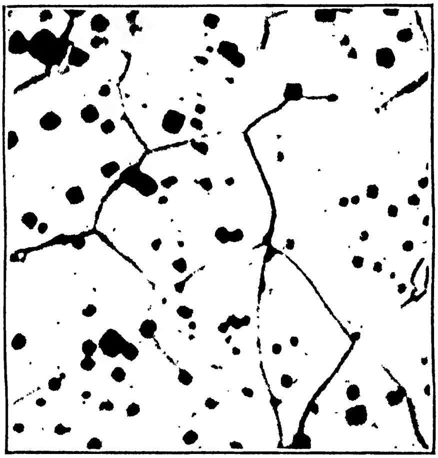

Fig. 44.—Wrought iron. Transverse section. Magnified 250 diameters. (*R. H. Greaves and Harold Wrighton.*)[1]

Wrought iron has a high electrical conductivity and can be readily magnetized, but it does not long remain in the magnetized state.

Wrought Iron of Inferior Grade.—All brands of wrought iron are not of equal quality. A good deal of the American product is made by piling wrought-iron scrap, wiring together, then heating to a welding heat, and rerolling. In most cases the scrap is indiscriminately collected and of non-uniform composition; besides it often contains intermingled steel scrap. For this reason the resultant product is not of high quality.

One of the common faults of low-grade wrought iron is "hot shortness" (page 241) caused by a high sulfur content.

Ingot Iron.—The term "ingot iron" is sometimes used to designate very mild, soft, or low-carbon iron. It differs from wrought iron in that it is obtained molten from the furnace and is therefore cast, while the wrought iron solidifies while being stirred in the presence of slag, with the result that the iron and

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[1] Reproduced by permission from Sauveur's "Metallography and Heat Treatment of Iron and Steel," 3d ed.

slag remain intermingled. Aside from the slag, ingot iron and wrought iron may have identically the same composition.

Welding.—Because of the ease with which it can be welded, wrought iron is usually demanded by the forge man. The weldability of iron products seems to be inversely proportional to their carbon content. Iron can be more readily welded by sprinkling over the parts to be joined, after heating, some borax or sand. By reacting with the iron oxide on the surface, these substances produce a readily fusible slag consisting of a borate or silicate of iron, which protects the iron from oxidation. As the parts are hammered together the slag is forced out and clean iron surfaces are brought into contact.

Carbon Steel

Relative Chemical Composition.—The ordinary, so-called "carbon steels," may, in a sense, be considered to be purified cast iron. They contain more iron and less carbon, silicon, sulfur, and phosphorus, while the manganese may or may not be less than in cast iron.

As compared to wrought iron, the steels will likely contain the more carbon, although this depends entirely upon the use for which the steel is designed. The sulfur and phosphorus in steel will average lower; the manganese, although it varies greatly, will be higher in steel than in wrought iron.

The following table, showing the percentage composition of the three commercial forms, should be studied carefully.

Composition of Cast Iron, Wrought Iron, and Steel in Per Cent

Kind	Iron	Carbon	Manganese	Sulfur	Phosphorus	Silicon
Cast iron	91 to 94	3.00 to 4.50	0.50 to 2.50	0.025 to 0.100	0.030 to 1.00	0.50 to 3.50
Ordinary steel	98 to 99.5	0.05 to 1.75	0.20 to 1.00	0.01 to 0.05	0.002 to 0.100	0.005 to 0.30[1]
Wrought iron	99 to 99.8	0.05 to 0.25	0.01 to .10	0.02 to 0.100	0.05 to 0.20	0.02 to 0.20

[1] In steel castings, the silicon will be higher, in the neighborhood of 0.60 per cent.

Definition of Steel.—Steel may be defined as an alloy of iron and carbon, with or without special alloying elements, which, while melted, was cast in a mass that is malleable at some temperature. This definition includes all except cement, or blister steel, which may be produced from wrought iron without melting, and therefore without casting. Such steel, however, is very little used. The definition sets no upper carbon limit, but the alloys containing over about 2 per cent carbon are excluded because they are not malleable. Such alloys fall into the cast-iron group.

The main distinguishing features of steel are indicated by the statement that it is cast and is malleable. Having been cast, *i.e.*, taken from the furnace in the molten state, it is relatively free from slag; this fact distinguishes it from wrought iron. Its malleability distinguishes it from cast iron. The fact that it is malleable when cast distinguishes it from malleable cast iron.

Manufacture.—Although there is a variety of processes by which steel may be made, they are all based on the purification of the metal by the oxidation of the undesired elements. The processes differ from each other only in the method by which this purification is accomplished. An exception may be considered in the making of cementation steel, in which case the purification is not considered a part of the steel-making process, but is secured in a prior operation.

The processes may be indicated as (*a*) the Bessemer process, in which the converter may have either an acid or a basic lining, although the basic Bessemer is not used in America; (*b*) the open-hearth process, both acid and basic; (*c*) the crucible process; (*d*) the cementation process; and (*e*) the thermoelectric process.

THE BESSEMER PROCESS

General Principles.—Of all the processes for the manufacture of steel, the Bessemer is the simplest. It consists essentially of blowing cold air under high pressure through melted pig iron in a suitably lined vessel, called a converter, until the silicon manganese, and carbon have been removed by oxidation. Under certain conditions, phosphorus, and to a large extent sulfur, may be eliminated also. Some iron is unavoidably burned; the iron and manganese oxides with the silica produced form a slag, while the oxides of carbon escape as gases. The oxidation of the elements named produces a great deal of heat, so that the temperature of the charge increases; in fact, the addition of cold metal or even steam is sometimes necessary to prevent it from becoming too hot.

The iron oxide tends to remain diffused through the metal to some extent, and if it is not removed, the quality of the steel is seriously impaired. Consequently, an important part of the process is the reduction of this oxide at the end of the "blow." Manganese is usually employed for this purpose.

Modifications of the Process.—There are two general modifications of the Bessemer method, known as the acid and the basic processes. The general principles involved in both cases are the same, but by the basic process it is possible to remove phosphorus and a part of the sulfur, which is not true of the other process. The basic process is so named because it employs a basic slag.[1] Lime is used to form the slag and as the phosphorus is oxidized to its pentoxide it combines with the lime to form probably the tetracalcium phosphate $(CaO)_4 \cdot P_2O_5$. Some of the sulfur is oxidized and escapes as sulfur dioxide, and some of it reacts with the lime to form a calcium sulfide.

Because a basic slag is required, and because an acid lining would be destroyed by a basic slag, it is necessary to line the converter with a basic lining. The basic process is used to its greatest extent in Germany, but it is employed considerably in other continental European countries and in England. For its successful operation, a high-phosphorus, low-silicon iron is needed; the burning of the phosphorus is depended upon as a source of heat. The silicon must be kept low, so that the silica produced does not destroy the basicity of the slag. The basic process is not practicable in America because American pig irons do not run high enough in phosphorus; at least 1.75 per cent is needed. Since silicon must then be depended upon for the production of heat, an acid slag and lining are required; the latter is formed of blocks of silicious material. Under such conditions no phosphorus can be removed; therefore, the charge must contain no more of this element than is allowable in the finished steel. This is generally less than 0.10 per cent. Because of the growing scarcity of ore capable of producing pig iron of this quality, the amount of Bessemer steel has been greatly lessened within recent

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[1] For a definition of the term "basic" in the metallurgical sense, see page 73.

years. The basic open-hearth product is taking its place. In 1906, more than half of all the steel produced in the United States was made in Bessemer converters, but now the Bessemer product amounts to only a little more than 10 per cent of the total.

The Converter.—Although converters vary considerably in details of construction, the type usually employed in America is an egg-shaped, steel receptacle with a capacity ranging from 5 to 25 tons. The bottom is detachable to facilitate relining, because it is subject to the greatest wear. To the bottom is attached a wind box with a space of an inch or so intervening between it and the bottom proper. About 20 fire-brick cylinders, called tuyères, lead from the wind box through the bottom lining to the interior of the converter. Each tuyère is about 7 in. in diameter and contains about 12 half-inch tubes.

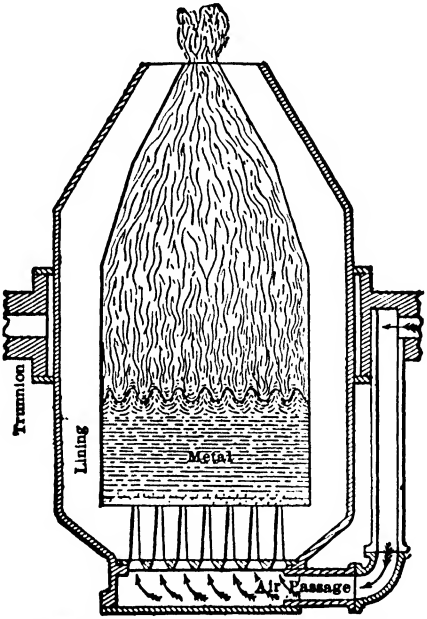

Fig. 45.—Bessemer converter purifying the metal. (*Lake.*)

The converter is mounted on trunnions attached to the side in such manner that it may be tilted or in some cases turned entirely upside down. One of the trunnions is hollow and serves to connect the blast main to a pipe leading down the side of the converter to the wind box. The nose of the vessel is formed by constricting the sides either concentrically or excentrically. In either case the construction is such that when the converter is lying on its side the charge may be contained without any of the tuyère holes being covered. This is necessary in order that the blast may be turned off without the metal running through the tuyères into the wind box.

The Charge.—The charge of the Bessemer converter consists of melted pig iron, which is obtained directly from the blast furnace as a rule; the output of two furnaces is required to keep one converter supplied. Blast furnaces cast at intervals of from 4 to 6 hr., yielding from 100 to 150 tons at each heat; consequently the output of the furnace must be stored to afford a continuous supply for the converter which uses only about 15 tons as a maximum. In order to make the operation of the furnace and converter as independent of each other as possible, the output of several furnaces is poured into a mixer.

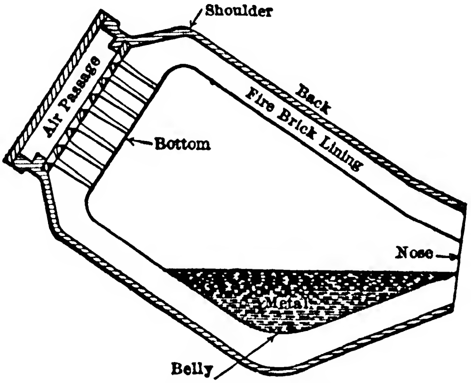

FIG. 46.—Bessemer converter tilted. (*Lake.*)

The Mixer.—The mixer is a larger reservoir, lined with a refractory lining. The larger ones are capable of holding as much as 1,200 tons. In addition to the storage feature, there is another advantage in using a mixer, which is that the composition of the metal supplied to the converter is more uniform. If a blast furnace fails to function properly, the irregularities of the metal cast for that heat are not so directly transmitted to the steel. Because they are constantly receiving additions of hot metal from the furnaces, it is rarely necessary to furnish heat to the mixers from any other source.

The "Blow."—The converter is turned on its side and a charge of about 10 to 15 tons is poured in from a ladle. This amount will form a layer about 18 to 20 in. deep when the converter is in the upright position. Before the converter is rotated to the vertical position, however, the blast is turned on. The blast carries a pressure of about 20 lb. per square inch. More than 5,000 cu. ft. of air pass through the converter per minute; although the layer of metal is comparatively shallow, practically no oxygen escapes uncombined. This high absorption of oxygen is due to the fact that the blast assumes the form of a spray of fine bubbles. In this way the silicon, manganese, and carbon are very largely burned out. The silicon and manganese are oxidized first; at a later period the carbon.

As the reactions proceed within the bath, there is a characteristic display at the mouth of the converter; thus the operator can follow the successive stages with his eye. At first there is a shower of sparks; then a volume of dense, brown fumes pours out. The brown fumes are soon followed by a dull-red, short, pointed flame, which gradually increases in length and brilliance until it is brightly luminous and about 30 ft. long. During this period the carbon is being removed. Toward the end of the blow, the flame begins to die away; before it has disappeared entirely, however, the blowing is stopped. The total time required for the blow is about 15 min.

Recarburizing and Deoxidizing.—It is possible to stop the blowing when the steel contains the required amount of carbon, but this method is more difficult and time consuming because tests are required in order to determine whether the amount of residual carbon is right. Hence, the blowing is usually continued until the carbon is practically all burned out, when the required amount is added.

At the end of the blow there is always a considerable amount of iron oxide as well as gases dissolved in the metal. If the oxide were allowed to remain, the steel would be brittle, and otherwise defective. Although both carbon and silicon will reduce iron oxide, it has been found that manganese is the best deoxidizer and will come nearest to freeing the metal of oxide.[1] If the iron oxide were not removed there would be a considerable amount of reaction between it and the carbon, with the result that gas flaws would be produced. Although manganese is employed, the formation of gas takes place to some extent, even up to the time that the steel solidifies.

The carbon and manganese are generally added to the bath in the form of a carbon-manganese-iron alloy. If an extremely soft steel, as for wire, material to be welded, as in making pipes, tubes, etc., is desired, then ferromanganese containing 80 per cent manganese and about 6 or 7 per cent of carbon is added. The required amount of manganese can thus be introduced without admitting too much carbon. If higher-carbon steel, as for rails, is wanted, melted spiegeleisen is added. This contains about 20 per cent manganese and as much as 6 per cent of carbon. Thus the required amount of carbon without too much manganese can be introduced. Sometimes anthracite coal or pig iron may be employed for the introduction of carbon.

The materials employed for deoxidation may be introduced into the converter and the blowing continued for the purpose of mixing. The blowing can be continued for only a very brief period, however, because otherwise the deoxidizer will be lost. Generally the deoxidizer and recarburizer are thrown into the ladle just as the melted metal is poured into it. In some cases the metal is stirred in the ladle to secure as uniform a mixing as possible. After the manganese has acted, a still more thorough deoxidation may be secured by using vanadium, titanium, or similar active element.

Teeming.—After the metal has been received into the ladle, it is "teemed," as it is called, into the ingot molds. The ladle is of the bottom-pour type; the tap hole in the bottom is controlled by means of a plunger lined with refractory material that extends down through the melted metal. The molds are bottomless casings that rest on metal plates mounted on small trucks. They vary in size according to the articles to be rolled, as struc-

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[1] It is interesting to note that during the early development of the Bessemer process, when working on low-manganese iron, the steel was almost invariably brittle when hot; the method seemed doomed to failure until the beneficial effect of adding manganese after blowing was recognized.

tural shapes, rails, etc. With steel containing approximately less than 0.5 per cent of carbon, a few ounces of aluminum in small pieces is added to the metal of each mold as it is being filled to secure further deoxidation.

$$2Al + 3FeO \rightarrow 3Fe + Al_2O_3$$

This is necessary especially if the steel shows a vigorous gas evolution during teeming. During the teeming of each ladleful, a sample of the steel is taken for chemical analysis.

After-treatment of the Ingot.—When the ingots in the mold have cooled off sufficiently to form a strong shell, the molds are lifted off, leaving the white-hot ingot exposed. The ingots are then removed to a furnace called a "soaking pit," where they are allowed to remain until they have reached the necessary uniform temperature throughout, after which they are rolled into the shape desired.

THE OPEN-HEARTH PROCESS

General Principles.—In this process, as in the Bessemer previously discussed, the manufacture of steel depends upon the oxidation of the impurities and the removal of the oxides through the slag or as gases. By using iron ore as an oxidizing agent, as is done in the puddling process for wrought iron manufacture, and by deriving the necessary heat from a fuel such as gas, instead of from the burning of the impurities in the metal as in the Bessemer process, the temperature of the bath is made independent of the purifying reactions. Although the whole process is slower, it is under much better control than is possible with the Bessemer process. As the name indicates, an open-hearth furnace is one with the hearth exposed to the flame, so that whatever lies upon it is exposed to the direct action of the burning gases in the combustion chamber above it. The gas with a quantity of air slightly more than sufficient to burn it, is introduced at the ends of the furnace alternately, so that the flame sweeps across the hearth first in one direction and then in the other; the reversals occur at about 15-min. intervals.

A very important feature of the process is that it is regenerative, which means that the hot products of combustion are caused to pass through a checker work of brick on their way to the stack; then the air is passed through the heated checker work and raised to a high temperature before entering the combustion chamber. Thus the brick work alternately stores up heat and in turn delivers it to the incoming gases. By this means only it is possible to develop the high temperature that is necessary. The regenerators are unlike the stoves of a blast furnace because they are not intended to be combustion chambers. The open-hearth is unlike the blast furnace because it employs only natural draft.

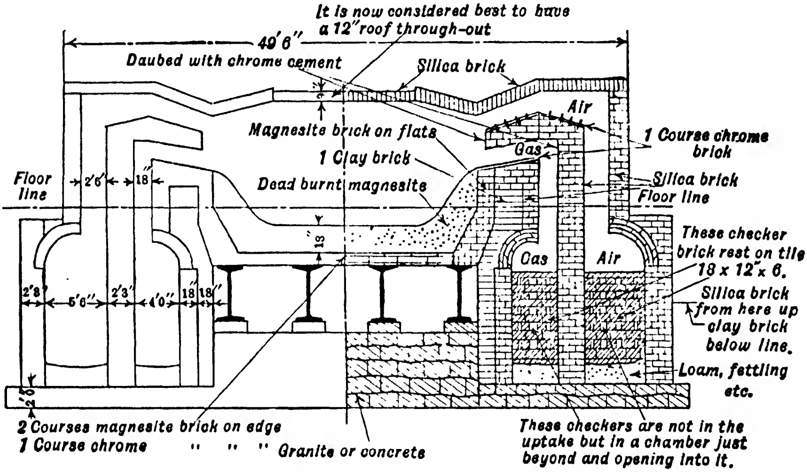

FIG. 47.—Materials of construction and lining for basic open-hearth steel furnace. (*Stoughton.*)

As with the Bessemer converter, there are two major modifications of the open-hearth, the acid and basic. Although in both cases the general construction is the same, the lining of the hearth is different. The character of the lining is determined by the character of the slag, and the character of the slag is determined by the reactions that must be brought about in the furnace. The reactions, in turn, are determined by the composition of the charge available.

Construction of the Furnace.—The details of construction of the open-hearth vary largely according to the size of the furnace, but the general principles are illustrated by the cross-section shown in Fig. 47. It is essentially a rectangular brick structure.

The exterior walls of its ends and sides are supported by vertical buck stays, held together at their tops and bottoms by suitable tie rods that extend across the furnace. The modern furnace will have a rated capacity of 80 to 100 tons; such a furnace will be from 15 to 20 ft. wide and 60 to 80 ft. long in outside dimensions.

An acid hearth is built up of fire-clay brick and silica sand; the whole lining is thoroughly sintered into place. It is then covered with a melted bath of old slag to fill in the crevices and to produce a smooth surface. For a basic bottom, although the details vary a great deal, the construction shown in Fig. 47 is illustrative. The depth of the hearth is such that the layer of melted metal will be from about 15 to 24 in. deep.

The walls and roof of both acid and basic furnaces are of silica brick. In the basic furnace, a layer of neutral chromite brick is employed to separate the acid wall from the basic bottom. The tapping hole and slag hole are placed in the back wall of the furnace; in the front wall are from three to five arched doorways, about 3 ft. wide and 4 ft. high, for charging. Both the doors and doorways have water-cooled cast-iron or steel frames. The doors are operated by hydraulic pressure or electric power.

The ports at the ends of the furnace for the introduction of the air and gas are set at such an angle that the flame is directed away from the roof, as even the most refractory brick would be melted by the extreme heat. Care must be exercised, too, that the flame does not strike directly upon the bath, or the charge will become excessively oxidized. For the same reason the air port is set above the gas port; this arrangement also promotes the mixing of the air and gas, since the gas is lighter and tends to rise.

At the ends of the furnace are the up- and downtakes. These are vertical flues that connect the ports to the slag pockets and thence to the checker-work regenerators. The slag pockets are chambers set at the bottom of the vertical flues, and are designed to receive the slag carried along by the blast so that it does not enter and clog the checker work.

The checker work is contained in large chambers, which are not built under the furnace as it may appear in the illustration, but usually under the charging floor in front of it. If producer gas is the fuel employed, one chamber on each side of the furnace will be used for gas and one for air.

The furnace may be either of the stationary or of the tilting or rolling type; each has its special advantages. Tilting furnaces rest on rollers, so that the furnace may be emptied by tilting, thus making a tap hole unnecessary. They are like the stationary furnace in shape and proportions, but the hearth is deeper and the frame is stronger in order to stand the additional stresses. Only the furnace proper (the hearth, walls, and roof) is movable; the ports and all other parts are stationary as in the ordinary furnace. Tilting furnaces are more expensive to build and to operate than stationary furnaces. Their advantages are that the troubles and delays arising from opening and cleaning out the tap hole are avoided, and that the slag may be poured off or the charge tapped at any time. The tilting type is used considerably for foundry work, where the capacity does not usually exceed 15 to 20 tons.

Charging.—The charge for both the basic and the acid furnace consists of a mixture of pig iron and steel scrap. The amount of scrap may vary from none at all up to 90 per cent; the actual proportions are determined by the relative cost of the materials. On an average, in America, the amounts will be approximately 50 per cent of each. The pig iron may be charged either melted or cold. If melted material is employed, it is added about 2 hr. after the charging of the solid material is begun. The melted metal is poured in from a ladle and is obtained from a mixer, the advantages of which were discussed under the Bessemer process.

The cold material is loaded into elongated, rectangular, steel boxes, which have a capacity of 16 cu. ft. or more. These boxes are inserted through the charging door by the charging machine, which manipulates the box on the end of a long steel bar. The box is emptied by rotating the bar. This method greatly facilitates charging, and is one of the important items in lessening the cost of the process.

The Fuel.—The fuels employed in the open-hearth may be natural gas, coke-oven gas, producer gas, powdered coal, fuel oil, and sometimes tar. The air for combustion is preheated. Only when producer gas is employed is the fuel preheated. If fuels of a hydrocarbon nature were preheated, they would decompose and clog the checker work with carbonaceous matter. The temperature developed varies at different intervals of the process, but averages between 1600 and 1700°C.

Acid Open-hearth Practice.—In the acid open-hearth, the elements removed from the melt are the same as in the acid Bessemer process, namely, silicon, manganese, and carbon. Since the scrap is always charged cold, and the pig iron frequently so, a considerable period, approximately 5 hr., is required to melt the charge. After melting, a little lime, about 10 lb. per ton of charge, is added to thin the slag that has formed from the oxides of iron, manganese, and silicon. The temperature is then increased. When hot enough to avoid chilling, the charge is fed with iron ore, but the slag is kept in a strongly oxidizing condition for a relatively short period only, about 2 hr. During this time the silicon and manganese will have been almost completely removed and the carbon will have been lessened considerably. For the 2 or 3 hr. following, no additions of ore are made. During this period the residual carbon reacts with the residual iron oxide with the result that both are eliminated to a great extent. This long and relatively quiet deoxidizing period greatly eliminates the tendency toward the formation of gas flaws, and allows opportunity for the oxides of manganese and silicon to separate from the metal. It is for these reasons that the acid-process steel is generally considered superior to the basic.

Toward the latter part of the heat, samples are taken and the percentage of carbon is determined by a rapid method of analysis. When the desired composition is obtained, ferrosilicon and ferromanganese are added to the melt while still in the furnace to complete the deoxidation as far as possible and to introduce the desired amount of silicon, manganese, and carbon into the steel. Generally, after these additions have been made, the bath is stirred or "rabbled" to insure a thorough distribution.

Basic Open-hearth Practice.—In basic practice, the usual charge consists of limestone, ore, scrap steel, and pig iron. The limestone is always charged first, ore or scale is charged above the stone, and scrap on top of this. The limestone is charged first because if it were placed above the metal it would insulate it from the flame and interfere with the melting. The melting period in the basic process is approximately the same as in the acid, about 5 hr. being required. If cold pig iron is used, it is charged with the scrap, but if melted metal is employed it is not added until about 2 hr. after the process has begun.

As in the acid process, silicon and manganese are first removed. The phosphorus is also rapidly attacked by the iron oxide, which not only oxidizes the phosphorus, but combines with the resulting oxide and forms an iron phosphate. Some sulfur is removed, but the removal of sulfur is somewhat uncertain and is usually not considered as one of the primary objects of the process. If the percentage present is high, a portion of it will be oxidized to sulfur dioxide (SO_2) and escape by way of the stack. A relatively small proportion is removed in the slag, probably as manganese sulfide (MnS). Carbon is being oxidized also at this time; the resulting carbon monoxide, which escapes in small bubbles, causes the slag to foam and become quite voluminous. The period during which these reactions occur is designated as the "ore boil." It is quite common practice to run off the slag formed during this period. It does not contain much lime, because the lime has not yet come up from the bottom, but it is rich in ferrous oxide and ferrous phosphate. Although the ferrous oxide is lost, the bulk of the phosphorus is removed from the metal in this way.

As the temperature of the furnace rises, the decomposition of the limestone, which has been proceeding slowly, becomes much more rapid. The evolution of the resulting carbon dioxide, with some carbon monoxide gas still being formed, causes a violent bubbling of the bath. This is referred to as the "lime boil." The stirring action brought about by the escaping gases is of considerable importance in promoting the oxidation by mixing the slag with the melt. During this period the lime rises to the top. It replaces the iron and manganese oxides in the phosphates, sulfates, and silicates of these metals, thereby forming the corresponding calcium compounds, which become a part of the slag. The iron and manganese phosphates are relatively unstable, and are easily reduced. If reduction occurs, the phosphorus returns to the metal. When the calcium phosphates are formed, however, they are very stable and the result is that the phosphorus is kept in the slag. This fact constitutes the outstanding difference between the acid and basic processes.

As soon as the charge is completely melted, which will not have occurred before the lime is up, samples are taken and analyzed for phosphorus and generally for carbon. If the carbon has been brought too low before the metal is hot enough, the percentage is raised by adding pig iron. To hasten carbon elimination, ore is added, but no ore is added usually within the last hour prior to tapping, since it is desired to have the ferrous oxide content as low as possible when tapped. Coincidentally with the adjustment of the carbon, the basicity of the slag is adjusted by adding lime; the desired fluidity is obtained by adding fluorspar; and the desired temperature is secured for tapping. When the desired composition and temperature have been secured, the metal is tapped.

The deoxidizers, such as ferrosilicon, ferromanganese, etc., which are necessary to eliminate the ferrous oxide, cannot be added in the presence of a basic slag since the phosphates present there would be reduced and the phosphorus would again enter the metal. Consequently, the deoxidizer and recarburizer are introduced into the ladle while the melted metal is flowing into it; the slag remains behind in the furnace. If it is desired to introduce more carbon than that carried in the ferro alloys employed, it is added in the form of crushed anthracite or coke contained in paper sacks.

The Talbot Process.—There are several modifications of the open-hearth process, both as to type of furnace and procedure. The Talbot process is one of the most noteworthy. A very large-capacity tilting furnace is employed; the charge amounts to over 200 tons in some cases. After the first charge has been purified to the required extent, a large part of the slag is removed, and about one-third of the metal is poured into a ladle and recarburized in the usual way. Limestone, ore, and pig iron are then added to compensate for the material removed. The reactions that take place are very vigorous due to the high temperature of the melt left from the previous heat, and in about 3 to 6 hr. the charge is again sufficiently purified so that more steel may be removed. The process is rapid and continuous; the residual steel in the furnace takes the place of the steel scrap that is melted down in the earlier stages of the process in ordinary practice.

The Duplex Process.—Although this term means literally the combination of any two steel-making processes, in America it is usually employed to mean a combination of the acid Bessemer with the basic open-hearth. Pig iron of the composition regularly employed in the basic open-hearth is first "blown" in the acid Bessemer; the silicon, manganese, and part of the carbon are quickly removed. This partly purified metal is then transferred to the basic open-hearth where the phosphorus and the remainder of the carbon are eliminated, after which the steel is finished according to the usual open-hearth practice. In this way, steel of open-hearth quality is produced in approximately half the time ordinarily required with the open-hearth furnace.

Quantity of Open-hearth Steel.—Of the total amount of steel now produced in the United States, about 85 per cent is made in open-hearth furnaces. Of the total open-hearth product, only about 2.3 per cent is acid steel. The reason for such a small percentage is, of course, that so little of the material available is suitable for conversion into steel by the acid process.

Cement or Blister Steel

The cementation process is the oldest method for making steel. By it, wrought iron, or at times low-carbon steel, is converted into high-carbon steel. The bars to be converted are packed in charcoal, sealed from the air, and heated to a temperature of from 650 to 700°C. In Sheffield, England, where this process is much used, 2 days are required for the furnace to reach the full heat; the heat is then maintained from 7 to 11 days longer, depending upon the product desired. The carbon penetrates, or is absorbed by, the iron at the rate of about ⅛ in. every 24 hr., a slow process. The saturation point is about 1.5 per cent of carbon, but the steel when finished usually contains about 1 per cent.

The product is called "cement steel" because ferrite of the wrought iron is converted into iron carbide or cementite by the addition of the carbon. It is called "blister steel" also because as the carbon migrates into the wrought iron it comes into contact with the slag which is rich in iron oxide and a reaction occurs that produces carbon monoxide, which causes blisters to form as the gas attempts to escape.

This steel is much used for tools bearing a cutting edge, but because the slag of the wrought iron still remains in the steel, the chance is great that the cutting edge will be imperfect. Hence, the steel is melted in crucibles to eliminate the slag. This double process greatly increases the cost of the product; therefore, more commonly, the carbon is introduced and the slag eliminated in a single operation known as the crucible process.

THE CRUCIBLE PROCESS

The making of crucible steel is essentially a refining process. The metal charged is either wrought iron or low-carbon steel, both of which have been subjected to previous purifying operations. Although produced in small quantities, the quality is exceptionally high.

The Furnace and Crucibles.—In America, the furnace is generally of the gas-fired, regenerative type; it is capable of holding six crucibles as a rule. In England, the furnace is generally coke fired and usually holds two crucibles. The American crucibles are made of approximately half graphite and half fire clay, are capable of holding about 100 lb., and may be used about six times. In England, the crucibles are made of clay only, hold about 50 lb., and are thrown away at the end of the third heat. The all-clay crucibles are necessarily smaller because they have less strength. There is a disadvantage with the part-graphite crucible because the steel absorbs some carbon from the graphite; it is difficult, therefore, to make low-carbon steel in graphite crucibles. Because of the service to which it is put, however, crucible steel generally contains more carbon than other steels. The crucible must be examined carefully for cracks before each heat to guard against the breaking of a crucible in the furnace. The bottom of the furnace is covered with granular coke to absorb the melted metal in the event of breakage, and a hole is provided to allow it to drain into a pit beneath.

The Process and the Product.—The metal charged is cut into small pieces and placed in the crucible with the required amount of carbon, usually in the form of charcoal, some ferromanganese, or spiegeleisen, and sometimes a small amount of glass or similar material to produce a neutral slag. If a special alloy steel is being made, then the special alloying element, as nickel, chromium, tungsten, etc., is also added. A cover is placed on the crucible and sealed with fire clay.

The charge requires about 3 hr. for melting after which the melt is allowed to stand quietly for an hour longer in order that occluded gases and slag may rise and produce a steel as sound as possible. Soundness is improved by the action of silicon reduced from the silica in the clay of the crucible, but the steel must not be allowed to stand too long in the crucible or it will be hard and brittle, probably because of the absorption of too much silicon.

When the steel lies quiet, the crucibles are lifted from the melting holes and the covers are taken off. The slag is removed from the melt by means of an iron bar carrying on its end a lump of cold slag to which the hot slag adheres. The steel is then poured into ingot molds, which are very much smaller than those employed in the Bessemer and open-hearth plants.

Crucible steel contains usually less than 0.4 per cent Mn, more than 0.2 per cent Si, less than 0.025 per cent P, less than 0.03 per cent S, and from 0.6 to 1.5 per cent carbon, depending upon the use to which the steel is to be put. It is used for cutting tools and drills for iron, brass and other alloys, rock drills, cutlery, wood-working tools, dies, files, springs, hammers, shafts, axes, and a great variety of other articles.

The amount of crucible steel now manufactured is very small. The thermoelectric product is taking its place.

THE ELECTROMETALLURGY OF IRON AND STEEL

The use of electric energy in the metallurgy of iron and steel may be divided into two major classes, as follows:

1. Thermoelectric Processes.—In the processes of this class, the electric current is used only for the development of heat; the reactions brought about do not partake of an electrochemical nature. There are several divisions under this head, such as:

a. The smelting of ores for the production of pig iron: This process is used to a considerable extent in Sweden, where abundant electric current may be obtained cheaply from water power, but it is not profitable at the present time in America.

b. The production of steel from pig iron, or from a mixture of pig iron with steel scrap: In general principle, this is similar to the open-hearth process, but aside from its greater cost it is much superior in many ways.

c. The super-refining of liquid steel made by other processes: This process has had the greatest development in America.

2. Electrolytic Processes.—In this class the reactions are distinctly electrochemical. The two outstanding examples are:

a. The electrolytic refining of cast iron, wrought iron, or steel scrap to produce practically pure iron.

b. The electrolytic production of iron direct from ores.

THE THERMOELECTRIC PROCESSES

Of the thermoelectric processes, only the steel-manufacturing methods shown as 1, *b* and *c*, in the preceding outline, will be discussed in this study. Before proceeding with the metallurgy involved, however, the types of furnaces that may be employed will be enumerated.

Electric Furnaces for Steel Manufacture.—The furnaces may be divided into two major classes according to the principle of heating involved, as follows:

1. *The Induction Type.*—With this type the metal on the hearth of the furnace is heated by its resistance to the flow of a heavy-density current induced in it.

2. *The Arc Type.*—This type may be divided into the following subdivisions:

a. That employing the indirect arc, in which the arc plays between the ends of the electrodes, so placed above the hearth that the hearth is heated by radiation from the arc.

b. That employing the direct arc with the hearth acting as a conductor. In this type the electrodes are suspended above and also set in the hearth so that the arc plays between the electrode above the hearth and the metal in it.

c. That employing the direct arc with the hearth a non-conductor. In this type the current is both brought in and carried away by the electrodes suspended above the hearth. Arcs play between the electrodes and the bath; the circuit is completed between the electrodes by way of the bath. The Heroult furnace, which is extensively used, is of this type.

THERMOELECTRIC STEEL

Steel Made from Pig Iron.—As has been indicated, where conditions warrant it, steel is made directly from pig iron in the electric furnace. In this case, the process may be divided into three periods: (1) the oxidizing, (2) the reducing, and (3) the finishing period.

The Oxidizing Period.—This is very similar to the first stage of the basic, open-hearth process. A basic, oxidizing flux is employed which consists of lime and iron ore. During the oxidizing period, the great advantage possessed by the electric process over the ordinary open-hearth is that no fuel is burned in the furnace chamber, so that no air need be introduced there. Because the oxidizing agent is the ore only, the intensity of the oxidation can be carefully controlled. Besides, the temperature is higher and the reactions proceed much more rapidly. In addition, there is a more certain removal of sulfur in the electric furnace. The disadvantage is the higher cost per unit of heat. When the silicon, manganese, and phosphorus have been practically eliminated, and the carbon has been reduced to the desired point, the oxidizing slag, which is black because of its metallic-oxide content, is carefully raked off. Afterward, a new reducing flux, which forms a white slag, is applied.

The Super-refining of Steel.—Although the oxidizing reactions for the purification of pig iron may be brought about in the electric furnace, as just described, the elimination of the manganese, silicon, phosphorus, and carbon can usually be more cheaply accomplished by other methods. Then, only the reducing and finishing periods involve the use of the electric furnace. These two periods constitute the super-refining of steel; since they are also a part of the thermoelectric process for the manufacture of steel from pig iron, the general principles involved may be considered as applicable to both.

The Reducing Period.—It is during the reducing stage that the electric furnace demonstrates its greatest superiority over other methods for manufacturing steel. In both the Bessemer and open-hearth processes, the sulfur, dissolved gases, and entangled oxides are only very imperfectly removed, so that the resulting steel is not of the highest quality. Crucible steel greatly excels the Bessemer and open-hearth products in these respects, but the process is costly and the output is small. The electric-refining process, when skillfully carried out, accomplishes the same results achieved by the crucible process, and it may be operated on a tonnage basis similar to that of the open-hearth.

Regardless of whether the oxidizing phase of the purification has been carried out in the open-hearth or electric furnace, when the reducing stage is begun, precaution must be taken to exclude all of the oxidizing slag because it contains phosphates. If the phosphates were subjected to reducing conditions they would yield phosphorus to the metal. Highly oxidized steel should not be used because it can never be restored to superior quality. It is for this reason that Bessemer steel is no longer super-refined, except in the so-called "triplex" process, where the metal goes from the Bessemer to the open-hearth and thence to the electric furnace.

The flux employed in the reducing period consists of 5 parts of lime, 1 part each of silica and fluorspar to render the slag sufficiently fluid, and about ¼ part of carbon in some form, such as anthracite coal. To exclude air as much as possible, the doors are closed and luted with fire clay. Then the temperature is slowly raised. As the steel is reduced, samples of slag will show a gradually lessening brown color. After about 1 hr. calcium carbide (CaC_2) will be formed in the slag. Its presence can easily be ascertained by the characteristic odor of acetylene gas when the slag is moistened. The steel is kept under the carbide slag until practically all oxygen and sulfur are removed.

The carbide slag is very important in basic, electric, open-hearth steel metallurgy. It is a good deoxidizer, acting in accordance with the following equation:

$$CaC_2 + 3FeO \rightarrow CaO + 2CO + 3Fe$$

It removes sulfur also, as follows:

$$CaC_2 + 2CaO + 3FeS \text{ (or } 3MnS) \rightarrow 3CaS + 2CO + 3Fe \text{ (or } 3Mn)$$

The Finishing Period.—After the steel is deoxidized, the elements desired, such as silicon, manganese, chromium, vanadium, etc., are added in the form of their ferro alloys. Nickel, which has practically no tendency to be lost through oxidation, is added much earlier. After adding these alloys, the steel is allowed to lie quietly for at least 45 min. before tapping in order that all slag and oxidized substances may rise, just as is done at a corresponding stage in the crucible process.

The total time for super-refining is approximately 4 to 5 hr.; the power consumed ranges from 100 to 200 kw.-hr. per ton of finished steel.

The quantity of steel refined by the thermoelectric process in the United States is steadily increasing.

ELECTROLYTIC IRON

The Process.—Electrolytic iron is obtained by the electrodeposition of the metal from an aqueous solution of an iron salt, such as ferrous chloride or sulfate, or the corresponding double ferrous-ammonium salts. The anode dissolved to maintain the concentration of the electrolyte may be cast iron or scrap steel. The cathode is a highly polished steel surface from which the deposited metal may be stripped.

Instead of employing iron or steel to maintain the concentration of the electrolyte, any iron ore capable of being dissolved may be used. For example, haematite ore may be dissolved in hydrochloric acid. The cheapest ores for this purpose are the very abundant iron sulfides, which cannot be smelted in the blast furnace without complete roasting, but they may be employed in the electrolytic process; their use here constitutes a very important metallurgical achievement.

The Product.—Depending upon operating conditions, the iron may be deposited in a brittle or in a malleable and ductile form.[1] The brittleness, which is due apparently to the hydrogen deposited with the metal, may be removed by annealing. In the unannealed form, the pure iron may be pulverized, in which condition it has several important uses, such as, for example, in magnet cores.

Boiler tubes consisting of 99.97 per cent of pure iron are formed by depositing this metal on a revolving mandrel from which it is stripped after annealing. The resulting tube may or may not be drawn through a die.

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[1] *Chem. Met. Eng.*, **37**, 357, June, 1930.

Pure iron is as soft or softer than copper, and has better cold-working properties than either copper or aluminum. It is cheaper, stronger, and more durable, and withstands heat better than either of these two metals. Besides it retains a bright surface well and probably resists corrosion better than copper or aluminum.

COMPARISON OF STEELS MADE BY DIFFERENT PROCESSES[1]

The several kinds of steel usually exhibit certain differences in their properties that are dependent upon the process by which the steel was made. These peculiarities are often noticeable regardless of the fact that the steels compared may be of the same composition, *i.e.*, in respect to the amounts of the elements shown by the usual chemical analysis of the steel.[2]

Crucible Steel Compared with Other Steels.—Crucible steel is the most expensive of the steels, and aside from steel made in the electric furnace it is the best quality steel. The reason for its superiority is that it is manufactured in a covered container that excludes the air and furnace gases. As a result, it contains less oxygen, hydrogen, and nitrogen. Because there is no violent agitation in the crucible, such as there is in the converter during the "blow," or in the open-hearth during the "boil," crucible steel will likely contain a much smaller quantity of occluded slag particles. Also, because its deoxidizer is added in the beginning of the process, the deoxidation is more complete and the mass more uniform. It is scarcely possible to get a gas-free "dead melt" of this sort in the open-hearth furnace, hence the open-hearth product will be likely to contain more blow holes in the ingot and resultant seams in the steel when rolled. In the crucible, because of the long contact with the manganese of the deoxidizer, the sulfur is largely carried into the slag as manganese sulfide. Also, the ingots of steel poured in the open-hearth plant are very large compared with those of the crucible works, and the chances for segregation are greater in the larger ingot.

Thermoelectric Steel Compared with Other Steels.—The thermoelectric steel is like the crucible steel in that no fuel has

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[1] STOUGHTON, "Metallurgy of Iron and Steel," p. 59.

[2] See p. 263.

been burned in contact with the metal, so that the impurities usually derived from the fuels are avoided; for the same reason the presence of air, which would contribute gases to the melt, is not necessary. The thermoelectric product is like crucible steel also, in that it has been subjected to reducing influences for a longer period than has the Bessemer or open-hearth steel. The same is true with regard to the quiet period allowed in order that the slag particles may have a chance to separate from the melted metal. Because of the high temperature employed, the sulfur in thermoelectric steel will likely be lower than in any of the other steels, although crucible excels Bessemer and open-hearth in this respect. The great advantage that the thermoelectric steel has over the crucible steel is that it may be produced more readily in large tonnage, which allows articles to be rolled from it that could be produced from crucible steel only with great difficulty and at great cost.

Acid and Basic Open-hearth Steels.—Since no effort is made to take out the somewhat difficultly removable sulfur and phosphorus in the acid process, the operations are shorter here than in the basic process. The charge is therefore for a less time exposed to the oxidizing conditions of the furnace, the slag is less highly oxidized, and the molten steel is more free from occluded gases and oxides at the end of the heat. Hence, there is less trouble from blow holes in the ingot. These blow holes roll out into longitudinal flaws and are considered as being responsible for the starting of cracks. It is for this same relative freedom from blow holes, that acid, and not basic steel is preferred for steel castings.

Another point in favor of the acid steel is that it is likely to be more uniform, since there is a better chance for the proper mixing of the deoxidizer and recarburizer with the steel. In the acid process the deoxidizer is added while the steel is in the furnace; in the basic process after it has been poured into the ladle. The ingot is cast by pouring from this ladle, so that thorough mixing is much less probable. On account of the more highly oxidized melt at the end of the process, more deoxidizer is needed with the basic steel, and this fact tends also to lessen the chances for uniform distribution.

The phosphorus and sulfur are lower in the basic than in the acid open-hearth steel, but this seems to be more than offset by the defects caused by the occluded gases and oxides, and the non-uniformity produced by the method of deoxidizing and recarburizing.

Because of the more expensive material for lining and slag, the operation of the basic open-hearth is more expensive than the acid. Because of the longer period, more fuel is consumed. But because of the cheaper stock used in the charge, basic steel is cheaper than that made by the acid process.

Basic Open-hearth and Bessemer Steels.—Basic open-hearth will likely be superior to Bessemer steel as the latter will contain more oxygen, nitrogen, hydrogen, and other gases, due to the intimate mixture of air with the steel when it is made. This is especially true if the "blow" is continued a little too long. The hydrogen, which is derived from the moisture in the air blast, is believed to have an embrittling effect on the steel.

In the Bessemer process all the carbon is removed, and then the total amount desired is added. In the open-hearth, the carbon is removed to a point only a little below the desired amount, and enough is then added to bring the total up to the desired point. The greater amount of recarburizer used in the Bessemer tends to cause the product to be less uniform, because the larger addition may not distribute itself uniformly.

Summary.—In general it may be said that the steels compared in the previous paragraphs stand in the following order as to cost and quality: (1) crucible and thermoelectric steel,[1] (2) acid open-hearth, (3) basic open-hearth, and (4) Bessemer.

Steel Used as Castings.—In view of the previous discussion relative to the soundness of steel, *i.e.*, freedom from gas flaws, slag inclusions, etc., and the fact that with castings there is no opportunity to compensate for unsoundness by mechanically working the steel, it is interesting to note the percentages of the total production of each kind used in cast form. For 1929 the percentages[2] were:

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[1] Although thermoelectric steel costs less to produce than crucible steel, they may be rated approximately the same as to quality.

[2] From *Annual Statistical Report* of the American Iron and Steel Institute, 1929.

Kind	Used as Castings, Total Production of Each Kind, Per Cent
Basic open-hearth	1.24
Acid open-hearth	48.5
Bessemer	0.43
Crucible	13.28
Electrically refined	44.06

The low percentages of basic open-hearth and Bessemer steel employed in cast form are especially noteworthy. With respect to the relatively low percentage of crucible steel employed in cast form, it should be remembered that a large part of this steel is used for tools which are generally wrought.

Influence of Carbon on Properties of Steel.—To illustrate the tensile properties of steel in the annealed condition, the following table has been quoted from Mills:[1]

TENSILE PROPERTIES OF ANNEALED STEEL

Class by uses	Carbon, per cent	Elastic limit, lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation, per cent in 8 in.
Boiler rivet	0.08–0.15	25,000	50,000	30
Structural rivet	0.15–0.22	30,000	55,000	30
Boiler plate	0.08–0.10	30,000	60,000	25
Structural steel	0.18–0.30	35,000	65,000	25
Machinery steel	0.35–0 60	40,000	75,000	20
Rail steel	0.35–0.55	40,000	75,000	15
Spring steel	1.00–1.50	60,000	125,000	10
Tool steel	0.90–1.50	80,000	150,000	5

SOLIDIFICATION AND STRUCTURE OF IRON AND STEEL

Alloys of Iron and Carbon.—Although the properties of the two are very different, both cast iron and steel are alloys of iron and carbon. The difference in their characteristics depends to a large extent upon the proportions in which the elements are present, but of no less importance are the relations that the constituents bear to each other. In order to understand the several relationships, it will be necessary to know something of the nature of alloys in general. For this purpose the st

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[1] "Materials of Construction," 3d ed., p. 292.

is referred to pages 161 to 172. Attention is directed especially to solid solutions and the formation of eutectics, because both items are of fundamental importance to the study of the structure and properties of the iron-carbon alloys. If these topics have not already been taken up, the pages to which reference has been made must be carefully studied.

Solidification of the Pure Iron-carbon Alloys.—In this discussion we shall consider the progress of crystallization during the freezing of the iron-carbon alloys, and in order to avoid as much complexity as possible, we shall consider first only the pure alloys, slowly cooled.

An iron-carbon alloy in the melted state may be considered to be a liquid solution of iron carbide and ferrite. When the melted alloy freezes, it depends upon the amount of carbon present whether it will freeze as a solid solution, or form a eutectic after the manner of the lead-tin alloys. More specifically, the manner of freezing depends upon whether or not the amount of carbon present is greater than that required to form a *saturated solid solution.* It has been found somewhat difficult to determine accurately this saturation point. It is given variously by different investigators, ranging from 1.4 to 2.2 per cent of carbon; for the purpose of this study, however, 1.7 per cent has been taken.[1] Regardless of the exact percentage required, the principle remains the same, *i.e.*, all alloys containing less than the amount required for saturation will freeze as solid solutions, while all those containing more will freeze with the formation of eutectics. On this basis, the alloys are classified either as steels or cast irons; the solid solutions are the steels and the eutectiferous alloys are the cast irons.[2] Thus, in Fig. 48, the steels are shown to the left of the line *XY* and the cast irons to the right of it.

Freezing of the Steels.—As an example of the freezing of the steels, we will consider an alloy containing 1 per cent of carbon. In the melted state, the carbon is in the combined form; consequently the steel contains 15 per cent of iron carbide. Assuming

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[1] Howe, "Metallography of Steel and Cast Iron," p. 127.

[2] For convenience in classification, the steels have been defined as the tiferous alloys, although, commercially, alloys containing carbon the saturation point are classed as steels.

a temperature of 1600°C., the steel will be melted as indicated by the point *m* in Fig. 48, and in cooling no change will take place until the temperature has fallen to the line *AB*. Here crystals of a solid solution of iron and iron carbide will form, and the crystallization will continue through the range below the line *AB* until the line *AI* has been reached. Although the concentration of the solution is not the same in all parts of the crystals at first, if the cooling is moderately slow, diffusion corrects this difference so that ultimately they form a homogeneous mass containing 85 per cent of ferrite and 15 per cent of iron carbide. If the steel had contained, say 1.5 per cent of carbon, then the ratio would be 77.5 per cent of ferrite and 22.5 (1.5 × 15) per cent of iron carbide. All alloys containing carbon not exceeding 1.7 per cent will solidify in a similar manner.

Austenite.—The solid solution formed as just described is called *austenite;* it may be defined as "a solid solution of iron carbide in iron." It will be apparent from the discussion that austenites of all degrees of carbon concentration, varying from the merest trace to a maximum of 1.7 per cent (25.5 per cent of iron carbide) may be formed. In this sense it is like an aqueous solution of a salt. For example, at 20°C., a solution of sodium chloride may be prepared containing any percentage of salt up to a maximum of about 36 per cent. Austenite containing the maximum amount of carbon is spoken of as *saturated austenite.* Crystals of this composition are formed in all alloys containing 1.7 per cent or more of carbon; they become, therefore, a constituent of the cast irons now to be considered.

Freezing of Cast Iron.—An examination of that part of the diagram lying to the right of the line *XY* in Fig. 48 will show it to be of the same character as that employed in Fig. 10, which was used to explain the freezing of the lead-tin alloys. This means, as stated before, that the cast irons form a eutectic during freezing. The eutectic in the cast irons has been found to contain 4.3 per cent of carbon. The alloys that contain less than this amount are spoken of as hypoeutectic (*hypo,* less than), while those that contain more are called hypereutectic (*hyper,* over) alloys.

We shall consider first an alloy containing 3 per cent of carbon. At a temperature of 1400°C., this alloy will be in the melted state, as indicated by the point *n* in Fig. 48. When it has cooled to the line *AB*, saturated austenite will crystallize out. In this way both iron and carbon will be removed from the melt. The melted alloy contained originally 3 per cent of carbon and 97 per cent of iron, but the crystals of saturated austenite contain only 1.7 per cent of carbon and 98.3 per cent of iron. Thus, since the austenite crystals formed at any instant in this alloy are richer in iron than the melt from which they separate, it follows that by the separation of such crystals the iron content of the residual melt is decreased, or the carbon content is increased. As a result, with a falling temperature and continued crystallization, the composition of the remaining unsolidified alloy will gradually move to the right, following the line *AB*, until finally a eutectic alloy containing 4.3 per cent of

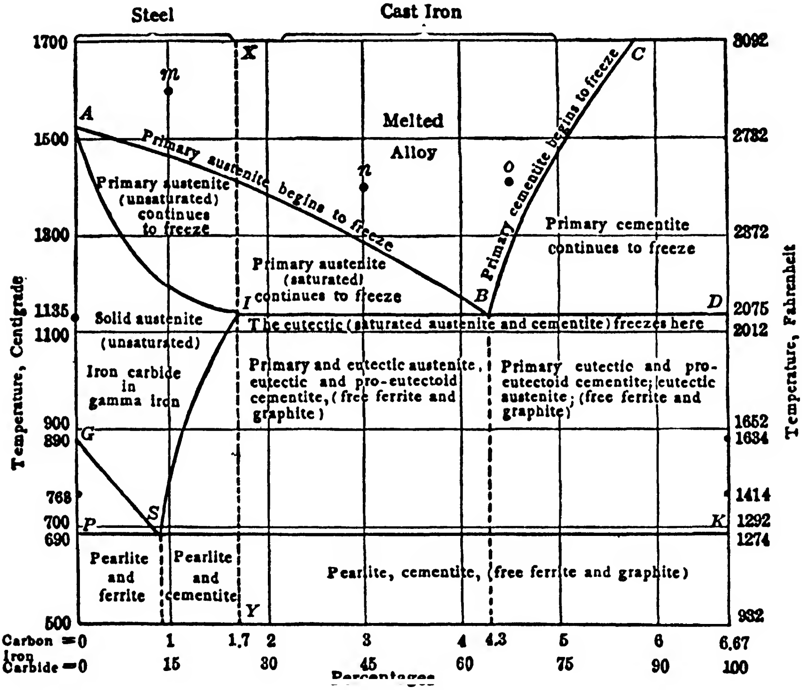

FIG. 48.—The freezing-point and solid-solution-decomposition curves of the iron-carbon alloys.

carbon. will be produced at *B*. In like manner any hypoeutectic alloy will solidify.

While the temperature is falling from the line *AB* to the eutectic line *IB* the metal will be in a mushy state like a mixture of snow and water. The melted portion will occupy a position beween the austenite crystals like the water between the little particles of ice. The austenite crystals formed prior to the solidification of the eutectic are called *primary austenite* to distinguish them from the finer austenite crystals formed when the eutectic solidifies. The gradual growth of such crystals is illustrated in a conventional manner in Fig. 50, where the cross-shaped masses represent the crystals of primary austenite

We shall next consider an alloy containing 4.5 per cent of carbon. At a temperature of 1450°C. this alloy will be in the completely melted condition as indicated by the point *o*, Fig. 48. When it has cooled to the line *BC*, crystals of iron carbide, known as *primary cementite*,[1] will separate out. The cementite crystals contain 93.33 per cent of iron, and 6.67 per cent of carbon, whereas the original alloy we are now considering contained 95.5 per cent of iron and 4.5 per cent of carbon. Thus, the crystals of primary cementite are richer in carbon than the melt from which they separate. Consequently, the percentage of carbon in the remainder of the melt grows gradually less; the composition moves to the left with a falling temperature, as shown by the line *CB*, until finally a eutectic containing 4.3 per cent of carbon is again formed at *B*, which represents a temperature of 1135°C.

As the temperature continues to fall and passes 1135°C., the eutectic also freezes, and its constituents separate completely. A conglomerate structure of alternate masses of saturated austenite and cementite is formed. In Fig. 49 the eutectic is the striated or banded structure indicated by *d*. Because the cast iron shown in this figure is a hypereutectic alloy, in addition to the

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[1] Although it is assumed by some writers that in the hypereutectic alloys carbon in the graphite form, rather than cementite, crystallizes out at this time, the view taken by Howe and Hadfield that the carbide first crystallizes and that the graphite is liberated by the decomposition of the solid cementite seems reasonable, and is here adopted. See Howe, "Metallography of Steel and Cast Iron," p. 216; and Hadfield, "Cast Iron in the Light of Recent Research," p. 7.

Fig. 49.—Hypereutectic cast iron. The white bands, *a*, *b*, and *c* are primary cementite; the striated mass *d* is the eutectic. Magnified 30 diameters. (*Howe.*)

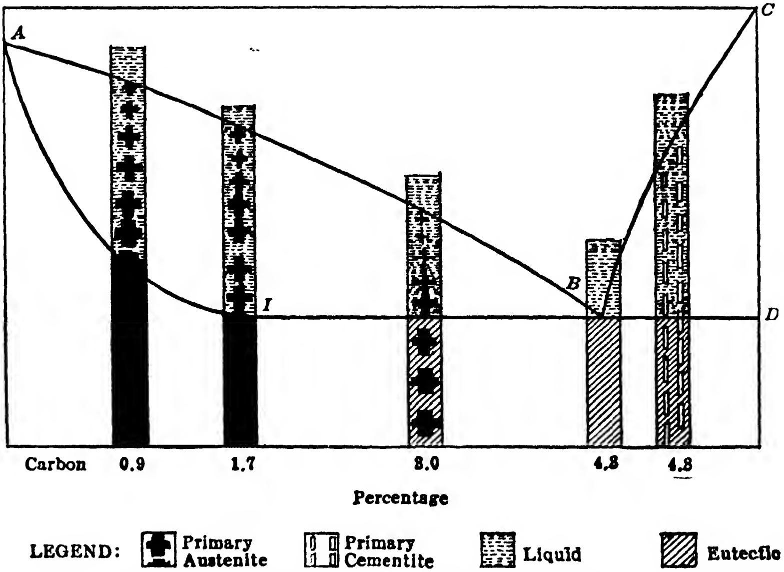

Fig. 50.—Sketches showing the progress of solidification in the iron-carbon alloys. (*After Howe.*)

eutectic, crystals of primary cementite are present; these crystals are indicated in the figure by *a, b,* and *c.*

Then, just as the solidification has been completed, the *hypoeutectic* alloys will be made up of a mass of primary-austenite crystals bound together by the eutectic that has solidified about them; the *hypereutectic* alloys will contain primary-cementite crystals in a solidified eutectic. If the original alloy was of exactly the eutectic composition, no primary crystals of either austenite or cementite will appear, but the whole structure will have the banded character that is normal to the eutectic. In Fig. 50, the several structures described are depicted in a conventional manner.

Transformations in Cast Iron after Solidification.—The freezing of the cast irons, *i.e.*, those alloys containing above 1.7 per cent of carbon, has been briefly described. Before leaving them it will be well to indicate briefly the structural changes that the constituents of the solid alloys undergo.

We have seen that the eutectic separated into saturated austenite and cementite, and that depending upon whether or not the alloy was of the hypo- or hypereutectic variety, this eutectic was interspersed with crystals of primary austenite or cementite. During the slow cooling of the solidified metal, the primary austenite of the hypoeutectic irons and the austenite of the eutectic (present in all irons) decompose, separating ultimately into cementite and ferrite. At the same time, unless the cooling is unusually rapid, the cementite, especially that of the eutectic, decomposes into ferrite and graphite. Before attempting to explain further the structure assumed by the cast irons, however, it will be necessary to consider more in detail the changes that take place in the austenite. Consequently, we shall leave the cast irons at this point and examine the structural transformations that occur in the steels, those alloys of iron and carbon which when pure and above their critical temperatures consist entirely of austenite.

STRUCTURAL CHANGES IN THE STEELS

Our knowledge of the structural changes in the steels has been arrived at largely by a study of their thermal critical temperatures and microstructure, and in order that the explanation may be as logical as possible, a brief review of some of the observed phenomena on which the explanation is based will be given.

Thermal Critical Points in Carbonless Iron.—If a piece of pure iron is heated to about 1000°C. and is allowed to cool slowly from that temperature, and the rate of cooling is carefully ascertained by a sensitive, accurate pyrometer, it will be found that at first the metal will cool at practically a uniformly retarded rate, the fall in temperature per equal unit of time becoming less and less as the metal cools off, in accordance with the general law for cooling bodies, until a temperature of about 890°C. is reached. At this temperature, a noteworthy phenomenon occurs. There is a marked slowing up in the cooling rate; in fact, the pyrometer may indicate a stationary temperature for a time, which shows that heat is in some manner being spontaneously evolved from the metal in an amount that compensates during a brief period for that given off in cooling. The cooling will then continue at a normal rate until the temperature has fallen to about 768°C., when the pyrometer will indicate a second evolution of heat, considerably less pronounced than the first one. After this the iron will again cool normally to atmospheric temperature.

As might be expected, with a rising temperature the reverse phenomena (whatever those phenomena may be) take place, *i.e.*, there is a momentary pause in the rise caused by an absorption of heat at the two critical points. At the upper point with cooling metal, there is, however, a slight lag, or hysteresis, so that the phenomenon takes place at a point about 20 to 30°C. lower than that at which the reversal occurs with a rising temperature. The lower point occurs at about the same place on the scale with both a rising and a falling temperature.

A Critical Temperature in Steel Containing 0.9 Per Cent of Carbon.—If instead of the pure iron, a steel containing about 0.9 per cent of carbon be employed as described in the previous paragraphs, there will be no retardations in the cooling rate at the temperatures recorded for pure iron. The metal will cool normally until a temperature of about 690°C. is reached, at which time a very marked retardation takes place. Heat is here evolved in much greater amount than at the critical points in pure iron; in fact, under favorable conditions the pyrometer will record a rise in temperature for a brief interval. If the experiment is carried out in a darkened room, the elevation of temperature will be apparent to the eye; a spontaneous glow will spread through the steel. Since the metal has become hotter, it is said to have "recalesced"; the name "point of recalescence" (literally the "point of reheating") is given to this temperature.

As was true with the critical points in iron, so with the steel, with a rising temperature the reverse phenomenon takes place, *i.e.*, there is a pause in the rise caused by an absorption of heat, although the absorption is not so spasmodic as to cause an actual lowering of the temperature in passing through this range. And, as with the upper critical point previously observed, the temperatures at which the change and its reversal take place are not exactly the same. With a rising temperature, it occurs at about 725°C., while with a falling temperature it is delayed and then occurs rather spasmodically at about 690°C., about 35° lower. This is a case of lag, or hysteresis, as stated before.

Notation.—In a report of some early investigations on the effect of the heat treatment of steel, Tschernoff indicated the temperature to which the steel must be heated in order to acquire hardness, when quenched, as the *A* point. This, as it is now known, is the point of recalescence. The *A* is derived from the French, *arrêt*, a stop, indicating an arrest in the cooling rate. Osmond, who was the first to determine accurately the position and magnitude of this point, and who discovered the two critical points in pure iron, adopted Tschernoff's previous notation and designated the point of recalescence as the A_1 point, and the two upper points in order as A_2 and A_3.

To distinguish the critical points on cooling from those on heating, the former were called the *Ar* points, the *r* referring to the French *refroidissement*—cooling; and the latter were called the *Ac* points, the *c* referring to the French *chauffage*—heating. Thus, with a falling temperature, the phenomena described are said to occur at the Ar_3, Ar_2, and Ar_1 points respectively, Ar_1 being the point of recalescence. With a rising temperature, the points in order are designated as Ac_1, Ac_2, and Ac_3.

Causes of the Critical Points in Carbonless Iron.—For a long time it was believed that the two thermal arrests observed in the cooling of carbonless iron were both due to a change of ferrite from one allotropic modification to another. Such changes in the chemical elements are not unusual. The cases of carbon, phosphorus and sulfur are well known. Sulfur, for example, exists as monoclinic crystals above 96°C., as rhombic crystals below this temperature, and as plastic, or amorphous, sulfur when rapidly cooled from just below its boiling point, 445°C. With iron, likewise, two allotropes have been definitely recognized. They are known as *alpha* and *gamma* iron. Alpha iron is the stable form at atmospheric temperatures, while the gamma modification becomes the stable variety when the metal is heated to above the Ac_3 point.

During the earlier investigations, the thermal discontinuity occurring at the A_2 point was also considered to mark a temperature at which an allotropic change took place. In accordance with this view, a form of ferrite, known as *beta* iron, was believed to exist between A_2 and A_3. It was noted from the first, however, that the thermal disturbance that occurs at A_2 is slight as compared to that which takes place at A_3, and that the shape of the ferrite crystals does not change in passing through the A_2 range. In addition, *x*-ray studies recently have revealed the fact that the structure of the iron atom remains as the body centered cubic lattice from atmospheric temperature to the A_3 point, where it changes into the face centered cubic lattice. In view of this information, it is now generally conceded that the thermal discontinuity at A_2 does not mark a change of phase. Ferrite exhibits only a feeble magnetic response above A_2, and a majority of those who have studied the subject believe that the interruption in the heating or cooling rate at A_2 is due largely to the adjustment incidental to the loss or gain of magnetic susceptibility by alpha ferrite. On heating the iron, therefore, the alpha modification persists to the Ac_3 point where it passes directly into the gamma form.

Comparison of Alpha and Gamma Iron.—Alpha iron crystallizes in the cubic system, but octahedra are the prevailing crystalline forms in gamma iron. At temperatures below 768°C. alpha iron has a high magnetic susceptibility, but the metal loses its magnetism when heated to above this temperature. Gamma iron is non-magnetic, is harder than alpha iron, and its electrical conductivity is about one-tenth that of alpha iron at ordinary temperatures.

Delta Iron.—Recently a fourth allotrope, known as delta iron, the transition point of which is located at 1400°C., has been reported. Very little is known concerning the delta modification, and since no practical applications of the new phase have been discovered, it has not been shown on the thermal diagram of the iron-carbon alloys (Figs. 48 and 51).

Thermal Critical Points in Austenite.—In austenite, a solid solution of iron carbide in iron, the A_3 point occurs at lower temperatures than in pure iron. Starting with a high temperature as in the case of pure iron, if the cooling rates of a series of low-carbon steels are accurately determined, it will be found that with increasing carbon content the Ar_3 point will be progressively lower until, with 0.9 per cent of carbon (13.5 per cent of iron carbide), it will merge with Ar_1, the point of recalescence, and produce an $Ar_{3\cdot 1}$ point. Thus, with a falling temperature, the gamma iron in an alloy of iron carbide and iron does not change to the alpha phase until the temperature drops below the line *GS* (Fig. 51) at a point that corresponds to the percentage of carbon in the steel.

Careful experiments have shown also that high carbon steels, at least those containing above 1.2 per cent of carbon, exhibit an upper critical point in addition to the point of recalescence. Because this point has been found to be connected with the separation of free iron carbide, or cementite, it has been designated by the notation A_{cm} (Ar_{cm} on cooling and Ac_{cm} on heating). As shown in Fig. 51, the A_{cm} point occurs at progressively higher temperatures as the carbon content of the steel increases.

Above the line *GSI* austenite is stable, but in a slowly cooled alloy, the solid solution decomposes as the temperature drops below this line. It is with the decomposition of austenite that we shall now have to deal.

Decomposition of Austenite.—When the solid solution, austenite, decomposes, it separates into iron carbide and ferrite. The manner in which it decomposes is illustrated in Fig. 51, where the solid solution is shown to exist within the range above the line *GSI*. In accordance with the principle already discussed in the case of liquid solutions (Fig. 9), p. 166, the temperature at which decomposition begins depends upon the amount of carbon present. If, for example, we start with a steel containing 0.5 per cent of carbon, which is equivalent to 7.5 per cent of iron carbide, at a temperature of, say, 900°C., it will cool without change until it reaches the Ar_3 point of the steel, which will be located on the line *GS* and will be equivalent to a temperature of about 785°C. At this point ferrite begins to separate from the solid solution. Because the temperature at which separation takes place is well below the Ar_3 point of pure ferrite, as it separates, the ferrite assumes the alpha form, but as long as it remains dissolved it continues in the gamma form. Just as was the case with liquid solutions, as the temperature continues to fall, assuming slow cooling, ferrite continues to separate, which thus increases the carbon content of the remain-

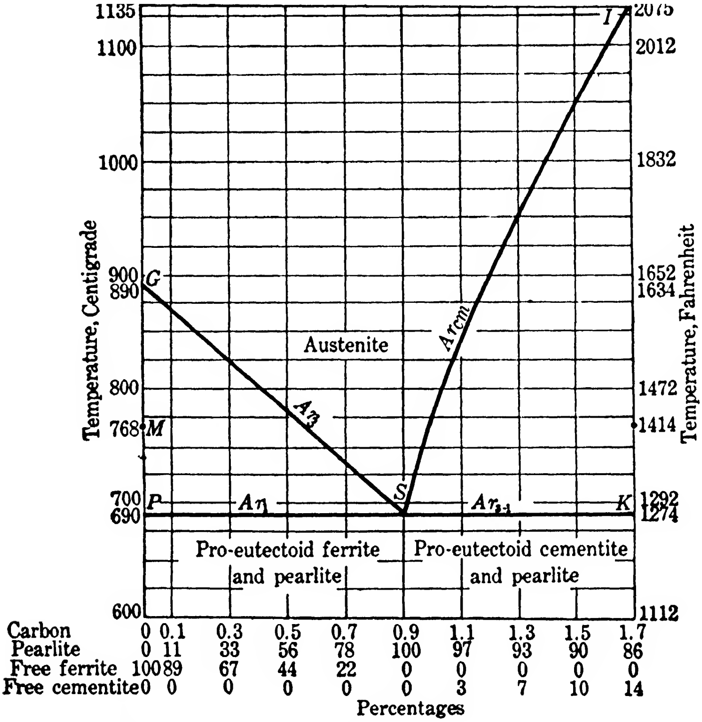

FIG. 51.—Thermal critical points in carbon steels.

ing austenite. The slope of the line *GS* indicates a progressive separation of ferrite with a falling temperature; that is to say, the carbon content and temperature of the austenite are at all times represented by the abscissas and ordinates of this curve. When the separated alpha ferrite reaches the temperature of 768°C., it acquires a magnetic susceptibility (p. 296), and any ferrite that separates from solution below this temperature at once becomes magnetizable alpha ferrite. Finally, by the continued separation of ferrite, the solid solution acquires a carbon content of 0.9 per cent, as indicated by the point *S*. In a similar manner, by the separation of ferrite, any slowly cooled steel containing less than 0.9 per cent of carbon will contain some austenite that has been enriched in carbon to the extent of 0.9 per cent by the time the Ar_1 point has been reached.

If, on the other hand, the steel should contain more than 0.9 per cent of carbon, when it is slowly cooled from above its Ar_{cm} point (on the line *IS*), iron carbide will separate out. This separation so decreases the proportion of carbon in the remainder of the solid solution, as indicated by the line *IS*, that when the point of recalescence (at *S*) is reached, this remainder will contain only 0.9 per cent of carbon.

From the previous explanation it is evident that the solid solution containing 0.9 per cent of carbon has the lowest decomposition point, and since in this respect it resembles the eutectic of a liquid solution, or alloy, it has been named the *eutectoid* alloy of iron and carbon. Also, steel containing this amount of carbon is known as a eutectoid steel. As a result of the selective separation, all steels, when slowly cooled from above the line *GSI*, to about 690°C. (the point *S*), will contain a certain amount of the eutectoid alloy. Depending upon the amount of carbon in the steel, the eutectoid alloy will be mixed with either crystals of ferrite or cementite.

It has been seen that the solid solution cannot cool below the line *GS* without precipitating ferrite, and it cannot cool below the line *IS* without precipitating cementite. But as it further cools and passes the point *S*, it crosses both lines. Therefore, the remainder of both the ferrite and cementite that now exist in the eutectoid solid solution are separated at this point. These two constituents separate from each other as fine crystals and may arrange themselves in the form of a laminated structure, as shown in Fig. 52. The name *pearlite* has been given to this structure, because under certain conditions it has an appearance resembling mother-of-pearl.

FIG. 52.—Eutectoid steel. Showing laminated pearlite. Magnified 750 diameters. (*Goerens.*)[1]

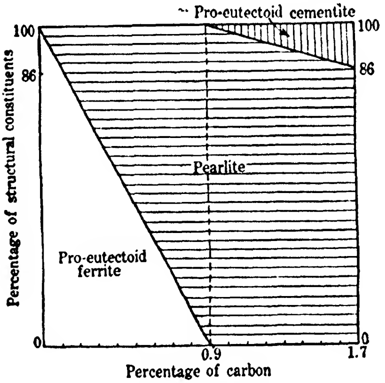

FIG. 53.—Percentages of structural constituents in steels.

The crystals of ferrite or cementite formed before the eutectoid point has been reached are called *free* or *proeutectoid* (*pro*, before) ferrite and cementite to distinguish them from the much smaller crystals of the same substances produced when the eutectoid austenite is converted into pearlite.

A graphic representation of the percentages of the structural constituents in steels containing pearlite ranging from 0 to 100

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

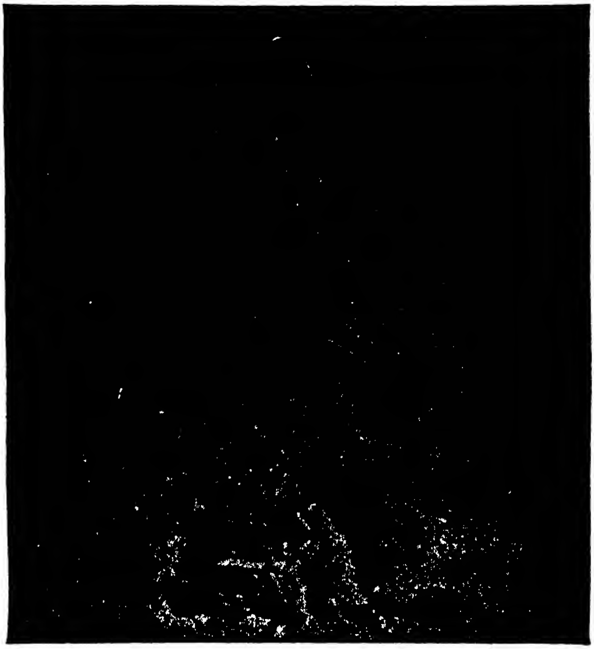

Fig. 54.—Steel containing 0.45 per cent carbon. Ferrite and pearlite. Magnified 1,000 diameters. (*Osmond.*)[1]

Fig. 55.—Steel containing 0.20 per cent carbon. Light areas ferrite, dark areas pearlite. Magnified 100 diameters. Etched.

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

per cent is shown in Fig. 53. Figure 54 shows a photomicrograph of steel consisting of grains of ferrite and pearlite. Since the carbon is only half that needed for a completely eutectoid steel, the excess ferrite has crystallized out in the form of separate grains. Such steels as this, that contain less than the eutectoid amount of carbon, are called hypoeutectoid steels. Figure 55 shows a hypoeutectoid steel of similar structure, but of insufficient magnification to show the lamellar nature of the pearlite. In Fig. 56 the structure of a steel containing more than the eutectoid amount of carbon is shown. Here the grains of pearlite are surrounded by free cementite. Such steels, containing above the eutectoid amount of carbon, are known as hypereutectoid steels.

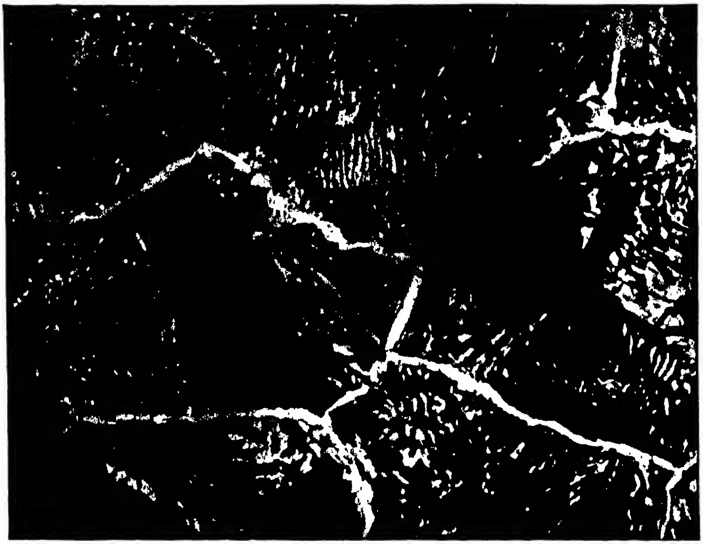

Fig. 56.—Steel containing 1.43 per cent carbon. Pearlite and cementite. Magnified 500 diameters. (*Boynton.*)[1]

Structural Changes during Heating.—The structural changes that occur in a steel during heating are the exact reverse of those that take place during cooling. If a eutectoid, pearlitic steel is heated to above its Ac_1 point, the components of the pearlite dissolve in each other or merge, and austenite is formed. If the steel had been either hypo- or hypereutectoid, so that either

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

proeutectoid ferrite or proeutectoid cementite crystals were mixed with the pearlite, then, as the temperature is gradually raised above the Ac_1 point, these crystals also dissolve in the austenite. Finally, when the temperature has been reached at which the first proeutectoid crystals appeared during cooling, they will all be again in solution; then the steel will be completely austenitic.

The Constituents of Hardened and Tempered Steels.—It has been determined that when the austenite of the eutectoid alloy is converted into pearlite, the change does not take place spasmodically, as might seem to be indicated by the point S, but in stages. In fact, the changes that take place in the region of which the point S may be considered the center extend over a range of at least 30°C.; they begin approximately 15° above the point S, and end a like number of degrees below it.

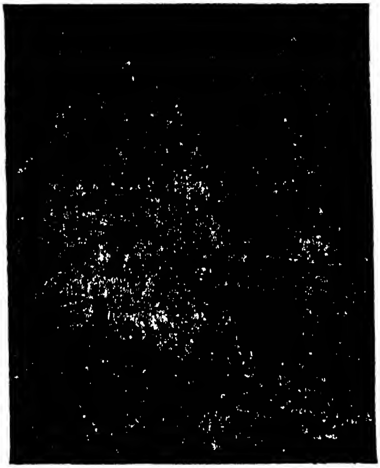

FIG. 57.—Martensite (black) in austenite. Magnified 100 diameters (*Stead.*)[1]

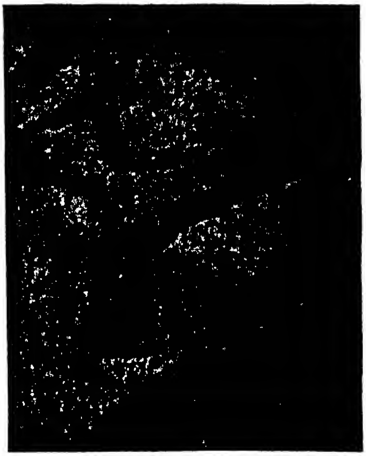

FIG. 58.—Ferrite F, martensite M, troostite black. Magnified 500 diameters. (*Howe.*)

In discussing Fig. 51, GSI was considered as a line, and any point upon it corresponding to a given percentage of carbon, was looked upon as the *critical point* or *temperature* for a steel containing that percentage. But since, as just explained, the structural changes do not in reality take place sharply, the critical

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[1] Reproduced by permission from Howe's "Metallography of Steel and Cast Iron."

temperatures are more properly spoken of as the thermal *critical ranges.* Because the structural change or transition from the solid solution, austenite, to the mechanical mixture, cementite and ferrite, called pearlite, is comparatively gradual, it can be caused to stop at certain points by rapid cooling. At least three incomplete stages of transition are commonly recognized; the constituents at these stages are known as transition substances. Named according to the degree to which the austenitic decomposition has proceeded, the series is as follows: austenite, martensite, troostite, sorbite, and pearlite, all of which can be recognized in suitably prepared specimens under the microscope. Photomicrographs are shown in Figs. 57 to 60. The names of all these constituents, except pearlite, have been derived from the names of noted investigators who have worked upon this subject.

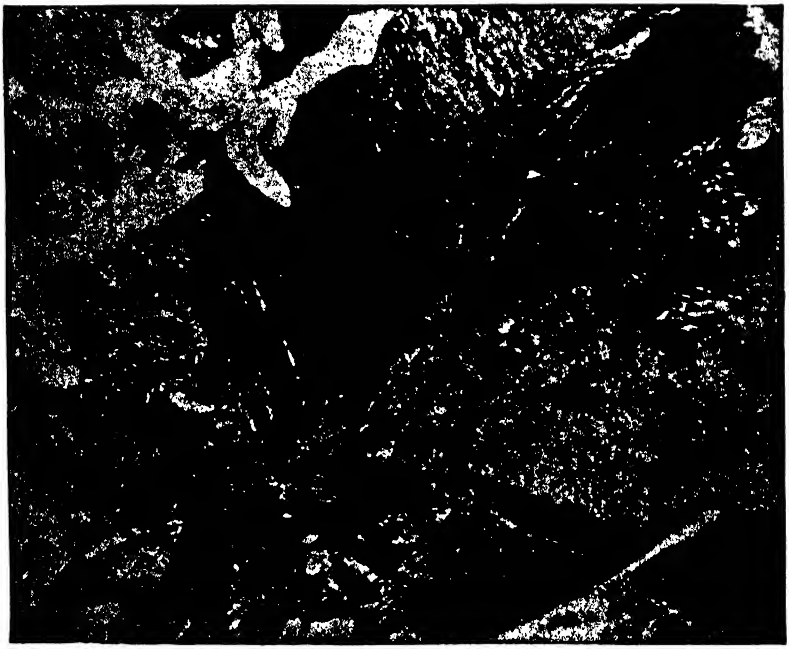

Fig. 59.—Hot-worked steel. Carbon 0.50 per cent. Magnified 650 diameters. The ill-defined constituent is sorbite.[1]

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

Although all the substances, except pearlite, exist naturally in a stable form only at comparatively high temperatures, it is possible, by rapid cooling under certain conditions, to cause them to be preserved until atmospheric temperatures are reached. Austenite will then be found in the steels most rapidly cooled. To preserve austenite, however, it is necessary that the carbon be above 1.1 per cent. Martensite will be found in those cooled with the next degree of rapidity, troostite in the next, sorbite in the next, and pearlite in those that are allowed to cool slowly.

FIG. 60.—Steel containing 1 per cent of carbon. Pearlite (laminated) passing into sorbite. Magnified 1,500 diameters. (*Osmond.*)[1]

Characteristics of the Constituents of Steels.—Austenite is very hard but *martensite is harder.* A polished surface of austenite can be plainly scratched with a steel needle, while a polished surface of martensite will be unaffected. Austenite does not occur in tempered carbon steels, but martensite will be found to a great extent in the harder varieties. Troostite is also

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

softer than martensite and occurs in great amount in tempered steels, especially in those quenched in boiling water, oil, and similar, less active, tempering media, as well as in steels that have been quenched and then tempered by reheating. Sorbite is softer than troostite; it is very close to pearlite in hardness. Pearlite is the softest of all. It occurs in slowly cooled or annealed steels. It is made up of alternate flake-like layers of alpha ferrite and cementite.

Hardening of Steel.—When a carbon steel in the softened condition is heated, pearlite persists, or is stable at any temperature below about 725°C., *i.e.*, the transition temperature on reheating. Hence, it is evident that a steel to be hardened must be heated to above that temperature to convert the mechanical mixture, pearlite, into the solid solution, austenite. If a pearlitic steel is heated to just below the Ac_1 point, no matter how rapidly it is cooled, it will still be in the unhardened state. If it is heated to above the Ac_1 point, however, even though but little, austenite will be formed. Then if it is rapidly cooled past this point, the complete change into pearlite will be prevented, *i.e.*, either martensite, troostite, or sorbite will be preserved, and the steel will be more or less hard. (It is very difficult to obtain the austenitic condition in ordinary carbon steel at atmospheric temperatures.) The degree of hardness of a steel containing 0.9 per cent of carbon is not dependent upon the distance above the Ac_1 point to which it may be heated. *Maximum* hardness may be obtained in this case by cooling with the greatest rapidity from *just above* this point. Besides a distinct ill effect is produced by heating to a higher temperature, because the crystal size is thereby increased.

The proper temperature from which a steel should be quenched to secure best results in hardening depends upon the amount of carbon it contains. Thus, for steels containing less than 0.9 per cent of carbon, maximum hardness and best crystal size may be obtained by quenching from just above the line *GS*. For steels containing over 0.9 per cent of carbon, maximum hardness results from quenching from just above the line *IS*. But since heating to the line *IS* produces large crystal size, it has been found that for these steels best general results are secured by quenching from just above the line *SK*.

A very reliable check to prevent excessive overheating can be had by noting at what point in the heating the steel loses its magnetism. This occurs at the Ac_2 point, *i.e.*, at 768°C.

Steel in the excessively hardened state, such as is obtained by quenching in water, is also very brittle—too brittle for use; some of this brittleness, therefore, must be removed. In lessening the brittleness some hardness is also unavoidably sacrificed. The process whereby the brittleness and hardness are lessened is known as tempering.

Tempering.—The austenite, martensite, troostite, and sorbite of the hardened steels are not stable in the ordinary sense at atmospheric temperatures. These constituents are prevented from decomposing in the hardened steel by the rigidity or immobility of the particles of the mass. To remove brittleness and soften the steel it is therefore only necessary to impart a certain amount of mobility to the molecules. This mobility can be caused by an application of heat, but since the degree of softening must be regulated, the heat must be quite accurately controlled. In the treatment of edged tools by the water-quenching process, only the tip is quenched, and then the desired amount of heat is allowed to flow into the tip from the uncooled shaft. By noting the color of the oxide developed upon the cleaned tip, the degree of heating may be judged, since the color of the oxide[1] changes with the depth of the layer, and this in turn bears a definite relation to the amount of heat applied. When this secondary heating has proceeded to the desired point, the influx of heat is stopped by quenching the whole of the hot portion. The secondary heating, or reheating, is often spoken of as the "drawing heat," or the temperature employed as the "drawing temperature."

The result of the tempering is, then, that the austenite or martensite of the steel is changed into some softer and less brittle form. The first heating causes the ferrite and pearlite of the steel to dissolve in each other, and the quenching keeps

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[1] The colors are due to the interference of light waves reflected from the inner and outer parallel surfaces of the oxide film. When the film is thin, the interference affects the blue and violet components of white light with the result that only the longer wave components, red and yellow, are visible. With a thicker film, the red and yellow components are cut out, and the film appears blue. This color effect is similar to that produced by films of oil on a wet pavement.

them dissolved, at least in large measure, by not allowing time for the separation to occur. Then, as heat is again applied, this interrupted separation is resumed and proceeds to an extent that depends upon the degree of heat and the time during which it is applied to the quenched steel.

It should be mentioned here, that because of the longer period during which the shaft of the tool is hot, its crystal size may be much increased, and that on this account fractures not infrequently occur at this point.

It is interesting to note that heat-treated steels change slowly at room temperature, although the rate of change is negligible, since apparently centuries are required for a steel to become noticeably softer when kept at about 20°C. At the temperature of boiling water, however, the softening is measurable; it is quite rapid at slightly above 200°C.

Combined Quenching and Tempering.—Instead of preventing the decomposition of the solid solution as far as possible by the rapid cooling in water, and then allowing a secondary influx of heat so that the decomposition may be resumed, the same result may be obtained by so regulating the rate of cooling that the decomposition proceeds to just the desired point in the first cooling. By choosing the proper cooling medium, any degree of hardness may in this manner be secured. Cooling media used in this way are molten solder, fused salts, oils of varying viscosities, solutions of salts, etc. The results secured by the use of these materials depend only upon the rate at which they are able to remove the heat from the steel. The steels are cooled rather rapidly past their critical temperatures, but not so rapidly that the proper amount of austenitic decomposition cannot take place.

These baths cool the steel less rapidly than water because of various factors, such as (1) the sensible heat of the bath, (2) the heat-conductivity of the bath, (3) the viscosity of the bath (liquids carry heat largely by convection), (4) the specific heat of the bath, (5) the volatility of the liquid (a cushion of vapor, which is a poor conductor, may form about the steel).

Some Illustrations Showing the Effect of the Cooling Rate.—If the steel is cooled slowly in the furnace, the excess constituent, either ferrite or cementite, will separate out completely and the pearlite will appear in the form of large plates. If the steel is cooled through its critical range relatively slowly, as normally in air, the pearlite will have a finely crystalline structure. If cooled in an air blast, it will be extremely fine.

If the steel is cooled from well above the critical range rather rapidly, as by quenching in oil, it will consist of martensite; if quenched in oil from the upper part of its critical range, it will consist of the excess constituent and troostite; if quenched in oil from the lower part of the critical range, it will consist of the excess constituent and sorbite.

FIG. 61.—Burnt steel. Carbon 1.24 per cent. Magnified 20 diameters. Quenched at a white heat. Unetched. (*Osmond.*)[1]

If the steel is cooled from well above its critical range at a very rapid rate, as by quenching in liquid air, it will consist of austenite; if quenched in liquid air from the upper part of its critical range, it will consist of the excess constituent and martensite.

Overheating (Commonly Called "Burning") of Steel.—Overheated steel may be really oxidized, *i.e.*, burned, or it may not. Overheating is recognized as existing in three stages. The

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

first stage exists when drops of melted metal have begun to form in the interior of the mass. This melted metal segregates or collects between the crystal faces and causes weakness. The second stage is reached when the molten drops segregate as far as the exterior and leave behind cavities filled with gas. The third stage occurs when sufficient gas is formed to force small drops of liquid steel through the surface of the piece. This produces the well-known scintillating effect seen at this temperature. The gas which collects is probably carbon monoxide, produced by the action of the occluded oxygen upon the carbon, or it may be the occluded nitrogen or hydrogen which steel almost always contains.

Air enters the cavities left by the forcing out of the molten portion, and produces ferrous oxide on the surface of the cavity. The crystal faces are then in reality burned. Steel in this last condition is useless. Because of the high heat to which it has been raised, burned steel is usually also coarsely granular in fracture.

Case-hardening.—When the manufactured steel article is required to have a tough core and a hard surface, it is case-hardened. The action in the case-hardening process is the same as in the production of cementation steel, except that the carbon enters to only a very slight depth, and the process requires but a few hours instead of several days.

The articles to be case-hardened are packed usually in nitrogen-bearing carbonaceous material, such as charred leather and other animal products, or in cyanides or ferrocyanides, since best results are produced by such materials. Steels suitable for case-hardening are those containing about 0.15 per cent carbon, and not above 0.25 per cent manganese because this element has a tendency to produce brittleness in the case. In case-hardening, it is necessary to heat the steel to above its critical temperature, which means for 0.15 per cent carbon about 900°C. Also, the carbonizing seems to proceed best when the iron is in the gamma condition. The steel apparently acquires carbon chiefly from the gases, carbon monoxide (CO) and cyanogen (CN), probably according to the equations:

$$2CO + 3Fe \rightarrow Fe_3C + CO_2$$

and

$$2CN + 6Fe \rightarrow 2Fe_3C + N_2$$

By case-hardening, the carbon in the case will be raised to about 1 per cent.

STRUCTURAL CHANGES IN CAST IRON

As explained on page 293, the consideration of the structural changes that occur in cast iron was deferred until a discussion of the structural changes that take place in steel had been presented. This was done because steels solidify entirely as austenite, and austenite appears as one of the major constituents during the solidification of cast iron.

Transformations in the Austenite of Cast Iron.—It was shown on page 299 that when hypereutectoid steels have cooled to their Ar_{cm} point (on the line SI), proeutectoid cementite begins to separate from the austenite and continues to do so until the Ar_1 point is reached. At this time the austenite that still remains will contain 0.9 per cent of carbon. Now in all cast irons, the austenite formed is identical with a 1.7 per cent carbon steel. Consequently, when the cast iron cools, all of the austenite present in it, both primary and eutectic, is changed in the same manner as in a hypereutectoid steel. Because the Ar_{cm} point of a 1.7 per cent carbon austenite is located at 1135°C. (Fig. 48), the decomposition begins as soon as the cast iron has solidified, and it continues through the usual range to the Ar_1 point, 690°C. By the time this temperature has been passed, assuming normal, slow cooling, the austenite will have been transformed into a mass of pearlite mixed with proeutectoid cementite. If the cooling is more rapid, the decomposition will be less complete, just as has been described for the steel.

The Decomposition of Cementite. Formation of Graphite.—It is possible that graphite, under certain conditions, may form directly from the melted iron or from crystals of austenite, but in the majority of cases, it is probable that it forms from the decomposition of cementite.[1] Cementite is an unstable compound and within a certain range of temperature changes over to the stable graphite and ferrite, as follows.

$$Fe_3C \rightarrow 3Fe + C$$

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[1] HOWE, "The Metallography of Steel and Cast Iron," p. 216.

In gray-iron castings, it is only at the temperature of solidification, about 1135°C. and immediately below it, that this reaction takes place to any extent. And all of the cementite of the iron is not available at that time. In the first place, there is no primary cementite in the commercial gray cast irons because they do not contain sufficient carbon to be hypereutectic. And at the temperature mentioned, very little cementite from the decomposing austenite could have had time to separate. Consequently, at the temperature of graphite formation, it is only the eutectic cementite that exists to any extent, and it is from this cementite that the graphite of the gray cast iron is produced.

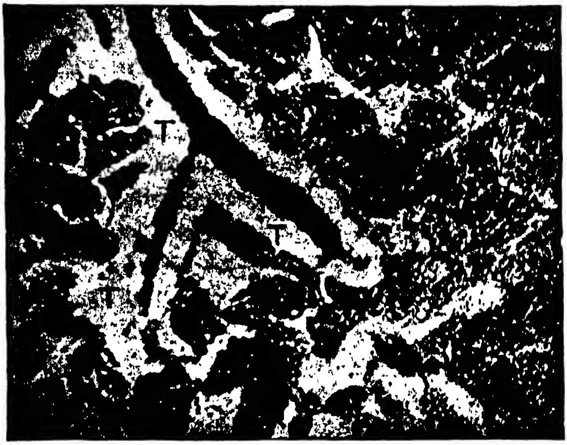

Fig. 62.—Hypoeutectic gray cast iron with hypoeutectoid matrix. Graphite (black) enclosed by free ferrite, T, T, T. The gray ground mass is pearlite. Magnified 180 diameters. (*Howe.*)

Since the carbon of the primary austenite is to a considerable extent not graphitized, gray castings usually contain more or less combined carbon; the amount ranges from a few tenths up to 1 per cent. As a result, the matrix or foundation structure partakes of the nature of steel; pearlite is found in these irons, as has been stated. This is illustrated in Figs. 62 and 63. In the former, the amount of combined carbon is less than 0.9 per cent. The matrix is, therefore, like a hypoeutectoid steel, it shows free ferrite (white) about the graphite flakes and pearlite in the shaded area. In Fig. 63, the matrix is hypereutectoid, since it contains more than 0.9 per cent of combined carbon; it shows graphite, pearlite, and free cementite.

Rapid Cooling and Impure Alloys.—It must be remembered that the structures just described result from the slow cooling of pure alloys. Rapid cooling tends to preserve both austenite and cementite, and the decomposition of the latter is greatly effected by the presence of impurities, as has been explained under Effect of the Impurities, on pages 239 to 244.

FIG. 63.—Gray cast iron with hypereutectoid matrix. Graphite, free cementite, and pearlite. Magnified 500 diameters. (*Wust.*)[1]

Residual Graphite in Melted Iron.—In the ordinary melting of cast iron, minute particles of undissolved graphite remain in suspension and act as nuclei for the formation of large crystals of graphite when the melted iron solidifies. If, however, the temperature of the melt is raised to 1565°C. (2850°F.) or higher, the graphite will all be dissolved, and there will be no nuclei to favor the growth of large crystals of graphite during the freezing of the metal.[2] As a result, the graphite precipitates in the form of much finer crystals than would have been produced if the melt had been heated to a lower temperature. Due to this fact, the strength of the casting is greatly increased.

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

[2] MOLDENKE, "Recent Developments in the Metallurgy of Cast Iron," *Metals and Alloys*, vol. I, p. 327, January, 1930.

"Pearlitic" Cast Iron.—It has just been shown that gray-iron castings, considered from the standpoint of microstructure, consist essentially of ferrite, pearlite, free cementite, and graphite. In the commercial irons there will be present also the usual impurities, iron phosphide and the sulfides of iron and manganese, in varying amounts. The ferrite is weak, and the presence of graphite increases this weakness. Pearlite is considerably stronger than ferrite. A method has been developed whereby cast iron is produced that has a much higher content of pearlite than is usual with gray-iron castings.[1]

In discussing the effect of the impurities on the condition of the carbon (pages 239 to 244) it was shown that silicon promotes and sulfur hinders the formation of graphite. In producing the highly pearlitic cast iron, the iron employed has a low silicon content, about 1.1 per cent, and a high sulfur content, about 0.15 per cent. If poured in an ordinary sand mold this iron would yield a white casting, but to secure the high pearlite content, the iron is poured in a mold heated to a temperature sufficiently high that the setting of the iron and its cooling subsequent thereto is delayed. Because of the slow cooling through the solidifying range, the primary austenite crystals become of fair size, but the low silicon and the high sulfur prevent the iron from becoming coarsely graphitic, a condition that the heated molds would otherwise bring about. The result is that sufficient carbon remains combined to form a considerable amount of austenite of approximately the eutectoid composition. When this austenite decomposes in cooling, more pearlite than is usual in cast irons is produced. Castings of this sort have been produced regularly, having tensile strengths ranging from 45,000 to 100,000 lb. per square inch, as compared with the 25,000 lb., or thereabout, of ordinary gray-iron castings.

Annealing of Gray Cast Iron.—In addition to the annealing of white cast iron, which produces the well-known malleable cast iron described on page 251, there has been developed a process for annealing gray cast iron which is said[2] to yield a product much superior in many ways to the usual malleable cast iron.

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[1] *Iron Age*, 112, p. 412, Aug. 16, 1923.

[2] *Iron Age*, **113**, no. 1, p. 15, Jan. 3, 1924.

Moreover, the time required is only about 45 min. instead of approximately 2½ days as required by the older method.

The process is very simple. It consists of heating the gray iron to a temperature of about 870°C. while it is protected in a wrought-iron muffle surrounded by a gas flame. The muffle is open at the top. As soon as the cast iron reaches the desired temperature, which requires about 30 min., the muffle and its contents are removed from the furnace and allowed to cool in air; the only precaution is that a cover is placed on the muffle to protect the iron from drafts. About 15 min. is required to cool to a black heat, after which the cast iron is removed from the muffle and allowed to cool to atmospheric temperature.

Gray cast iron annealed in this way is said to possess a much higher combined malleability, ductility, pliability, and resiliency than the gray iron before annealing. In its resiliency it most resembles steel, since it possesses this property both before and after distortion. A thin bar of it may be coiled and used as a spring, although it would be less strong and resilient than a tempered steel spring.

In microstructure, the annealed iron is not unlike that described under Pearlitic Cast Iron. In ordinary gray cast iron, the ferrite is rendered discontinuous by the coarse flakes of graphite, which cleave readily. At the annealing temperature employed in this process, some of the graphite is absorbed by the solid solution existing then. With the moderately slow cooling that follows, the solid solution decomposes into ferrite and pearlite, intermingled with fine particles of carbon surrounded by the ferrite from which they have separated. The greater resiliency it possesses as compared to that of the older product is no doubt due to the presence of pearlite rather than the ferrite, which is the main constituent of the ordinary malleable cast iron.

It is not known just why the effects observed are produced by this method. It is significant to note, however, that muffles made of the usual refractory materials, clay and graphite, and of cast iron, ingot iron, and steel, were used without success. It is believed that the reason for the failure in these cases was that the materials mentioned are more porous than wrought iron and that hydrogen from the products of combustion found its way through the muffle to the cast iron. It is known that hydrogen is present in the products of combustion and that it has a deleterious effect upon iron and steel. This conclusion seems to be borne out by the fact that when a crack appeared in the wrought-iron muffle, a hard spot opposite it appeared in the iron being annealed.

ALLOY STEELS

The steels known as alloy steels are those that owe their properties, in a very large measure at least, to the presence of one or more elements other than carbon, although carbon is always present, whereas the properties of the older type of steels depend largely upon the percentages of carbon they contain. For distinction then, in commercial terminology, the latter are designated as *carbon steels,* and the former as *special* or *alloy steels.*

The alloy steels are divided into two classes: Those that are made up essentially of iron, carbon, and one special element, as nickel, manganese, chromium, tungsten, and others, are called *ternary alloy steels.* Those that contain essentially iron, carbon, and two special elements, as nickel-chromium, tungsten-manganese, tungsten-molybdenum, or other combinations, are known as *quaternary alloy steels.*

The results obtained by the addition of the special element are usually very marked and often very unexpected, so that the properties of the resultant steel cannot accurately be forecast; they must be determined by trial. This procedure is especially necessary with the quaternary steels, for in some cases the effect of the two elements, working in conjunction, is directly opposed to the effect of each element alone in steel. The whole subject of special steels is still quite new and much remains to be done, both in preparing new combinations as well as in further investigating the properties of those already prepared.

The process of manufacture is practically the same as for the making of the more ordinary carbon steels. They are usually made in the open-hearth, crucible, or electric furnace. The special elements are added usually at the time when the deoxidizer or recarburizer is added in the normal practice for each of the processes mentioned. An exception should probably be made in the case of nickel, which is usually added in the early stages of the open-hearth treatment, since it has no great tendency to be lost through oxidation.

Structure and Properties.—Guillet has investigated the structure and properties of the alloy steels, and the following statements concerning ternary steels are based on his results, as quoted by Sauveur.[1]

If into a carbon steel, which when slowly cooled is pearlitic, a small amount of the special element is introduced, the steel will at first remain pearlitic, but, if the carbon remains constant, and the special element is increased in amount, it will become martensitic, then austenitic, and finally cementitic, depending upon the amount introduced. The terms employed are used to signify that the steels naturally assume these structures as their stable condition when slowly cooled in air. *Cementitic steels* are those in which the austenitic condition does not appear, but in its stead there is a structure made up of particles of the double carbides of iron and the special element contained in a matrix of martensite, troostite, sorbite, or pearlite. A result similar to that produced by increasing the amount of the special element may be obtained by keeping the special element at a constant percentage and increasing the quantity of carbon. Hence, as either of the two constituents is increased in amount, the less will be the quantity of the other needed to produce a different structure. In brief, the desired structure may be obtained by increasing either carbon or the special element, but it may be obtained more quickly by increasing both. As would be expected, the alloy steels may be caused to assume, by suitable heat treatment, other structural forms than those which they acquire when slowly cooled in air. A martensitic steel, for example, may be made austenitic by quenching and pearlitic by cooling slowly in the furnace.

The fact that the special elements are able to produce in steel the austenitic or martensitic condition on slow cooling depends upon an ability they have to lower the critical temperature to such an extent that before it is reached the mass has become so rigid that the decomposition is either prevented altogether or else is inhibited to such a degree that only the martensitic stage is reached. The conclusion drawn from many observations

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[1] "Metallography of Iron and Steel," lesson xvii.

seems to be, according to Sauveur, that when the critical temperature remains above 300°C. the steel, when slowly cooled, will be pearlitic. At this temperature the particles are sufficiently mobile that the transformation can take place. When the critical temperature is below 300°C., the steel will be martensitic. When the critical point is lowered to atmospheric temperatures or lower, the structure will not be decomposed at all, and will therefore be austenitic.

TYPES OF ALLOY STEELS

On the basis of the preceding explanation the special steels are divisible into at least four classes: (1) cementitic, (2) austenitic, (3) martensitic, and (4) pearlitic.

FIG. 64.—Showing the structure of cementitic tungsten steel. Tungsten 39.96 per cent. Carbon 0.867 per cent. The white crystals are the double carbide. Magnified 200 diameters. (*Guillet.*)[1]

Cementitic Steels.—Certain elements, for example, chromium, tungsten, molybdenum, and vanadium, when present in steel in sufficient quantity, cause crystals of the double carbide of iron and the special element to separate out when the steel is slowly cooled. These crystals may be set in a matrix of pearlite or some harder constituent and then exhibit a structure such as is shown in Fig. 64. The cementitic steels have less strength and

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

ductility and more brittleness than austenitic steels. When such steels are heated to about 1250°C., however, so that these carbides go into solution, and are then cooled at a proper rate so that the carbides are held dissolved, the steel has the remarkable property of retaining its hardness at a red heat. It may then be used for high-speed tools.

Austenitic Steels.—The austenitic special steels have properties very similar to those of the austenitic carbon steels, *but unlike the quenched austenitic carbon steels, they are stable at all temperatures below their solidifying point.* Hence they are only with difficulty affected by heat treatment. Austenitic steels are moderately tough, but are very ductile and have a low elastic limit (page 82). They have a great resistance to wear by abrasion and to rupture by shock. They are very hard. Since austenite does not contain alpha iron these steels are *non-magnetic.* Their chief objectionable features are their low elastic limit and the extreme difficulty with which they may be machined. Some steels that are austenitic when cooled in air become martensitic or troostitic when slowly cooled in the furnace.

Martensitic Steels.—These steels generally contain less carbon and special elements than the austenitic steels. They are very hard—harder than the austenitic steels. They are brittle, which is one of their chief disadvantages. Besides, because of their hardness, it is almost impossible to machine them. Some martensitic steels can be made pearlitic by slow cooling in the furnace and austenitic by quenching in water. This property is a distinct advantage. The steel may be machined, for example, in the pearlitic form and hardened by allowing it to become martensitic again by cooling in air, a process that eliminates the risk of cracking during quenching and tempering.

Pearlitic Steels.—The pearlitic special steels have a higher elastic limit and are frequently harder than the pearlitic carbon steels. They are usually tougher and better able to resist rupture by shock than the carbon steels. These superior qualities are probably due, partly at least, to the fact that the pearlitic structure is made up of finer layers in the special steels.

By increasing the amount of carbon in the exterior by casehardening, the pearlitic special steels may be given a hard martensitic or tough austenitic shell when cooled in air. In this way the risk of fracture which attends quenching from above the critical temperature is avoided.

COMMON PEARLITIC ALLOY STEELS

Nickel Steel.—The nickel steels are the most used of all the alloy steels. They may contain as much as 42 per cent of nickel for special uses, but the steels of the greatest commercial importance contain about 3.5 per cent of nickel and about 0.5 per cent of carbon. These are pearlitic. Within the range of 10 to about 28 per cent the steels are martensitic, with higher percentages they are austenitic.

The 3.5 per cent nickel steels exhibit the properties described under the general head of pearlitic steels. With this amount of nickel, the steel has an elastic limit about 50 per cent greater than a similar steel would possess without the nickel, and the ductility is only about 15 to 20 per cent less. According to Stoughton, it is probably due to the high elastic limit of nickel steel, that it so well resists what is called "fatigue." This means that it resists rapidly applied, repeated, and alternating stresses. All steels ultimately break down under such stresses, even though the load is far less than the steel could bear indefinitely if constantly applied. The 3.5 per cent of nickel increases the resistance of steel to such stresses about six times. It is also because of the higher elastic limit that nickel steel is used in bridges, and in automobile and airplane parts.

The crystalline structure of nickel steel is much finer than that of carbon steel; this is probably the reason for its increased toughness. Microscopic cracks, if started, develop much more slowly than when the crystals are larger, and the cleavage planes therefore greater.

Although the 3.5 per cent nickel steel is much harder than carbon steel, it can be machined without difficulty. Because of its hardness, it is excellent for use on railway curves where abrasion is great. Nickel steel has also a low coefficient of friction, and on this account is well suited for making axles for automobiles, etc.

It has a very great shearing strength and so is well adapted for use in making rivets. Nickel segregates very little and seems also to lessen the segregation of other elements. Nickel steel has a lower melting point than the ordinary carbon steel. It is easily cast, and makes exceptionally sound castings, but it welds less readily than carbon steel.

Steel containing from 22 to 24 per cent of nickel is used for electric resistance units, such as in toasters, flatirons, and other heating devices.

Nickel steel corrodes very little. For this reason, with 30 per cent of nickel, it has been found very serviceable in making boiler tubes.

When the amount of nickel present is about 36 per cent, the coefficient of expansion is practically zero. This alloy is called "invar." It is used for balance wheels in watches, pendulums, surveyors' tapes, etc. With about 42 per cent of nickel, the steel has about the same coefficient of expansion as glass, so that it was at one time used in electric-light bulbs for fusing into the glass, where the joint must be kept airtight. Such metal has been called "platinite," because originally platinum only was used here. Platinite has not proved entirely suitable for lamps and now a compound wire, having a 38 per cent nickel-steel core encased in copper and sometimes coated with platinum is employed. Nickel steel is used in the "armored glass," so much employed for fireproofing.

In general, then, this steel is very suitable where exceptional strength, hardness, toughness, abrasion resistance, and corrosion resistance are required.

Chromium Steels.—Depending upon the amount of chromium present, the chrome steels may be pearlitic, martensitic, or cementitic. Those generally prepared contain under 3 per cent of chromium, and from 0.8 to about 1.5 per cent of carbon. With this composition they are pearlitic when slowly cooled. Chromium seems to affect the position of the critical point but little. It causes the structural transformation to take place more slowly, however, so that the steel can be easily made martensitic by quenching.

Unlike nickel, which dissolves in the iron and becomes associated with the ferrite, chromium forms a carbide and becomes associated with the cementite. In this way, it imparts great hardness to the steel. Because of its hardness, chrome steel is used for files; several thousand tons, containing about 1.3 per cent carbon and 0.5 per cent chromium, are employed annually for this purpose. Because chromium increases the elastic limit and lessens the liability to rupture by shock, chromium steel is much used for the wearing parts of plows and rock-crushing machinery.

Heat-treated chrome steel is characterized by an extreme fineness of grain, which imparts the valuable property of toughness. With chromium from 1 to 1.5 per cent and the carbon about 1.1 per cent, chromium steel is used for ball and roller bearings, for which purpose it is well adapted because of its great hardness, resiliency, and compressive strength. It has a tendency to crack during heat treatment.

Nickel-chromium Steel.—According to a recognized authority on the heat treatment of steel, the chrome-nickel steels probably represent the best all-round alloy steels in commercial use for general purposes. They appear to have combined in them the desirable effects of both nickel and chromium. To the increased ductility and toughness conferred upon the ferrite by the nickel is added the mineral hardness given to the cementite and pearlite by the chromium. Because of its great combined toughness and hardness, the largest amount of nickel-chrome steel was formerly used for armor plate. Relatively little armor plate, however, has been manufactured since the first Naval Armament Conference at Washington.

The usual percentages employed are from 1.5 to 3.5 per cent of nickel and from 0.6 to 1.5 per cent of chromium. The nickel-chromium steels have a very wide application. Their use may by typified by mentioning automobile parts, as crankshafts and gears.

¶ **"Stainless" Steels.**—Several non-tarnishable steels, varying somewhat in composition, have been patented, and are manufactured under such names as *Krupp-Nirosta's* KA_2, *Allegheny Metal,* and *Rezistal Steel.* All of these steels contain a high percentage of chromium. As given by Nelson,[1] the following composition is typical: carbon, 0.07 to 0.15 per cent; silicon under 0.75 per cent; nickel, 8 to 10 per cent; and chromium 16.5 to 19.5 per cent. With this composition, the steels are austenitic. These alloys cast well, are malleable and ductile, and may be

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[1] "Chrome-nickel Alloy Steels," *Iron Age*, p. 888, October, 1929.

rolled both hot and cold. They do not corrode or tarnish, have a high acid and flame resistance and are non-magnetic. Because of their excellent mechanical properties and high corrosion resistance, the steels are used for table and kitchen cutlery, heads of golf clubs, skates, rifles, harness hardware, steam traps, water meters, valves on gasoline engines, turbine blades, parts of pumps for acid waters, chemical equipment, structural work, etc. Due to the highly infusible chromium oxide that is formed by the oxidizing flame, the steel offers a high resistance to the "cutting" action of the oxyacetylene torch. The Rezistal steel has been reported to be from ten to twelve times harder to cut with the burglar's torch than a 1 per cent chromium steel.[1]

The nickel-chromium steels of this type are susceptible to a high polish and are now being used for bright trim on automobiles and for similar uses. Just as chromium plating supplanted nickel plating for such purposes, the "stainless" steels are now taking the place of chromium plating. Since the bright work formed of it has the same composition throughout, there can be no peeling.

Vanadium Steel.—Vanadium seems to have but little effect upon the critical temperature of steel. Any steel that contains less than 1 per cent of vanadium will be pearlitic. In the commercial steels, the vanadium scarcely ever exceeds 0.2 per cent, hence, they are pearlitic when slowly cooled. With the single exception of carbon, no element is so powerful in its effect on steel; even 0.1 per cent will produce very noteworthy results. Ordinarily, vanadium ranges from 0.12 to 0.15 per cent, carbon from 0.25 to 0.55 per cent, and manganese from 0.5 to 1 per cent. Usually, about 1 per cent of chromium or nickel is used in the vanadium steels; hence, they may be considered quaternary.

A very noteworthy point is that the vanadium is an exceedingly active deoxidizer; it lessens blow holes and apparently segregation. Because of the great readiness with which it combines with oxygen and perhaps with nitrogen also, it must be added to the steel only after the addition of manganese and carbon has been made. It would be lost otherwise.

The properties of the pearlitic vanadium steels are in many ways similar to the pearlitic nickel steels. They have a high

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[1] "Nickel and Its Alloys," *U. S. Bur. Standards Circ.* 100, 1924.

combination of elastic limit and ductility, are very hard and tough, and seem to be especially able to resist shock and vibratory stresses. Unlike nickel steel, vanadium steel welds readily.[1]

Chrome-vanadium Steel.—This steel is similar to chrome-nickel steel, but it is said to be more easily machined and more free from surface defects, such as scale pits and seams. It probably has also a higher combined ductility and elastic limit than chrome-nickel steel. In the hardened state, chrome-vanadium steel may be had with a tensile strength of 250,000 lb. per square inch and an elastic limit of 210,000 lb.[2]

Chrome-vanadium steel is used for driving axles and other locomotive forgings, automobile springs and axles, air flasks, torpedo tubes, gun forgings, etc.

For springs, the chromium will range from 1 to 1.25 per cent, and the vanadium from about 0.15 to 0.25 per cent, but for other purposes the chromium will range from 0.8 to 1.1 per cent.

Silicon Steel.—Silicon has no very noticeable effect on the thermal critical temperatures of steel. It exists probably as a silicide (FeSi) in solid solution in the iron. If the silicon does not exceed 5 per cent, the steel is pearlitic; with more than this amount, some graphite is formed.

There are two types of silicon steel, one employed for electrical, and the other for mechanical construction. For electrical purposes, the steel contains from 3 to 5 per cent of silicon and the smallest possible amounts of carbon, manganese, and other elements. The most important uses of this alloy depend upon its magnetic properties. It has a higher degree of magnetic permeability than the purest iron. Its hysteresis is low, *i.e.*, it does not persist in a state of magnetism after the magnetizing force has been removed. For these two reasons it is very useful in constructing electromagnets and electric generating machinery. It has a high electric resistance; this lessens the effect of the "eddy currents" which detract from efficiency.

For mechanical purposes, the alloy contains less silicon, from 1.5 to 2.0 per cent; and considerable manganese, from 0.5 to 0.8 per cent. The carbon ranges in the neighborhood of

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[1] For properties of vanadium steel, in detail, see pamphlets issued by the American Vanadium Company.

[2] Stoughton, "Metallurgy of Iron and Steel," p. 448.

about 0.5 per cent. This alloy is used for the leaf-type springs such as are employed in automobiles. For this purpose it seems to be well suited because, when given a double heat treatment, it has a very fine grain, a higher strength, and lower deflection under load than carbon steel, and is relatively cheap.

SELF-HARDENING STEELS

Some of the alloy steels remain austenitic upon being slowly cooled in air. They owe this property to the fact that the special element or elements they contain lower the critical temperature to a point below the temperature of the atmosphere. On this account they cannot be very appreciably softened by heat treatment. *Being austenitic, these steels are all non-magnetic.*

Manganese Steel.—The usual manganese steel is that which contains about 12 to 14 per cent of manganese and about 1 to 1.3 per cent of carbon, except steels to be rolled, which contain less carbon.

When this steel is cast and slowly cooled, it is hard, brittle, and non-ductile. If heated to 1000°C., or more, and then quenched in oil or water, it will have pronounced ductility and toughness; the ductility is about equal to that of low-carbon steel or wrought iron, although the tensile strength is about three times as great. This toughening by quenching is interesting since it is the very opposite effect from that produced by similarly treating carbon steel. Although tough, the steel, when quenched, is practically as hard as before, so that it cannot be machined or drilled and there seems to be no way of making it softer.

Manganese steel has a low heat conductivity and so must be heated slowly and uniformly to avoid cracking. It is very difficult to forge and roll successfully. This is particularly true of the high-carbon manganese steels. When Hadfield first produced manganese steel it was impossible to produce a manganese steel low in carbon, because the only ferromanganese available was the product of the blast furnace, which is almost saturated with carbon. Since manganese, practically carbon free, has been produced in quantity in the electric furnace and by the thermit process, low-carbon manganese steels have been produced that are relatively much more workable. Manganese steel has a rather low melting point, about 1360°C.

It is used wherever extreme hardness and abrasion resistance are required; for example, the wearing parts of rock-crushing machinery, the teeth of steam shovels, railroad and trolley frogs, crossings and curves, mine-car wheels and burglar-proof safes are made of it. Its uses are somewhat limited by the fact that it must usually be cast into finished shape. It can be rolled, nevertheless, and railroad rails are made of it.

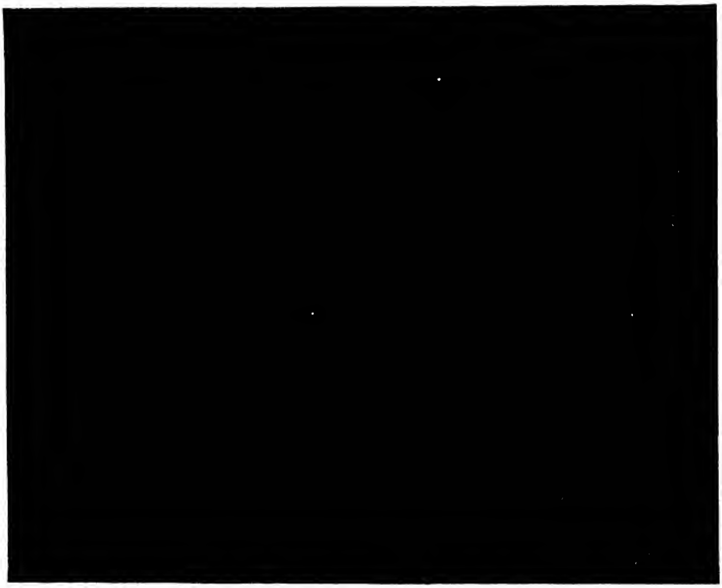

FIG. 65.—Manganese steel. Austenitic. Cast. Magnified 50 diameters.[1]

Manganese-tungsten Steel.—This steel has been usually known as "Mushet steel" because it was first produced by Robert Mushet. Although the proportions of the elements vary, the following is a very good example: tungsten 9 per cent, manganese 2.50 per cent, and carbon 1.85 per cent.

The steel is very hard and durable. Tools made of it are used for cutting extra hard metals. It is considered economical, regardless of its higher cost, because it will take such deep cuts and last so long without regrinding. With the proportions given, it is not a high-speed steel.

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

HIGH-SPEED TOOL STEEL

The name "high-speed steel" is used to indicate those alloy steels that do not lose their hardness and toughness at a red heat. Consequently, in the form of tools, they can be used to do cutting work at a speed so great that the cutting edge is raised to and kept at a red heat by the frictional resistance. Tungsten, either alone or in combination with chromium and vanadium, seems to be best able to confer this property.

Composition.—Although the amount of tungsten employed may range between 8 and 24 per cent, perhaps in nine-tenths of all the steel of this kind produced, it ranges between 16 and 20 per cent. Chromium may range between 2 and 8 per cent, but averages about 4 per cent. Its effect is to increase the hardness. Although molybdenum has been employed as a substitute for chromium, it does not seem to yield results that are entirely satisfactory. The amount of vanadium generally used ranges in the neighborhood of 1 per cent. Aside from its beneficial cleansing action, it seems to impart a certain added hardness.

The tungsten combines with the carbon of the steel, which runs from about 0.6 to 0.8 per cent, to form tungsten carbide. The tungsten carbide crystallizes with iron carbide as a double carbide, which is soluble in austenite at high temperatures, although with the amount of tungsten employed, there is more of the carbide present than can dissolve in the austenite at any temperature. Some of the tungsten, as well as some of the chromium and vanadium, dissolve as such in the ferrite of the austenite.

Heat Treatment.—The first step in the heat treatment given the steel consists of heating it to incipient fusion, a temperature of about 1250°C., which would ruin an ordinary carbon steel. This is done to put as much of the double carbide into solution in the austenite as possible. Then the steel is quenched in oil. Depending upon the temperature of the oil, varying amounts of austenite are preserved; the remainder passes into martensite. Scattered through the austenitic-martensitic matrix are many particles of free double carbide, globular in outline, that give evidence of never having been in solution in the matrix at any stage of the heat-treating process (Fig. 66).

For tools designed for use on lathes and planers, the usual treatment is that described; for milling cutters and similar tools, a secondary or "drawing" treatment is generally given. For the drawing treatment, the quenched steel is heated to about 595°C. for 30 min., when the austenite that was preserved by the quenching passes into martensite, with the result that the hardness of the steel is increased.

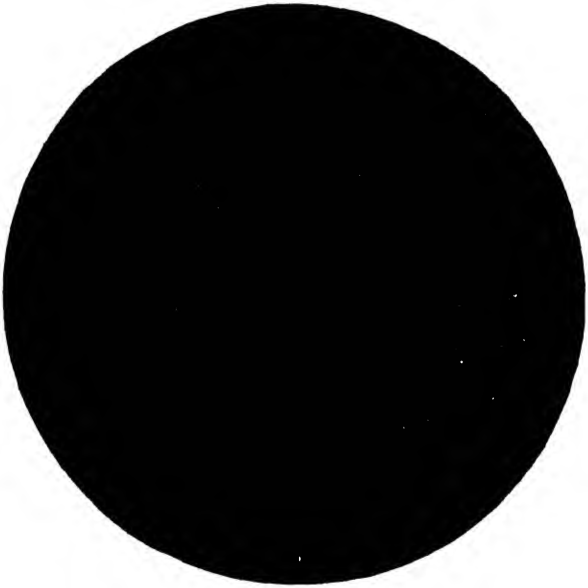

FIG. 66.—High-speed steel. Quenched at 1280°C. Magnified 1,500 diameters. Tungsten 17.87 per cent; chromium 3.46 per cent; vanadium 0.81 per cent; carbon 0.65 per cent. (*Emmons.*)[1]

When thus heat treated, the steels retain their hardness at all temperatures up to about 550°C., or somewhat higher. Metals have a visible glow in moderate light at about 450°C., consequently, heat-treated tools of high-speed steel can be used while red hot without losing their hardness and toughness, and therefore their capacity for work.

Reason for Hardness at Red Heat.[2]—When the steel is heated to above 595°C., the ferrite grains and the iron-tungsten carbide

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[1] Reproduced by permission from Sauveur's "Metallography of Iron and Steel."

[2] BAIN and JEFFRIES, *Iron Age*, **112**, 805, Sept. 27, 1923.

particles increase in size and the steel softens rapidly. This is the same reason that causes ordinary carbon steel to soften, *i.e.*, increase of grain size, although the action occurs at a much lower temperature.

The reason for the retention of fine grains in the *ferrite* of the high-speed steel below 550°C. is that their growth is obstructed by the elements dissolved in the ferrite and the presence there of the great number of carbide particles. The reason for the retention at a red heat of *carbide particles* of small size is the great stability of the iron-tungsten carbide and the large size of the tungsten atom. Because of its great stability, this double carbide forms in preference to the other carbides; it is produced whenever the necessary atoms are available. Its formation requires a number of tungsten atoms, which can be supplied only by diffusion through the ferrite. The large size of the tungsten atom prevents this diffusion until a temperature of about 595°C. is reached.

CHAPTER VII

CORROSION OF IRON AND STEEL

Introduction.—The five metals used most in the industries are iron, copper, lead, tin, and zinc. Of these, iron is for many reasons by far the most important. Its various commercial forms together form the largest manufactured product in the world. But iron is also one of the most perishable of the industrial metals. In the presence of water and air, it is all too rapidly converted into a loosely coherent compound called *rust.* The term "corrosion" is usually applied to the process by which the metals are, by natural agencies, converted into compound forms, but the term "rusting" is applied more specifically to the corrosion of iron. The compounds formed are as a rule insoluble, and are produced by a combination between the metal and some negative ion derived usually from the surrounding air or water. In the case of iron, the compound that is generally formed is the red oxide, which, disregarding the water it contains, very closely resembles one of the most important ores of iron. In fact, the corrosion of iron may be considered to be nothing more or less than the reversion of the metal to the state in which it existed before it was smelted or reduced in the blast furnace. It is not at all unreasonable to suppose that the deposits of ore now found were at one time deposits of iron in the metallic state.

Although iron, when unprotected and exposed to the weather, lasts as a rule only a comparatively brief period, there have been a few cases observed of very remarkable resistance. The most noted is that of the iron pillar at Delhi, India. This is a forged iron column, 16 in. in diameter and 22 ft. high, which was erected to commemorate the glory of an ancient monarch in the year 900 B.C. It has been standing exposed to the weather in an open court yard for more than 2,800 years, and is scarcely more than tarnished. Photographs of the pillar are shown in Figs. 67 and 68.

Then, there are the chains of the old suspension bridge across the Merrimac River at Newburyport, Mass., which were taken down in 1909, after having been in use for 99 years. Although during most of this time they had no protection, they were found to be in such excellent condition that they appeared to be good for another hundred years of service. Their unusual resistance seems not to have been due to any property inherent in the metal, for when some of the links were heated and rolled down to sheet form and exposed, in some instances at least, they rusted like modern material.

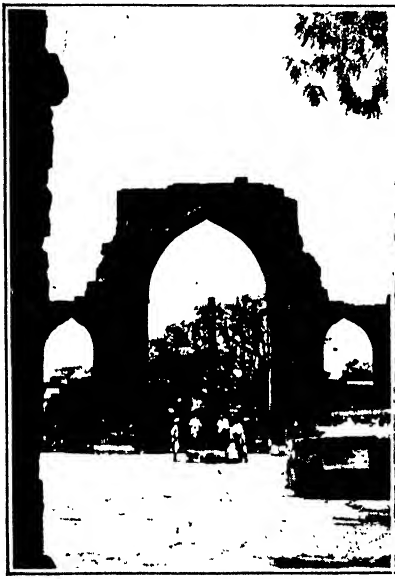

Fig. 67.—Pillar of forged iron at Delhi, India. Erected 900 B.C. Practically free from rust.

Fig. 68.—Base of the pillar shown in Fig. 67. Roughness of the base is due to imperfect forging.

During the past 10 or 15 years a great deal of time has been spent on the corrosion problem. The best efforts of our ablest scientifically trained men have been devoted to the study of the subject. Although much has been learned, there are many points about which our knowledge is very imperfect. We do know some of the facts, however, and an effort will be made to present them in the following pages.

Composition, Weight, and Bulk of Rust.—As has been indicated, iron rust consists essentially of the ferric oxide, but it is usually more or less hydrated, so that its composition may be represented by the formula $Fe_2O_3 \cdot xH_2O$. Although the amount of combined water varies, in the following study it will be considered as the ferric hydroxide $Fe(OH)_3$, the equivalent of which, when written so that the anhydride is expressed, is $Fe_2O_3 \cdot 3H_2O$. In addition to having an indefinite amount of combined water, the degree of oxidation varies slightly; that which is nearest to the iron is somewhat more ferrous, or in a lower state of oxidation.

If we consider rust as the ferric hydroxide, the weight of the rust is nearly twice (1.91 times) the weight of the iron from which it was formed.

The bulk of the rust is even more increased. Bauermann[1] says that 1 volume of wrought iron when completely rusted, produces 10 volumes of rust. Because of the volume increase, iron, when corroding, manifests a force comparable to that of water during freezing.

Theory of Corrosion.—There have been many theories proposed at various times to explain the mechanism of the process involved in the corrosion of iron, but now the electrochemical theory seems to be almost universally accepted. In the words of Whitney,[2] who first formulated this theory, in undergoing corrosion,

> . . . the iron always passes through or into a state of solution, and, as we have no evidence of iron going into aqueous solution except in the form of ions (probably electrically charged atoms), we have really to consider the effects of conditions upon the potential difference between iron and its surroundings. The whole subject of corrosion is therefore an electrochemical one and the rate of corrosion is simply a function of electromotive force and resistance of circuit.

Whitney developed his theory in considerable detail. And, although he expressed his views many years ago and a great deal of corrosion research has been carried out since, it is interesting to note that the theory still accounts for the essential facts, as far as they have been observed. We cannot attempt

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[1] *Jour. Iron Steel Inst.*, **2**, 135.

[2] *Jour. Amer. Chem. Soc.*, **25**, 394, 1903.

here to deal with all the concepts as Whitney expressed them, but the central idea is that the corrosion of iron depends upon the same sort of reactions and controlling factors that have to do with the working of primary electric cells. We must, therefore, study first the fundamental processes involved in the operation of such cells.

Primary Electric Cells.—The subject of primary electric cells is treated more fully in Chap. XVIII, page 614. Only a partial review or synopsis of the several factors involved can be taken up here.

Electrolytic Dissociation.—In accordance with the theory of Arrhenius, when an acid, a base, or a salt dissolves, it dissociates at almost the same instant into charged particles called *ions.* The dissociation reaction is reversible. If we employ a salt, say copper sulfate, the process may be represented as follows:

$$CuSO_4 \rightleftarrows Cu^{++} + SO_4^{--}$$

The reaction proceeds in both directions simultaneously until equilibrium is established; the relative amounts of molecules and ions are determined by the concentration of the solution and the temperature employed.

Osmotic Pressure.—The dissolved molecules and ions exhibit a tendency to move from the region where the concentration is greater to some other where the solution is more dilute. If we place a concentrated solution of copper sulfate in the bottom of a tall glass cylinder, and then pour on pure water in such a way as to produce a sharply defined layer, it will be seen after a time that some of the salt has passed upward a considerable distance. It is evident that some force is driving the dissolved particles through the water against gravity. This driving force is known as osmotic pressure. We know very little about the manner in which the pressure or driving force is developed, but it has been found that it operates according to the gas laws; it is greater with increases in both concentration and temperature.

Solution Pressure and Precipitation Pressure.—Osmotic pressure plays a part in determining the degree of solubility of substances. When crystals of copper sulfate are placed in water, the tendency that the salt manifests to pass from the solid into the dissolved state is called its solution pressure. The salt in solution has also a tendency to pass from the dissolved to the solid state. Nernst[1] assumes that osmotic pressure is a measure of this tendency. Then, for any given temperature, when the osmotic pressure of the dissolved salt is equal to the solution pressure of the salt in the solid state, no more will dissolve; the solution is said to be saturated.

Electrolytic Solution Pressure and the Electrostatic Double Layer.—Metals, like their salts, exert a pressure that tends to cause them to dissolve in water and aqueous liquids, but when metals dissolve, they can send only positively charged ions into solution; no negative ions are formed as when a salt dissolves. We denote the pressure that forces the positively charged ions into solution as the electrolytic solution pressure. It is common to all metals, but some possess it to a much greater degree than others. In the following table, the more common metals are arranged in the order of their diminishing solution pressures according to the hydrogen scale:

Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Copper
Bismuth
Antimony
Mercury
Silver
Platinum
Gold

We may conceive of the positively charged state of the ions as being due to the absence of certain negative electrons which remain behind on the metal when the ion enters solution. Thus, if we place iron in faucet water, or in a suitable aqueous solution, the metal acquires a negative and the solution a positive charge; a potential difference is developed between them that may be measured as an electrical pressure or electromotive force. The negatively charged metal attracts the positively charged ions in solution and prevents them from diffusing away from the interface, *i.e.*, the surface of contact between the metal and liquid. An electrostatic double layer is formed at the interface, consisting of negative charges on the metal opposed by positive charges in solution. This tends to prevent the further forma-

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[1] "Theoretical Chemistry," 4th Eng. ed., p. 143.

tion of ions. Such a condition may arise before a weighable quantity of iron has passed into solution.

If we now furnish some other path by which the opposing charges may be neutralized, iron will continue to dissolve, although the tendency to do so is still opposed by the osmotic pressure of the ions already in solution.[1] We may supply such a path by dipping some other metal that has a lower solution pressure than iron, such as copper, into the liquid, and connecting it to the iron by means of a copper wire. We have now constructed a very simple form of primary electric cell, as illustrated in Fig. 69. In order to facilitate later discussion, it will be advisable to define some of the terms commonly employed in connection with such cells.

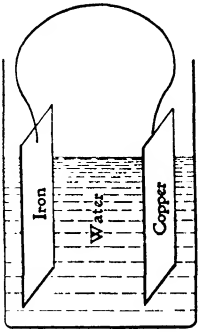

FIG. 69.—Iron-water-copper cell.

Electric-cell Nomenclature.—Primary electric cells are often called *galvanic* or *voltaic cells*, in honor of Galvani and Volta, who were pioneer investigators in this field. The liquid in the cells is called the *electrolyte;* it is so named because the electric current decomposes it. The surfaces of the metals employed in the electrolyte are called the *electrodes*, or, in distinguishing them from each other, the active, dissolving electrode is called the *anode*, and the other the *cathode.* In the iron-water-copper cell, the iron forms the anode and the copper the cathode. Ions that move through the electrolyte towards the anode are called *anions;* those that move toward the cathode are called *cations.* The connecting wire in the cell described forms the *external circuit.* The electromotive force developed by the cell is measured in terms of a unit called the volt (page 625).

Electrochemical Action in the Cell.—Although iron by itself tends to become negatively charged when placed in water, there is a tendency to keep it electrically neutral in the iron-water-copper cell. This results from the fact that negative electrons flow from the metal side of the double layer at the anode (iron) surface through the external circuit to the cathode (copper)

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[1] In pure water, the opposing force due to the osmotic pressure of the dissolved ions will not be very great because the product formed (ferrous hydroxide) is not very soluble.

surface, and positively charged hydrogen ions discharge there, which is to say, they take on negative electrons at the cathode surface and become electrically neutral atoms. Hydrogen ions are always present due to the slight ionization of water, as:

$$H_2O \rightleftarrows H^+ + OH^-$$

Because of the lessening of the electrostatic attraction resulting from the removal of negative electrons at the anode, more iron ions can now pass into solution. Hydrogen ions are resupplied at the cathode both from hydrogen cations moving forward through the electrolyte, and from the further ionization of water adjacent to the cathode. The hydroxyl ions are the anions, and move to the anode, where they combine with the ferrous ions as they enter solution, thus forming ferrous hydroxide, as:

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2 \text{ dissolved} \rightarrow Fe(OH)_2 \text{ solid}$$

When the limit of solubility of ferrous hydroxide in water has been reached, it precipitates from solution as indicated. We shall show later how this ferrous hydroxide is converted into rust.

Metal-like Characteristics of Hydrogen.—In an electrochemical sense, hydrogen acts like a metal. It possesses an electrolytic solution pressure and tends to throw positively charged ions into solution. Although its pressure is comparatively low, it is greater than that of the metals following it in the table shown on page 334. Metals with low solution pressures revert from the ion to the atom rather easily, while those with high solution pressures can be made to do so only with comparative difficulty. Accordingly, hydrogen discharges and passes to the electrically neutral atomic condition more readily than the metals above it in the potential series, but less readily than those below it. As a result, if the relative solution pressures are the controlling factors, the metals that have a higher solution pressure than hydrogen will replace it in solution, while those below it will not do so.

Polarization by Hydrogen.—In the primary cell we have been considering, electrons will flow through the external circuit for a time, as was stated, but an opposing force is soon encountered. While the cell is working, hydrogen ions are continually discharging at the cathode, and they eventually cover it with a layer of electrically neutral hydrogen atoms. We now have in effect a hydrogen cathode; the cell is said to be polarized by hydrogen. The solution pressure of the hydrogen tends to develop an electromotive force operating in the reverse direction to that which was first established. This so-called "back electromotive force" causes it to be less easy for the negative electrons to pass from the iron to the solution by the path provided, and the inhibitive tendency of the electrical double layer at the anode remains more effective. The result is that the electrochemical action in the cell becomes very much less.

Hydrogen Overvoltage.—If the electromotive force that tends to maintain the electron stream in the cell were of sufficient magnitude, the monatomic hydrogen would be converted into molecular hydrogen. Then, assuming such conditions, when the concentration of hydrogen reaches a point above that corresponding to atmospheric pressure, the hydrogen will escape as gas bubbles. The energy consumed in converting the monatomic hydrogen into molecular hydrogen is called the hydrogen overvoltage. It varies according to the kind of metal and the state of the surface on which the hydrogen has been plated out. In the following arrangement, the metals shown are listed according to their hydrogen-overvoltage values, running from high to low:[1] mercury, zinc, lead, tin, copper, nickel, silver, platinum, and iron.

It would be easily possible to increase sufficiently the energy made available by the cell to cause the evolution of molecular hydrogen. It can be done by increasing the hydrogen-ion concentration of the electrolyte to the required degree by the addition of an acid. Less acid will be required if the electrolyte is heated.

Depolarization.—With the iron-water-copper cell, the energy developed will be insufficient to evolve hydrogen in the gaseous form to any extent, but if some suitable oxidizing agent is present the hydrogen will be removed from the cathode by being oxidized to water. The cell will then continue to act. Oxygen from the air dissolved in water will serve for this purpose, and it operates in this manner in ordinary corrosion, where its effect is of great consequence. The removal of the hydrogen from the cathode is spoken of as depolarization.

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[1] Chapin, "Second Year College Chemistry," p. 293.

Adjacent Areas Assume the Anode-cathode Relationship.—Thus far we have stated that the mechanism of the corrosion process may be explained on the basis of the reactions occurring in a primary electric cell, and have discussed rather briefly the several factors involved in the operation of a cell of this type. It is not intended, however, to convey the impression that iron will corrode only when in contact with another metal capable of acting as cathode to it. Adjacent areas on the surface of the iron itself assume the anode-cathode relationship, although in some instances we are unable to say just what predetermines their location. It is obvious, of course, that with an impure metal in which the impurities are segregated, numerous voltaic cells will be established on the surface of the metal when it becomes wetted with water or an aqueous liquid. They will result from the difference in solution pressure that is caused by the difference in composition.

With the ordinary, commercial, ferrous metals, there would be no difficulty in demonstrating a lack of uniformity in composition sufficient to induce electrochemical action when the metal is placed in an electrolyte. Such lack of uniformity may be shown by an examination under the microscope. In discussing the methods of manufacture, we have pointed out some of the difficulties encountered in securing a uniform product. And, although the metal might be fairly uniform in composition when melted, there is a tendency toward selective crystallization even in those cases where solid solutions are formed. The unavoidable segregation of the impurities will cause the solution pressure to be greater at one point than at another, and the areas with the higher pressures will become anodic to those with less. Hence, when the surface of a piece of iron or steel becomes coated with a conducting film of water, currents flow through the film from the anodic to the cathodic areas. Iron ions enter solution at the anodes and hydrogen ions are discharged at the cathodes. It is an observed fact that corrosion does not begin or take place evenly; some spots are more liable to attack than others, although as the corrosion proceeds, layers having a different composition may become exposed or other conditions may become changed, so that eventually the whole of the surface may be corroded.

For the cases described, the explanation that has been given is supported by the evidence, but even pure metals corrode. It appears that actual difference in composition is not necessary to develop anodic and cathodic areas; even a slight difference in the state of the surface or the degree of finish seems to be sufficient. That it may be caused by a surface condition seems to be shown by the ease with which the location of the electrodes becomes changed when determined by the Cushman-Walker ferroxyl indicator.[1] With regard to this Walker[2] has pointed out that if a piece of chemically pure iron, free from mechanical strains and evident crystallization, is immersed in the indicator, the position of the anodes and cathodes may be located almost at once. Then, if the reagent be removed and the surface of the specimen be cleaned by rubbing with a dry towel, and the indicator be again applied, the anodes and cathodes will again be indicated but in entirely different relative positions.

With regard to these facts, Walker stated that the anodic-cathodic relationship could be accounted for by assuming an unequal concentration of oxygen on different parts of the specimen, even though its presence there could not be demonstrated by discernible differences in the character of the surface. In 1927, 20 years after this tentative explanation was offered, through additional research on the passivity of metals, experimental evidence was obtained by which the validity of this conjecture is supported.

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[1] This indicator may be prepared and used as follows: Dissolve 1½ g. of agar in 100 cc. of distilled water by the acid of heat, filter through loose cotton, add 1 cc. of a 0.5 per cent solution of phenol phthalein, and titrate to neutrality with decinormal caustic soda or hydrochloric acid as required. Then add about 7 cc. of a 1 per cent solution of potassium ferricyanide that has been freshly made, and stir thoroughly. Pour a little of the reagent into the tray or vessel to be employed, allow to cool and gel, place thereon the carefully cleaned specimen and cover with more of the reagent.

Iron ions enter solution at the anodic areas on the surface of the specimen, and form Turnbull's blue. Hydrogen ions discharge at the cathodic areas. Thus, an excess of hydroxyl ions is left in the reagent, and this causes the phenol phthalein to turn pink in this region. Because the gel prevents convection currents, the colors remain where developed. The maximum development of color is obtained after a lapse of a day or two, but the location of the anodes and cathodes is apparent almost from the very first.

[2] *Jour. Amer. Chem. Soc.*, **29**, 1262, 1907.

The Passive State of Iron.—When iron is immersed for a brief period in a solution of potassium chromate or dichromate of suitable concentration, is subsequently washed, and is dipped into a cold, dilute sulfuric-acid or copper-sulfate solution, no hydrogen is evolved or copper is precipitated, as would have occurred if the iron had not been treated with the chromate solution. The iron is passive.

On becoming passive, no change in the appearance or in the weight of the metal can be detected, and the determination of the cause of passivity was a problem that engaged the attention of research workers for a great many years. Now, however, Evans[1] has shown that passivity is due to a film of transparent, non-magnetic ferric oxide, too thin to be visible, and even too thin to give the first yellow interference tint.[2] Working with strips of electrolytic iron, Evans caused the iron to become passive by suitable treatment. He then made a deep scratch along the middle of each strip and clamped it in such a way that it was held vertically in a 10 per cent solution of potassium iodide saturated with iodine. The attack of the iodine was found to be most intense along the line of the scratch and near the surface of the solution. When the metal had been sufficiently dissolved away by undermining[3] most of the surface was found to be covered with a transparent film that could be easily removed. Although the film was invisible while on the iron, when detached, it became visible in water.

The presence of the thin oxide film on the iron is the cause of the passivity of the metal. The very thinness of the film is proof that it is protective and renders the metal inactive. If it did not inhibit its own growth, the film would become thick enough to be visible.

Iron is not the only metal that may be rendered passive. This property is possessed by several metals, and many reagents

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[1] Evans, U. R., "Passivity of Metals," *Jour. Chem. Soc.*, **130**, pt. I, p. 1020, 1927.

[2] Thin films of transparent substances, such as a layer of oil on water, or a layer of oxide on polished metal, show colors by reflection in white light. These colors represent that portion of the composite white light remaining after the elimination of the waves of one or more colors through interference of wave systems reflected from the two parallel surfaces of the film.

[3] *Loc. cit.*, p. 1024; see also Evans and Stockdale, *Jour. Chem. Soc.*, **132**, 2651, 1929.

other than the chromates may be employed to bring it about. Some metals, such as chromium, become passive in air. On iron exposed to the air, some primary oxide forms always, and whether or not the metal becomes passive depends merely on the condition of the film.[1] If the film cracks, or becomes discontinuous for any cause, the passive metal tends to become active again.

The Oxygen Concentration Cell.—With a variable oxygen concentration, adjacent areas on the surface of a piece of pure iron develop the anodic-cathodic relationship. Which area becomes anodic, and which cathodic, depends upon the condition of the primary oxide film, whether it is in good or bad repair. Where the oxygen is relatively abundant, the film is kept in good repair, and that area becomes cathodic to the area where the oxygen supply is less.

With strips of electrolytic iron supported vertically in a quiescent solution of sodium chloride, Evans[2] has shown that the corrosion is greater at the lower end of the strip. In the undisturbed solution, oxygen can reach the lower zone of the liquid only by diffusion or some other slow process.[3] At the bottom of the strip, therefore, the oxygen does not arrive fast enough to keep the primary oxide film intact, and that area becomes anodic to the upper part, which is kept passive because the oxygen supply is greater nearer the surface of the liquid, and film repair is more rapid there.

If the oxygen concentration is kept fairly uniform over the whole surface of the metal, as may be done by constantly stirring the solution and taking suitable precautions with regard to the support of the specimen so as not to interfere with the free access of oxygen to the metal at any point,[4] the anodic-cathodic areas caused by varying oxygen concentration may be eliminated. Because the stirring brings a good oxygen supply to the bottom of the solution, the tendency of the metal to become passive and cathodic is as great at the lower end of the strip as it is at the top. In pure water, if the oxygen concentration is kept uni-

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[1] Tronstad, L., *Nature*, **124**, 373, 1929.

[2] Public lecture at Carnegie Inst. Technol., Pittsburgh, Mar. 11, 1929.

[3] *Phil. Mag.*, **45**, 835, 1923.

[4] Evans, U. R., "The Corrosion of Metals," 2d ed., p. 108.

form, electrolytic iron may become entirely passive, and remain free from rust, but this does not happen in a solution of sodium chloride because chlorine ions tend to penetrate the primary oxide film.

Evans[1] has demonstrated the principle of the oxygen concentration cell also by placing a weighted watch glass on lead covered with a solution of potassium chloride. Because the oxygen is largely kept away from the area on which the glass presses, that area becomes anodic to the surrounding area.

The same principle may be illustrated by placing a drop of salt water on bright, electrolytic iron. The metal under the middle of the drop will be anodic, the outside rim will be cathodic (passive), and a ring of ferrous hydroxide will form at the junction where the ferrous cations and hydroxyl anions meet. As the moderately soluble ferrous hydroxide diffuses outward and oxidizes, a membrane of ferric hydroxide will form just inside the border, with a ring of uncorroded metal beyond it, but within the confines of the drop.

Effect of Strain on Corrosion.—The fact that localized strains have a very important bearing on the corrodibility of metals, has also been shown by Evans. The primary oxide film that forms on strained metal cracks readily. It was found that when electrolytic iron was cleaned with fine abrasive, the passivifying oxide film cracked less than when the metal was cleaned with coarse abrasive. This is due to the fact that the deeper gouges produced by the coarser grit cause greater strain.

When the strips of electrolytic iron, free from physical defects such as would cause the film to break down, were corroded in stagnant sodium-chloride solution, as described under the previous topic, the corroded area extended upward along the sides of the specimen as illustrated by sketch No. 1 in Fig. 70. The marginal corrosion increases toward the bottom due to a combination of two factors: first, along the edge of the strip there is excessive cracking of the oxide film on account of the strained condition of the metal caused by shearing the strips; second, the repair of the film is progressively less perfect at the lower levels, due to a constantly diminishing oxygen supply.

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[1] *Loc. cit.*, p. 91.

The effect of strain is, perhaps, more definitely shown by specimens No. 2 and No. 3 in Fig. 70. Like No. 1, these test pieces are samples of electrolytic iron. One of them was marked by a deep, jagged scratch, and the other was bent sharply and then straightened. In both cases a strained condition (page 177) was produced in a line running longitudinally through the specimens, as shown in the sketches. The effect of the strain in accelerating corrosion is very apparent. Oxygen, diffusing in from the air, tends to repair the film which the strain causes to crack, but as is shown by the area that is corroded, the completeness of the repair diminishes as the distance below the surface of the liquid increases. Only where the air touches the solution is the film repair sufficiently rapid to prevent the strained metal from becoming definitely anodic.

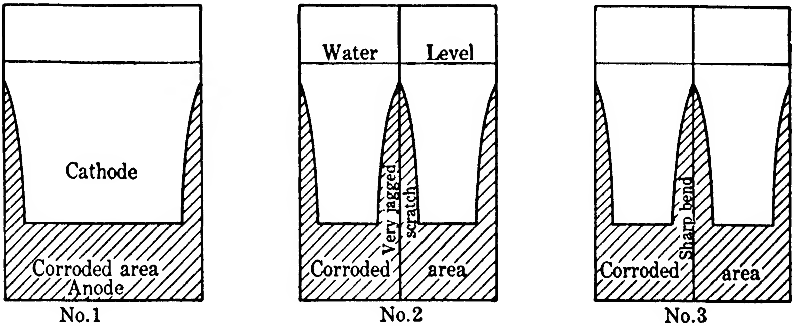

FIG. 70.—Corrosion of electrolytic iron in areas unprotected by primary oxide film.

The anodic-cathodic relationship has been frequently observed between strained and unstrained portions of iron and steel in service. Corrosion in the neighborhood of punched holes is greater than in the neighborhood of drilled holes. Scratches and indentations made by tools are almost always anodic to surrounding areas. In these cases, just as with the test pieces of electrolytic iron, the passivity of the metal is destroyed by the cracking of the film, which results from the strained condition of the metal.

Summary.—In summing up, it may be said that the corrosion of iron is due to an electrochemical action that takes place between adjacent parts of the metal. The location of the electrodes is determined (1) by differences in the composition of the metal in adjacent areas, (2) by differences in the degree of passivity of adjacent areas, and (3), in some cases, by other factors. With regard to differences in composition, it appears that although ferrous metals will corrode even though as pure and homogeneous as it has been found practicable to make them, if other conditions are equal, a lack of uniformity has a tendency to intensify corrosion locally. The variation in the degree of passivity depends upon the condition of the primary oxide film, which in turn depends upon its tendency to crack, and upon the supply of oxygen available for its repair.

The formation of local passive (cathodic) areas by the primary oxide film does not lessen the *rate* of corrosion: the rate is determined by other factors as will be later explained. Because it confines the total corrosion to restricted anodic areas, and thus intensifies it there, localized passivity may actually hasten the failure of the metal.

Reactions Occurring during Corrosion.—The initial reaction that occurs in the iron corrosion cell consists of the conversion of anodic iron into ferrous ions, as follows:

$$Fe + 2H^+ \rightarrow Fe^{++} + 2H \qquad (1)$$

The atomic hydrogen separates at the cathode, and as the reaction continues, the cathode tends to become polarized. In explaining the principles of operation of a primary cell, mention was made of the fact that unless the polarizing film of hydrogen on the cathode is removed in some way, the action of the cell will not long continue. This statement applies with equal force to the ordinary corrosion of iron. In the most usual cases of such corrosion, the hydrogen is oxidized to water by means of the oxygen dissolved from the air,[1] as:

$$2H + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad (2)$$

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[1] According to the suggestion of Whitman, Russell, and Altieri, *Jour. Ind. Eng. Chem.*, **16**, 665, 1924, when oxygen is present in sufficient concentration about the cathode, it is not necessary to conceive of the hydrogen as having been plated out and then oxidized to water, since a similar effect would be accomplished by the formation of hydroxyl ions at the cathode. In accordance with this view, instead of negative electrons being removed from the cathode by the discharge of hydrogen ions, the reaction represented by the following equation occurs:

$$H_2O + \tfrac{1}{2}O_2 + 2\ominus \rightarrow 2OH^-$$

The hydroxyl ions then diffuse away toward the anode.

In ordinary natural waters, the electromotive force developed by the corroding iron is usually not able to cause the evolution of hydrogen to any extent on account of the hydrogen overvoltage, but if the water is practically oxygen free, a relatively small amount of gaseous hydrogen may be produced, as:

$$2H \rightarrow H_2 \text{ (gas)} \qquad (3)$$

This accounts for the appearance of small quantities of hydrogen in closed-system, hot-water radiators, where there is almost no dissolved oxygen. Under such conditions, however, the corrosion is very little.[1]

It has been shown experimentally and by observation of metals under service conditions, that with natural waters, the rate of corrosion is directly proportional to the amount of dissolved oxygen present. This means that even in natural waters, Reaction (1) produces atomic hydrogen more rapidly than it can be converted into water by the oxygen that is available for this purpose. *Reaction (2), therefore, becomes the controlling reaction and determines the rate of corrosion.* We shall repeatedly have occasion to refer to this fact.

There is another reaction in which the dissolved oxygen plays a part that should be mentioned, although it is a secondary one and of importance chiefly because it helps to consume the oxygen supply. This is the oxidation of the ferrous hydroxide to the ferric state. The ferrous hydroxide referred to is that formed by a combination between the ferrous ions produced by Reaction (1) and the hydroxyl anions, as shown on page 336, thus:

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2 \qquad (4)$$

The ferric hydroxide is then produced as follows:

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3 \text{ or } Fe_2O_3{\cdot}3H_2O \qquad (5)$$

The ferric is less soluble than the ferrous hydroxide, so that the effect of the oxidation is to remove iron ions from solution. This reduces the osmotic pressure of the ions, and might seem to be a factor tending to promote corrosion, because it lessens the opposition to Reaction (1). It probably has no actual effect

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[1] Wilson, "The Mechanism of the Corrosion of Iron and Steel in Natural Waters and the Calculation of Specific Rates of Corrosion," *Jour. Ind. Eng. Chem.*, **15**, 127, 1923.

in this direction, however, because the speed of Reaction (1) tends to exceed that of Reaction (2) even when the electrolyte is saturated with ferrous hydroxide. Of much more practical importance is the fact that the precipitated ferric hydroxide forms a coating that has an effect on corrosion, as will be explained later.

Reactions Occurring when Iron Corrodes in Hard Waters.—In water containing calcium-sulfate hardness, the calcium sulfate is at least partially ionized. In the operation of the corrosion cell the calcuim ions migrate to the cathode, and the sulfate ions to the anode. Because the calcium ions have a lower discharge tendency (higher solution tension) than hydrogen, they are not discharged at the cathode, but hydrogen ions discharge, as has been explained. At the cathode the calcium ions unite with the hydroxyl ions, left in that vicinity by the discharged hydrogen, to produce calcium hydroxide, $Ca(OH)_2$. In a similar manner, the sulfate ions, collecting at the anode, combine with the ferrous ions entering solution there and form ferrous sulfate ($FeSO_4$). Because the anodes and cathodes are not far apart in a corrosion cell, the calcium hydroxide and ferrous sulfate, both being soluble, meet by diffusion. Where they meet, a reaction, represented by the following equation, occurs:

$$Ca(OH)_2 + FeSO_4 \rightarrow CaSO_4 + Fe(OH)_2$$

By continued diffusion and reaction, an amount of these reaction products is formed that exceeds their solubility in water, and a precipitate appears. If a specimen of iron is placed vertically in stagnant water, the calcium hydroxide will be formed at the top, because the top of the specimen will be kept cathodic by the oxygen diffusing in from the air. The line formed by the precipitated ferrous hydroxide and calcium sulfate will appear just at the lower edge of the cathode.

In water containing bicarbonate hardness, calcium hydroxide is formed at the cathode and ferrous acid carbonate at the anode. Where these soluble substances meet by diffusion, the reaction represented by the following equation occurs:

$$2Ca(OH)_2 + FeH_2(CO_3)_2 \rightarrow 2CaCO_3 + Fe(OH)_2 + 2H_2O$$

In tanks and other receptacles containing hard waters, these insoluble reaction products clinging to the metal are frequently observed.

Illustrations of the Effect of Dissolved Oxygen.—There are many illustrations that may be cited to show the effect on corrosion produced by the presence or absence of oxygen. It is well known that iron which is alternately wet and dry corrodes more rapidly than that which is permanently wet. The reason is obvious; under these conditions there is a plentiful supply of both water and oxygen. Anodic and cathodic areas become established either because of impurities in the metal, which cause the solution tension to vary, or because of differences in the condition of the primary oxide film. The more rapidly the hydrogen is oxidized at the cathodes by the free oxygen derived from the air, the more rapidly will iron dissolve at the anodes.

For the same reason, iron that is partly immersed corrodes most rapidly near the surface of the water. The most rapid corrosion does not occur in the zone adjacent to the water line, but generally a little below it. At the water line, the metal tends to remain passive, because of the repair of the oxide film there, but in the anodic area just beneath it, corrosion is intensified. As was just pointed out, if the atomic hydrogen on the cathode is speedily removed, the functioning of the corrosion cell will be less inhibited.

In a hot-water supply system, where the water is being changed constantly, and the oxygen supply therefore kept up, the corrosion is greater than in a closed heating system, where the water soon becomes and remains substantially oxygen free. Speller[1] says that the most striking fact in practical pipe experience is that hot-water *heating* systems invariably show no corrosion to speak of after 35 or 40 years' use, whereas frequently hot-water *supply* systems operating at the same average temperature with the same water last only 6 or 8 years. Corrosion will be less, moreover, if the water is not changed in the heating system each season. The oxygen effect also accounts for the greater corrosion at the inlet end of the supply system. After the oxygen supply has been consumed by the corrosion of the storage tank and the part adjacent to it, the water can less readily corrode other parts of the system through which it passes afterward. Use is made of

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[1] *Trans. Amer. Electrochem. Soc.*, **39**, 141, 1921.

this principle in a commercial method, known as the "deactivating process," for removing the dissolved oxygen from water. The heated water is passed through a storage tank containing a large quantity of expanded steel plates, by the corrosion of which the dissolved oxygen is used up. If it is to be employed for domestic purposes, water treated in this way should be filtered to remove the rust. In another method, known as the "deaerating process," the quantity of the dissolved gases is lessened by the application of a partial vacuum to the water.

Stationary Liquid Films.—Since Reaction (2) is generally the controlling reaction in under-water corrosion, the rate at which oxygen can be transported from the main body of the liquid to the surface of the metal becomes an important factor. When water flows through a pipe, there is always a film of water that remains stationary next the metal. Although the bulk of the liquid may be charged with oxygen, the depolarizing reaction can go on only as the free oxygen diffuses through the stationary layer. It is necessary, then, to take account of the *velocity of flow*, because the greater the velocity, the thinner is the quiet layer next the metal through which the oxygen must diffuse. In commenting upon the data obtained by Speller and Kendall,[1] Wilson[2] says that their results indicate that the rate of corrosion in pipes is very low, and increases but slowly at low velocities where straight-line flow is known to prevail, but then rises sharply in the critical region, and continues to increase, though less rapidly, as the velocity increases through the turbulent-flow region. The increased corrosion with the higher velocities is due, without doubt, to the thinner liquid films that exist under these conditions.

Effect of Continuous Coatings.—With muddy water, corrosion is often less than with clear water. As the mud settles out of the water, a more or less continuous coating is formed on the metal. When the oxygen next to the metal has been used up, a new supply can reach the hydrogen on the cathodes only as it slowly diffuses through the mud layer. A more or less continuous deposit of the ferric hydrogel itself, formed from the dissolved ferrous hydroxide, as shown by the equation for Reaction (5),

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[1] "A New Method of Measuring Corrosion in Water," *Jour. Ind. Eng. Chem.*, **15**, 134, 1923.

[2] *Jour. Eng. Chem.*, **15**, 129, 1923.

will also retard the ingress of the depolarizing oxygen. Coatings that protect in this way may be formed from the bicarbonates and sulfates that are generally present to some degree in the water supply (page 346). The results of observations show that in cities where the water supply is notably "soft," other things being equal, the corrosion is greater than in those localities where the water is "hard."

A device has been recently developed to serve as an adjunct to the domestic hot-water supply system that constantly feeds a small amount of a specially prepared sodium silicate into the water with a view to forming a protective silicate coating in the system. As far as the results have shown, a considerable benefit is derived from this practice.

Fig. 71.—Corrosion products covering pits in steel pipe.

Discontinuous Coatings. Pitting.—When the deposit on the metal is discontinuous, as in the case of the blisters of rust in Fig. 71, the damage done by corrosion is aggravated. Pits form under the blisters. The coating of rust cuts off the oxygen supply and keeps the pit constantly anodic. The wide, clean cathode areas allow a speedy removal of hydrogen, and the rate of formation of iron ions in the pit is increased in proportion. With corrosion locally intensified in this manner, it does not take long for the metal to rust through entirely. If the article is a pipe, boiler tube, or tank, its value is destroyed. With the same amount of corrosion more uniformly distributed, the life of the container will be greater.

Effect of Temperature on Corrosion.—It has been found that the amount of iron corrosion increases as the temperature increases. This is no doubt due in largest part to the much lower viscosity of water at the higher temperatures, and the resulting increase in the rate of oxygen diffusion. Speller[1] says that measurements have shown that at 135°F., a pipe lasts twice as long as when the water is heated to 180°F. In an open system the maximum-temperature effect seems to be reached at about 180 to 190°F.; the separation of the dissolved air, which occurs because of the reduced solubility at the higher temperatures, begins to have a retarding effect then.

In addition to increasing the rate of oxygen diffusion, the lower viscosity of water at the higher temperatures will promote corrosion in another way. The lower the viscosity, the thinner will be the quiet film next the metal through which the oxygen must diffuse.

Effect of Alkalinity on Corrosion.—Because the ferrous hydroxide formed in the region of the anode is somewhat soluble, there is a tendency to keep the stationary liquid layer, or film, next to the corroding surface in an alkaline condition. In natural waters, the acidity is usually insufficient to neutralize this alkalinity because the ferrous hydroxide is being formed continually. The result is that in such waters corrosion occurs under conditions that are practically constant with respect to hydrogen-ion concentration, even though in the main body of the liquid the hydrogen-ion concentration may vary through a rather wide range. If the alkalinity of the main body of the liquid is increased sufficiently, there will be a tendency to increase the alkalinity of the liquid layer next the metal, with the result that the solubility of the ferrous hydroxide will be decreased and a more protective coating will be formed. On this account the diffusion of oxygen will be retarded and corrosion will be inhibited. This effect is, however, not apparent with only slight additions of alkali. It has been found that increasing the calculated alkalinity from 0 to 100 parts per million by the addition of sodium hydroxide to Pittsburgh water did not appreciably affect the corrosion in hot-water pipes.[2] The exact degree of alkalinity necessary to produce the well-known retarding effect depends somewhat on other conditions, but it usually does not exceed the equivalent of a small fraction of a per cent of caustic soda.

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[1] "Plumbers' Handbook," edited by Dibble, p. 171.

[2] *Jour. Ind. Eng. Chem.*, **15**, 128, 1923.

Effect of Acidity.—Theoretically, we might anticipate an increased corrosion rate due to the presence of an acid in solution, because of the resulting increase in the concentration of hydrogen ions, and the neutralization of the alkaline film. With slight acidities this effect is not observed. With an increasing amount of acid, a point will be reached eventually when the alkalinity of the liquid film next to the metal will be neutralized, and the ferrous hydroxide will be rendered more soluble. Under these conditions the tendency to form a protective coating will be lessened. Ultimately, gaseous hydrogen in bubble form will be produced. At this time the total corrosion will consist of that depending upon gas evolution and that depending upon depolarization by oxygen. The latter will be accelerated by the former because the escape of gas bubbles tends to disrupt the liquid film normally quiescent against the metal.

In a quiet liquid, as soon as the evolution of gas bubbles becomes at all rapid, the effect of the presence or absence of oxygen will be practically negligible. Hydrogen overvoltage is the most important single factor then; Reaction (3) will control the rate of corrosion. Under these conditions the corrosion will be accelerated by the presence or absence of impurities in the iron, because of their usually low hydrogen overvoltages.

At comparatively high velocities in acid, depolarization may still be the controlling factor because of the increased amount of oxygen that reaches the metal surface.

Effect of Carbon Dioxide.—In connection with the effect of acidity on the rate of corrosion it should be remembered that carbon dioxide forms an acid with water. Because the carbonic acid tends to neutralize the alkaline film, it tends to increase the rate of corrosion. An example of this effect may be found in the return line of a steam-heating system. From boiling water, the dissolved air, which is richer in both oxygen and carbon dioxide than normal atmospheric air, is driven out with the steam. When the steam condenses in the radiator, the carbon dioxide, being the most soluble in water of all the atmospheric gases, dissolves in the condensate that returns to the boiler. Since the condensate is sufficient in amount to form only a small rivulet flowing along the lower side of the pipe, corrosion is largely confined to this narrow area. Due to its acidity, this trickle of water is exceptionally corrosive, and a deep, narrow gutter is cut in the pipe.

The reactions involved in carbonic-acid corrosion are illustrated by the following equations:

$$4CO_2 + 2Fe(OH)_2 \rightarrow 2FeH_2(CO_3)_2$$
$$2FeH_2(CO_3)_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3 + 4CO_2$$

It will be seen that all of the carbon dioxide used in the beginning is set free at the end of these reactions. Consequently, a little carbon dioxide will, in time, bring about a great deal of rust formation.

Corrosion Stimulated by Contact with Other Materials.—When iron is in electrical contact with any material capable of acting as cathode to it, corrosion will be intensified because of the greater area over which hydrogen may be discharged, and the greater amount of depolarization that can go on per unit of time. Whitman and Russel[1] found that the amount of total corrosion on the surface of steel was the same as when 75 per cent of it was coated with copper. In the latter case of course, because only one-fourth the area was exposed, the corrosion was four times as intense. The hydrogen deposited on the copper was oxidized as fast as the oxygen diffused in, which is just what happens on the same area of cathodic steel surface. With a larger cathode area, the total amount of oxygen that can diffuse through the liquid layer is increased.

Iron railings fixed in stone copings by means of lead are most rapidly corroded where iron joins the lead, because lead is cathodic to iron. For this reason it would be better to use spelter in place of lead, because zinc is anodic to iron and protects it by causing the iron to become the cathode on which the hydrogen is discharged.

The effect of "mill scale" is important in this connection. If a continuous layer of it could be kept on the surface of the metal, it would form an excellent protective coating, because it is very insoluble. But because it is very brittle, it is practically always flaked off in spots. Then, where the iron is not covered by the scale, the corrosion is much intensified because the scale acts as cathode to it. On this account it is generally good practice to

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[1] *Jour. Ind. Eng. Chem.*, **16**, 276, 1924.

remove the scale completely. With boiler tubes, the interiors are generally reamed out with this object in view.

In some cases, cathodic substances have lower hydrogen overvoltages than iron, so that it becomes possible to remove hydrogen by Reaction (3). The rate of corrosion is then not limited by the rate at which oxygen can diffuse inward to the metal.

Action of Cinder and Soot.—Cinder is found to be extremely active in accelerating the corrosion of iron as well as of other metals buried in it. This is due to the fact that in addition to being cathodic to iron, the cinder is porous and contains both carbon dioxide and sulfur dioxide, which gases form acids with water. In Fig. 72 is shown a section taken from a line of lead pipe that passed through a cinder fill. There is evidence of considerable action, although lead has a rather high resistance to corrosion. Metal pipe lines should not be laid in cinder, but if cinder is unavoidable, the pipe must be protected in some way, as by a heavy coating of asphalt. Or the trench may be filled with clay for about 8 to 10 in. about the pipe.

FIG. 72.—A section of lead pipe showing the corroding action of cinders.

Accumulations of soot in flues, etc., have a very decided accelerative action on the corrosion of the metal. Furnace soot consists of approximately half carbon, which serves as an excellent cathode on which the hydrogen may be oxidized. In addition, analyses show that such soot deposits contain a noteworthy amount of sodium chloride and other salts, which have been volatilized in the furnace and condensed in the flue. Such salts help to maintain a high moisture content and increase the electrical conductivity of the soot.

Electrolysis as an Aid to Corrosion.—When an electric current, for example, a stray current leaking from some electric system, passes through water or an aqueous solution, with iron, or other soluble metal, acting as anode, the rate at which the metal is converted from atom to ion may become enormously great. The amount of corrosion is determined by the quantity or amount of electricity flowing through the system (amperes × time). Corrosion of this sort may occur at the joints in pipe lines, between the pipe and the ground, between metal and moist wood or masonry, between structural metal and the foundation, or even between the reinforcing rods and the concrete encasing them. But it is always the anode only that is corroded. An example of the effect of electrolysis is shown in Fig. 73. This is a section cut from a brass pipe where it passed through a board partition in a damp basement. An electric system having been grounded to the pipe, the electrolysis occurred where a part of the current passed to the earth by way of the damp boards.

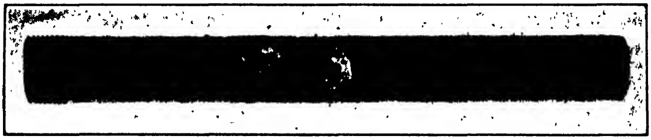

FIG. 73.—Showing a section of brass pipe corroded by electrolysis.

A very troublesome point about this sort of corrosion is that it usually goes on in some unexposed situation where an inspector cannot see it. Great care must be exercised, therefore, to prevent currents from passing through such metallic systems. In some cases, electrolysis may be prevented by making the metallic connection continuous as, for example, by soldering.

PROTECTION OF IRON AND STEEL FROM CORROSION

The methods employed for protecting iron and steel from corrosion may be classed under three heads: (1) the application of an extraneous material as a coating, which either simply adheres to the metal as a distinct layer as in the case of a paint, lacquer, or enamel, or may form an alloy as in the case of some of the metallic coatings; (2) the treatment of the surface of the metal either to develop a definite layer of iron oxide, as in the case of "black sheet iron," or to render the iron passive; and (3) the introduction of an element or elements into the metal while in the molten state, thereby forming a solution or alloy that is resistant.

1. Extraneous Coatings.—Among the most important materials of this class are the paints and lacquers. They are discussed rather fully in Chap. XIII, page 467, so that only brief mention will be made of them here. A *paint* may be defined as a fluid preparation, consisting essentially of a mineral pigment ground in oil, designed to be applied as a surface coating for the purpose of protection or decoration, or both. The oil used must be of such character that when exposed to the air in a thin layer, it will oxidize and harden either spontaneously or by the aid of driers, and form an elastic film. Films produced in this way from oil alone are, however, more or less porous and permeable to water, and lack wearing qualities. It is to remedy these defects that the mineral pigment is incorporated. The function of the pigment is to close the pores and to supply hardness and strength to the film. Although linseed oil is the most widely used paint oil, there are several others that may be employed.

Aside from the general protective value of the paint coating due to its ability to exclude air and moisture, it has been found that the pigments themselves may contribute a distinct effect. Some of them exhibit a definite retarding action on corrosion, while others accelerate it. There are many, however, the value of which in this respect seems to be indeterminate (page 524).

A *lacquer* is essentially a spirit varnish consisting generally of a resin, as shellac, or a resin-like substance, as nitrated cotton, dissolved in a volatile solvent. Upon application, the solvent evaporates, leaving the dissolved material in the form of a film. Because the film is more nearly impermeable, lacquers furnish better protection as a rule than ordinary paints. When the lacquer has been baked after drying, the article is said to be *japanned*. Baking renders the coating harder and more durable. A *black japan*, sometimes called an enamel, consists of asphaltum dissolved in linseed or similar oil and thinned with petroleum naphtha. Black japans may or may not be baked. The black japan is applied to hardware, conduits for electric wiring, etc.

Metallic paints, known as *gilt*, *bronze*, or *aluminum paints*, such as are applied to radiators, for example, consist of oils, lacquers, or varnishes in which have been incorporated thin flakes of metal. Flaky pigments of this sort are especially good for outer coats. They make a film that is impermeable and strong. Aluminum flake reflects light, a fact that is important because it lengthens the life of the oil. Any pigment that keeps out the light, other factors being equal, tends to make the paint more durable. Light causes the oil to be oxidized to destruction more rapidly.

A coating that is sometimes employed for water pipes is known as the *Angus Smith solution.* It consists generally of a mixture of coal tar, tallow, rosin, and quicklime. This mixture is heated nearly to the boiling point, and then the carefully cleaned pipes are dipped into it and allowed to remain until they acquire the temperature of the bath. Upon being removed and allowed to cool, the coating solidifies. To overcome "pin holes" two coatings are usually applied. It has a very excellent protective value. There is some objection to this treatment because unscrupulous manufacturers make use of the coating to cover defects in the pipe.

Metallic Coatings.—Coatings of other metals may be applied to iron in a variety of ways; by dipping the iron or steel article into a molten bath of the metal to be applied, by electrolytic deposition, by the metal-spray method, etc. In all cases the article to be coated must be carefully cleaned beforehand. This is generally done by "pickling" (acid treatment).

The methods of applying zinc coatings, called *galvanizing*, may in the main be classified under three heads: (1) the hot-dip process (hot galvanizing or pot galvanizing), (2) the electrolytic or electroplating process (cold galvanizing), and (3) the sherardizing or dry-dust process. In the *hot-dip process* the carefully cleaned article is dipped into a bath of molten zinc. This method is much used for water pipes, and is always used for sheets. The markings or spangles on the surface of the galvanized sheets are due to the crystallization of the zinc. The rate of cooling determines the size of such markings. In the *electroplating process*, the metal is deposited from a water solution of a zinc salt or salts. In the *sherardizing process* the cleaned article is heated in a revolving drum with zinc dust or blue powder (page 122). As in the hot-dip process, the zinc appears to form a true alloy with the iron. The sherardizing process does not, however, tend to modify the conformation as does the hot-dip process, *e.g.*, threaded pipes can be galvanized by this process without destroying the usefulness of the threads. Further, the threads are galvanized more uniformly than by the electrogalvanizing process. As usually manufactured, the thickest coatings are generally produced by the hot-galvanizing method, with sherardizing and electrogalvanizing following in the order named. Since zinc protects iron at the expense of its destruction, the life of the coating is a function of its thickness. In exposure tests carried out by the author on samples of galvanized electric conduits, those coated by the hot-dip process were found to have a longer life, but in all these cases the coatings applied by this process were much thicker than those applied by the other processes. The argument for thin coatings is that they are less likely to be cracked and flaked off by bending than are the thicker coatings. But because iron that is exposed by a crack in the zinc coating is cathodic to zinc, the zinc will protect iron that it does not actually cover. On this account, cracks in the zinc coating may be less detrimental than the thinness of the coating. It must be remembered, of course, that zinc can extend its protective effect over uncovered areas only within limits.

In salt water, because zinc is dissolved wastefully, a coating of aluminum is better than a coating of zinc. But in water containing bicarbonate hardness, which most waters carry, aluminum is not attacked readily enough to provide protection. When a perforation in the aluminum coating is formed, rusting starts at once.

Cadmium, like zinc, protects iron and steel by anodic action, and recently this metal has come into use in the automobile industry for the plating of small parts, such as bolts, nuts, etc. It adheres to the steel better than zinc or nickel (page 129).

Tin plate is manufactured by a modification of the hot-dip process. The cleaned-iron or steel sheets are passed through pots of molten tin between driven pairs of rolls. The last pair squeezes off the surplus tin. In the finished product, the weight of the tin in the coating ranges from 1.4 to 2.6 lb. per base box of 112 sheets, 20 by 20 in. in size. It constitutes only a very thin layer, which at the junction forms an alloy with the steel.

Except that the bath consists of an alloy containing usually about 70 per cent tin and the remainder lead, *terne plate* is made in the same way as tin plate.

Nickel plating and *copper plating* are usually done by the electrolytic method. Copper may be deposited upon iron and steel (also upon lead and tin and their alloys) from an acidified solution of a copper salt by a purely chemical reaction. To immerse the cleaned article in the solution, or apply the solution with a brush is all that is necessary. A substitution reaction occurs in which the copper is thrown out of the dissolved salt and an equivalent amount of iron passes into solution. The copper coating produced in this manner is not substantial, is easily rubbed off, and has very little protective value. A somewhat improved coating is obtained by placing the article to be coated in a tumbling barrel with sawdust saturated with the copper-salt solution. The burnishing action of the sawdust improves the coating, but the protective value is not high.

Schoop Metal-spray Process.—All of the metals commonly employed as coatings may be applied by the metal-spray process. In this method a spray of the finely divided metal is thrown forcibly against the object to be coated. As in all other processes, the surface of the metal being coated must be thoroughly cleaned before the coating is applied. In the form of wire, the metal to be applied is fed into the spraying device, where by means of a specially constructed oxyhydrogen torch it is melted. An excess of hydrogen is employed in order that the melting may be done in a reducing atmosphere. In the nozzle of the torch is a central tube carrying compressed air which causes the melt to be projected forward at the rate of about 3,000 ft. per second. In the form of a fine mist it impinges upon the object, which is placed about 6 in. from the nozzle. By means of the expanding air, the sprayed metal is cooled to such an extent that it may be directed against wood, paper, and even delicate fabrics without injury. It is supposed that the heat set free by the impact of the minute droplets of metal upon the surface to be coated brings about the formation of a solid continuous layer.

Zinc, Copper, Nickel, Lead, and Tin Coatings Compared.—If the iron is coated with copper, nickel, lead, or tin, when the coating is broken, these metals become cathodes to the exposed iron.

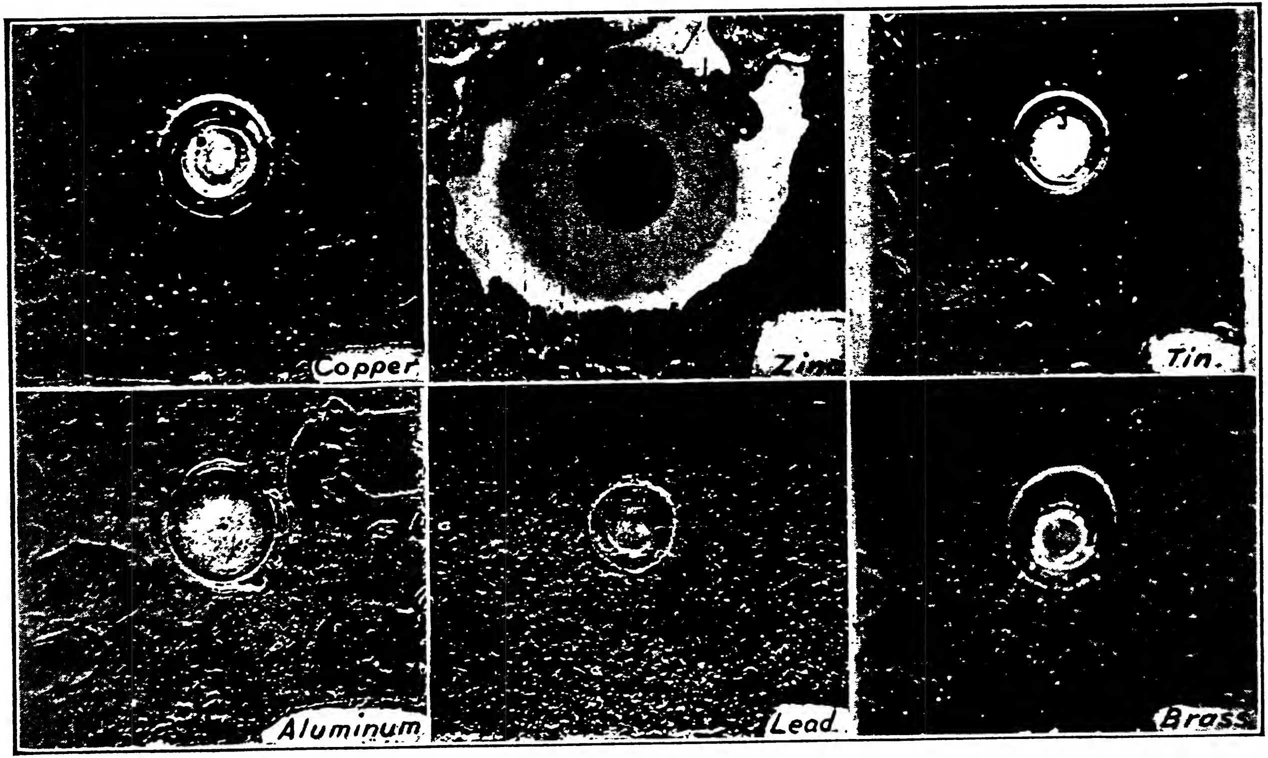

FIG. 74.—Corroded wrought iron plates containing buttons of other metals fused in place. Zinc protects the area adjacent to it; copper, tin, lead, and brass accelerate the corrosion where they join the iron.

With zinc, under the same conditions, the relationship is reversed; the zinc becomes the anode and the iron the cathode. As long as the copper, nickel, lead, and tin coatings are *unbroken*, they have excellent protective values, and last almost indefinitely. Most of the early failure of zinc coatings is due to the fact that they are made so very thin. This is done partly, of course, to prevent the cracking of the coat during the bending of the coated article, but as can be seen the cracking is not nearly so serious as the thinness of the coating.

All coated articles that are subjected to rough usage are almost certain to be scratched, and besides, small "pin holes" exist even in the original coating. And when openings are present in the copper or tin coatings, it may be said that these metals become stimulators of corrosion, because they act as cathodes and enable iron to go into solution more rapidly. Nickel does not bring about corrosion in a perforation at a rate above that which would occur if no coating were present.

The effects produced by different metals in contact with iron are illustrated in Fig. 74. The plates were cut from wrought iron, 3/8 in. thick, drilled with a 5/8-in. drill to produce a depression in the center, and then the cavities were filled by fusing therein the metals indicated in the presence of a suitable flux. After the specimens had been planed and ground to a smooth surface, they were placed in faucet water and allowed to corrode. Copper, tin, lead, and brass caused the corrosion to be accelerated; the rust was built up in the form of a ridge where the metals joined (page 342). Zinc caused an area adjacent to it, several times as large as the area of the zinc itself, to remain clean and free from rust by keeping it in the cathodic condition.

Silicate or Vitreous Enamels.—These are coatings consisting essentially of a special form of glass. The glass is first prepared, and while in the melted state is run into water to shred or "frit" it, after which it is converted into a cream-like produce by grinding it with clay in water. This cream-like preparation is then applied to the metal by dipping, brushing, or spraying, after which it is dried and fired until fused. This produces the glazed coating. The glaze may also be applied in a finely ground, dry condition by sifting it upon the hot article being enameled. Two or more coatings are usually applied (see Sanitary Ware, page 465).

Protection of Iron by Concrete.—A concrete containing Portland cement would naturally be expected to protect iron from corrosion, first, because it has a distinctly alkaline character, and, second, because it tends to prevent the free passage of oxygen to the metal. The effects of both of these factors have been explained. The alkalinity is due to the presence of a considerable amount of calcium hydroxide. This is produced both by the hydration of the free lime that is always present to some extent in the cement, and by the reaction between water and the basic calcium silicates. A normal cement is made up of more than half calcium orthosilicate which reacts with water as follows:

$$(CaO)_2 \cdot SiO_2 + \text{water} \rightarrow CaO \cdot SiO_2 \cdot 2\tfrac{1}{2}H_2O + Ca(OH)_2$$

Although the calcium hydroxide in the exterior layers of the concrete structure soon becomes carbonated by the carbon dioxide in the air, the formation of the more dense calcium carbonate makes the concrete less porous and the further penetration of the carbon dioxide more difficult. Still, it is very obvious that the metal should not be allowed to be too near the surface of the concrete.

Much can be done to insure the protection of the encased iron by properly proportioning the concrete so that it is as free from voids as possible, because voids allow an easier penetration of water containing dissolved air and carbon dioxide.

As far as corrosion is concerned, round rods are better than square or twisted rods, because the chance for the formation of voids is less. And the concrete should be of a sufficiently wet mix for the same reason.

Cinder concrete should never be used for reinforced work, because it is almost certain to cause corrosion if water is present.

It is, then, reasonable to assume that under normal conditions the reinforcing rods will not corrode, if the concrete is well made, and, in general, this assumption has thus far been confirmed by the facts. In concrete structures that have been torn down after many years, the metal has been found clean and free from rust.

There are, however, two factors that may accomplish the destruction of reinforced-concrete structures. These are the presence of cracks and voids, and the action of electrolysis. If cracks and voids of sufficient magnitude exist, corrosion of the encased metal will occur, and since the bulk of the rust is greater than that of the iron, the increase will widen the opening so that the final result will be disastrous. Also, if conditions should happen to be such that electrolysis occurs about the rods, corrosion of the metal in the anode position will certainly take place; the presence of the alkali will not prevent it.[1]

2. Corrosion-resistant Surfaces.—Iron and steel may be rendered more or less able to resist corrosion by certain methods of treating the surface. This may be accomplished by developing on the surface a layer of magnetic oxide of suitable thinness and flexibility, and by making the metal passive.

Iron-oxide Coatings.—Iron and steel articles that have been given a coating of the magnetic oxide of iron (Fe_3O_4) are designated by such names as *black iron* (black sheet iron), *blued iron*, *Bower-Barffed iron*, *Russia iron*, etc. There are various methods by which the oxide may be developed. In the Bower-Barff process, for example, which is employed chiefly for small articles of hardware, the metal to be treated is heated to about 980°C. in a closed retort, and steam heated to about 540°C. is then introduced. The iron and steam react to produce the magnetic oxide with the liberation of hydrogen. In the place of steam, air and carbon monoxide may be employed. The carbon monoxide serves to reduce any ferric oxide that may have been formed.

Like the coatings of copper and tin, the magnetic oxide is good protection only as long as it is entirely continuous and not broken or scratched, for under these conditions it acts as a cathode, and the corrosion of the exposed iron will be very much intensified. Because flaws ("pin holes") are present in the original coating, metals with iron-oxide protection are not suitable for outside exposure. The oxide coatings are always oiled, which undoubtedly accounts for some of the protective value.

Protection by Means of Passivity.—An explanation of the passivity of iron has been given on pages 340 to 343. As was pointed out on those pages, when completely passive, iron does not corrode. Use has been made of this fact in methods of

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[1] For a more complete discussion of electrolysis in concrete, see Rosa and McCullom, "Electrolysis and Its Mitigation," *U. S. Bur. Standards Tech. Paper* 52, 1915.

rust prevention. To the water in tanks, boilers, cooling systems, and the like, film-repairing reagents are added to maintain the passivity of the metal. Care must be exercised to use enough of the reagent to insure complete passivity, or spots that have a strong tendency to be anodic will remain active. Then, because most of the metal is passive, the corrosion will be localized and very intense in the infrequent anodic areas. In most cases, passivity may be produced by 200 parts per million of sodium dichromate with sufficient sodium hydroxide to form the normal chromate.[1] Sixty parts per million of sodium hydroxide, or 80 parts per million of sodium carbonate, will convert the 200 parts of sodium dichromate to the normal salt.

Although the passivifying reagents are usually employed to prevent under-water corrosion, an instance may be given where the practice was successful in arresting atmospheric corrosion. The rusting of badly corroded steel-hopper cars was stopped by spraying them with an aqueous solution of chromic acid. This method was found to be more satisfactory than cleaning and painting, because the cars were frequently subjected to ill-treatment by being loaded with hot cinders and the like, which destroyed the paint.

Effect on Corrosion Produced by Elements Alloyed with the Iron.—The most noted example of a corrosion-resistant alloy formed by the addition of a small amount of another element to iron, is that of *copper steel.* Only about 0.2 to 0.4 per cent of copper is employed, but the effect is relatively great. The increased resistance seems to be due to the formation of a thin layer of oxide that adheres very tenaciously, which is to say, the steel forms its own protective covering. In the early stages, before the oxide has had a chance to form, corrosion appears to proceed at the usual rate. The disadvantage with the steel is that the protective layer is formed only when the oxygen concentration is high, as when exposed to air; in under-water service, it seems to act about as ordinary steel.

Nickel has a marked influence in causing the steel to resist corrosion. The effect increases with the nickel content, and with 30 per cent of nickel, the alloy is practically non-corrodible (page 321).

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[1] SPELLER, "Corrosion—A Problem of Protective Coatings," *Jour. Ind. Eng. Chem.*, **21**, 508, May, 1929.

Chromium has a tendency to lessen corrosion. This is especially true when the amount of chromium exceeds about 6 per cent. That which is known as *stainless steel* contains about 16 to 20 per cent of chromium.

Some of the elements that occur normally in iron and steel have an effect on corrosion; some seem to accelerate, and others to retard it. Tiemann[1] says that under 0.2 per cent, *carbon* has very little influence on corrosion, but that from this amount up to about 0.9 per cent there is a gradual increase in the corrosion rate with additional carbon. From about 0.9 up to 1.26 per cent, the corrosion gradually decreases, but in all cases the effect of carbon is very slight. When the metal is exposed to the air, *sulfur* causes the corrosion rate to increase directly with the amount present, particularly if the alloy is at the same time comparatively free from copper. Opinion is divided as to the effect of *manganese.* It is believed by some that it increases and by others that it decreases the corrosion rate. *Phosphorus* has little or no direct influence on corrosion. Phosphorus occurs, however, in the form of a phosphide in the iron, and if this is segregated, as it very frequently is, corrosion is stimulated because the phosphide acts as a cathode. *Silicon,* in the amounts normally present in open-hearth and Bessemer steel, has no influence on corrosion.

[1] "Iron and Steel," p. 366.

CHAPTER VIII

FOUNDRY SANDS[1]

Classification of Foundry Sands.—Foundry sands may, in general, be divided into two classes, molding sands and core sands. The former are used for the mold proper, while the latter are employed to make the cores with which the hollow parts of the casting are formed. Because the properties required of the two sands are different, they will be treated separately.

MOLDING SANDS

Definition.—A molding sand has been defined by Littlefield as any material which, when moist, can be formed into a mold from which usable metal castings can be made.[2] Molding sands, as a rule, are in reality mixtures of sand and clay; the latter is necessary to make the parts cohere. Sand is called sharp when its grains are angular; dull, when round; strong, when it retains a shape given it; weak, when it does not. If the amount of clay and all other factors are equal, the sharper the sand the stronger it will be; but the sharpest sand is weak without some cementing or bonding material. Usually molding sands contain more clayey matter than core sands, but this distinction is not sharp because both classes vary greatly in this respect and often overlap. The sands that contain the higher percentages of bonding material are those employed for making

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[1] For a further study of foundry sands, and for methods of testing sands, see the following publications: Report of Ries and Rosen on Foundry Sands, publ. by Board of Geol. Survey of Mich., 1907; the Tentatively Adopted Methods of Tests and Résumé of Activities of Joint Committee on Molding Sand Research, organized by Amer. Foundrymen's Assoc. and National Research Council, 1924; Littlefield's Report on Natural-bonded Molding Sand Resources of Illinois, publ. as *Bull.* 50 by Div. of Geol. Survey of Ill., 1925; and Molding Sands of Pennsylvania, publ. by R. W. Stone and Amer. Foundrymen's Assoc. as *Bull. M* 11 of Topogr. Geol. Survey of Pa., 1928.

[2] *Ill. Geol. Survey Bull.* 50, p. 20.

castings of iron, brass, bronze, and aluminum. For steel castings, sands containing very little bonding material are employed. Sands of this sort are used in the steel foundry because other considerations are overruled by the need for high refractoriness or resistance to fusion. A pure silica sand has a much higher resistance to fusion than a sand that is mixed with clay.

The sand-clay mixtures employed for molding may either be found in nature as such, or may be prepared artificially by thoroughly mixing, in suitable proportions, sand and clay of the proper quality. The former are spoken of as natural-bonded sands and the latter as synthetic molding sands.

Origin of Natural-bonded Molding Sands.—Natural-bonded molding sands have been formed either directly or indirectly by the weathering of rocks. The term "weathering" is used here to include both the mechanical and chemical processes involved in the change. If physical agents break down the rock structure without destroying the identity of the constituents, the process is known as disintegration; if some chemical reaction takes place that transposes the mineral particles into new compounds, the process is called decomposition.

Mechanical Processes.—In the physical disintegration of rocks, the principal agents are temperature variations and mechanical abrasion. Temperature changes, both diurnal and seasonal, have a disintegrating effect through the changes in volume they cause. The different mineral entities of rocks have different coefficients of expansion or contraction, and change in volume at different rates; as a result, through long periods of time, the grains of the rock become loosened. Water finds its way into the minute cracks that are formed in this way, as well as into pores that previously existed in the rock, and freezes there. Alternate freezing and thawing greatly accelerate the disintegration. Working concurrently with these forces, through the agency of wind and water, mechanical abrasion is also an important factor in breaking down rock formations.

Chemical Processes.—Of the chemical processes, which bring about the decomposition of the component minerals of rocks, the most noteworthy are hydration, oxidation, and the action of carbonic acid. Although not strictly a chemical process, the leaching effect of water is also important here.

The term hydration, as used in this connection, denotes the process in which addition products are formed by chemical reaction between the mineral substance and water. Because the volume of the material after hydration is greater than before, it is very probable that the reaction may cause further physical disintegration. If the reaction products are not soluble in water, the volume of the hydrated material may be more than double that of the original mineral, but usually the increase is less than 50 per cent.

The process of oxidation is of considerable importance in the decomposition of rocks. It is generally accompanied by hydration, and these two processes together account for the formation of the hydrated ferric oxide that has been found to exert such a marked influence on the cohesiveness and durability of molding sands. In the weathering of biotite, or iron-magnesia mica (H_2O or $K_2O{\cdot}2MgO$ or $FeO{\cdot}Al_2O_3{\cdot}3SiO_2$), or in the weathering of a hornblende ($CaO{\cdot}3MgO$ or $FeO{\cdot}4SiO_2$), the ferrous-oxide component is converted into the hydrated ferric form ($Fe_2O_3{\cdot}3H_2O$). The reddish or yellowish color of clays and sands is due to this compound.

Another common example of this type of reaction is the wet oxidation of the very prevalent iron sulfides, such as pyrite and marcasite, FeS_2. The products are basic ferric sulfate and free sulfuric acid as shown by the following equation:

$$4FeS_2 + 15O_2 + 6H_2O \rightarrow 4Fe(OH)SO_4 + 4H_2SO_4$$

The sulfuric acid becomes an active agent in further decomposing the minerals of the rock.

The carbon dioxide of the atmosphere, as well as that which results from the direct oxidation and bacterial fermentation of organic matter in the earth, combines with water to form carbonic acid, and this reagent brings about an enormous amount of rock dissolution. Many soda, potash, magnesian, calcareous, and ferruginous silicates, and other compounds as well, yield to the action of this acid with the formation of soluble carbonates or bicarbonates, which are gradually leached out. The sodium and potassium carbonates that are formed, are themselves active in breaking down silicates.

To illustrate with an actual case the formation of a clayey sand by weathering, we shall consider the decomposition of the components of a granite. The granites are igneous rocks; they have been formed by the solidification of fused material. They consist largely of quartz, feldspar, mica, and hornblende. One of the common feldspars, called orthoclase, has the composition indicated by the formula, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. The micas and hornblendes, as have been shown, are complex silicates of such basic anhydrides as soda, potash, magnesia, iron oxide, lime, and alumina. All of these silicates may weather to form clay. In the weathering of orthoclase, the potash and two-thirds of the silica are removed, and water combines with the remainder to form a hydrous alumina silicate, as follows:

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2 + 2H_2O + CO_2 \rightarrow Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 4SiO_2 + K_2CO_3$$

Pure hydrated alumina silicate is white. It is known as kaolin, and also by such names as China clay, porcelain clay, pipe clay, etc. The clay produced by the weathering of granite, of course, is not pure; it will likely be colored reddish or yellowish by iron oxide, and will be mixed with free silica and other material. The silica liberated as shown in the preceding equation may be set free as colloidal silica or may be formed into quartz grains. It is more likely to be colloidal if the reaction takes place in the presence of organic matter. Among the products of weathered granite, quartz grains will be present, of course, due to the crystals of quartz that were initially present in the granite.

Transporting Agencies.—If a clay or a sand, or a mixture of these materials, produced by weathering, remains where formed, it is spoken of as *residual;* if carried away and deposited elsewhere, it is called a *transported* clay or sand. Molding sands are practically always derived from transported material; the sorting effect that occurs during transportation is an important item. The agents that built up the deposits were gravity, wind, water, and ice of the glacial period. Some of these agencies are still operative.

Of all of the transporting agencies, gravity is probably the least important. As an example of its action, mention may be made of the collecting of eroded matter at the base of a cliff.

Landslides, of course, are also due to the force of gravity, but there is practically no sorting effect in such movements of earthy material and, consequently, there is little likelihood of molding sand deposits being formed in this way.

The wind, as a rule, will transport only sand, silt, and clay. Because the lighter particles are lifted higher and carried farther, the wind has a pronounced sorting effect. The coarse grains of sand remain nearest the source, and tend to be collected in dunes. The sand in dunes is remarkable for the uniformity in the size of its grains. The finer silt and the clay removed by the wind from a valley floor, where it was first put down by water or ice, will be deposited on the slope and rim of the valley wall, and on the plateaus or hilltops beyond.

Glacial ice has been an important agency in the transportation of earthy material, but direct deposition from glacial ice tended to produce an unsorted mixture of clay, sand, gravel, and boulders. Such deposits are, therefore, not likely to be prolific sources of good molding sand. The turbid streams that began at the melting edge of the ice sheet sorted the material, and in this manner, indirectly, glacial ice has been responsible for the formation of many valuable deposits of molding sand. The mechanical disintegration that resulted from the grinding action of the moving ice, was also an important factor in producing sand from coarser rock structure.

The Clay Bond.—There are apparently three ways by which the clay bond of molding sand was developed.

1. Some clay was, of course, produced by the initial weathering of rock and was transported and finally deposited with the sand as already described.

2. In all water-borne and wind-borne deposits that consist of sand and clay, there is also intermediate material, such as silt and fine sand. Deposits occur, however, that consist only of fairly coarse sand and clay, without intermediate material. Such mixtures, obviously, were not deposited as such. It is probable that grains of quartz and grains of other material were deposited together, and that the clay was formed subsequently by the chemical decomposition of the unstable minerals originally present in granular form. If the mechanical disintegration of the rock had been brought about rapidly, as by the grinding of ice,

the slow process of chemical decomposition of the mineral substances may not have had time to take place. Thus grains of such minerals, which originally were approximately of the same size as the quartz grains and were therefore placed with them by the sorting agency, water for example, may have been converted into clay by a subsequent weathering process. In this way a sand of well-sorted grain size may have become a suitably bonded molding sand.

3. According to Littlefield,[1] there seems to be evidence that the clay in some molding-sand deposits has been received by infiltration from the layer of soil above. The vegetable matter in the surface soil, decaying, yields a water-soluble extract that acts as a protective colloid, which helps to transpose the clay into the colloidal condition (page 579). In the colloidal state, clay is more readily carried in suspension in water. The protective colloid, being organic and relatively unstable, may soon be oxidized to destruction by the free oxygen dissolved in the water. In accordance with this view, the colloidal clay would not be carried far through the sand by the percolating water before the protective colloid would be destroyed. The disappearance of the protective colloid would tend to cause the colloidal clay to flocculate and precipitate within the interstices of the sand. Thus, it is conceivable that in this manner also a previously unbonded sand might acquire a bond.

Chemical Composition of Molding Sands.—Excluding core sands and the sands employed in steel foundries, both of which are described later, the approximate ranges of the percentages of the constituents of molding sand are represented by the following table:

	Per Cent
Total silica (SiO_2)	70 to 90
Alumina (Al_2O_3)	5 to 12
Ferric oxide (Fe_2O_3), less than	6
Lime (CaO), less than	2
Magnesia (MgO), less than	1
Alkalies (K_2O and Na_2O), less than	5
Titania (TiO_2), less than	1.5
Loss on ignition	2 to 4

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[1] *Loc. cit.*, p. 60.

It is understood, of course, that the analyses of many molding sands will show percentages that do not fall within these limits, but the figures given serve to illustrate the composition of sands that are employed for cast iron and the non-ferrous metals and alloys.

Because alumina and part of the silica are combined in the form of clay, the following table may furnish a better conception of the range covered by the two chief mineral components:

	Per Cent
Free silica, chiefly quartz	52 to 83
Clay	12 to 30

Quartz is generally present in molding sands in large quantities; it is the shrinkage-resisting and refractory component. After washing with water, the grains may be pearly white but they are generally colored by iron oxide, which in the form of a film, clings tenaciously to them. This film can be removed by leaching the grains with warm hydrochloric acid that has been diluted with an equal volume of water. After this treatment the quartz grains may be identified by visual examination, particularly with the aid of the microscope. The size of the grain may vary from fine silt to particles as large as a pinhead or larger; the size determines in a large degree the use for which the sand is suitable. Since quartz confers refractoriness, the amount of it present should be as high as possible without displacing necessary bonding material. Quartz itself is practically lacking in cohesiveness.

Clay.—In molding sand, clay is next in abundance to quartz. Since it furnishes the bonding power, a certain amount is necessary, but an excess is undesirable because it lessens porosity, and shrinks and cracks when heated. It should be understood that the amount of bonding power is not dependent alone on the amount of clay, since different clays possess this property in different degrees.

Because methods have recently been devised for evaluating molding sands on the basis of physical properties, chemical analyses are now less frequently made than formerly. The making of a chemical analysis of a sand is a long and tedious process. It does not, moreover, furnish information of a value comparable with its cost. Permeability, crushing strength,

strength in shear, and cohesiveness are much more quickly and cheaply determined, and besides furnish a much better basis for judging the suitability of the sand for the use intended. There seems to be no relation between the percentage of alumina, present as clay, and the degree of plasticity. Sands are used satisfactorily for the same purpose that are entirely unlike in chemical composition.

Refractoriness.—The refractoriness of foundry sands should be sufficiently high that it will prevent the pores from being closed by fusion during casting. Several factors such as fineness of grain, chemical composition, and the uniformity of the distribution of the components influence refractoriness, but none of these alone is determinative. The alkalies, lime, magnesia, and iron oxide are known as fluxes. Sands containing high percentages of such materials are less refractory than those in which these anhydrides are relatively absent, but refractoriness cannot be predicted on this basis because texture plays such an important part. A coarse-grained sand is much more refractory than a fine-grained one of the same composition.

The fluxes react with the silica in the sand and form silicates that have rather low melting points. The alkalies K_2O and Na_2O are the most objectionable in this respect. Highly siliceous sands are more refractory than those containing much clay partly because it is the clay that carries most of the fluxing constituents. Especially the alkalies will be present in the clay if it contains much unweathered feldspar.

Iron oxide has a fluxing action particularly if it is present in the ferrous condition, or if it is present in the ferric state in conjunction with reducing material such as carbonaceous matter. The fluxing action of iron oxide becomes noticeable when the amount present exceeds about 3.5 per cent. It forms an iron silicate which is known as black slag. Metallic iron does not react with the sand, but, during casting, the surface of the hot metal oxidizes and this oxide combines readily with the silica.

Moisture.—The amount of moisture that must be present in the sand is not determined arbitrarily; it varies with the size of the casting, the amount of clay in the sand, the grain fineness, and many other factors. The permeability and cohesiveness of the sand depend to a large extent upon the moisture content.

The amount of water employed should be that which will develop these properties to the greatest degree. Good permeability is generally more important than high bonding strength, and since the same percentage of moisture does not usually produce the maximum of both of these properties, permeability should be given first consideration.

It is generally good practice to keep the moisture content as low as is compatible with the requisite permeability. If this is done, less steam will be formed and there will be less likelihood of forming gas flaws in the casting. Too little moisture is also objectionable, because, if the sand is too dry, it may be detached from the surface of the mold as the iron flows along. This difficulty may be overcome by harder ramming, but hard ramming makes the sand less permeable, and gas flaws may result from this cause. The correct percentage of moisture must be determined for each sand; generally it will be found to be between 6 and 10 per cent.

Selection of Molding Sands.—Although the main essential features of the composition of a molding sand are expressed by the statement that it consists of grains of sand bound together with clay, such mixtures vary so greatly in physical properties that the requirements to be met must be clearly understood before a suitable sand can be chosen. The refractoriness required of the sand, for example, will depend upon the melting point of the metal or alloy to be cast. The permeability to gases, the cohesiveness, and shearing strength that the sand must possess will depend upon the size of the casting to be made. The durability or length of life of the sand, its degree of fineness, and other properties are all important. Until comparatively recently, these properties were judged by the foundryman largely by the feel of the sand and its appearance to the eye. Now, however, through the work of the American Foundrymen's Association and the National Research Council, together with the splendid pioneering work of a few individuals, the measurement of the required characteristic has been reduced to a quantitative basis. With the help of these tests, a new sand may be selected to take the place of an old one or to fill any given set of requirements.

Fineness.—The degree of fineness is the most important single factor in determining the suitability of a sand for making a particular type of casting. In this connection, the word fineness is used with two meanings. It is employed, of course, to refer to the relative size of the particles, as when we speak of fine, medium-fine, and coarse sands, but the term has acquired also a technical meaning. It is used to denote the *distribution of grain sizes* as determined by the percentages of the sand that remain on screens of different mesh. The distribution of grain sizes may be very different in two sands that by touch and visual examination would be rated as having the same relative fineness. The variation in the proportion of grain sizes has a noteworthy effect on the strength of bond and permeability of the sand.

The Fineness Test.—In the fineness, or grain-size-distribution test, tentatively adopted by the American Foundrymen's Association, a series of U. S. Bureau of Standards' sieves is employed. The sieves selected consist of Nos. 6, 12, 20, 40, 70, 100, 140, 200, 270, and bottom pan. The sample of sand, usually 50 or 100 g., is placed on the top screen of the series stacked in the order given, and the stack is agitated by a mechanical shaking and jarring device for a given period. The weight of sand that remains on each sieve is carefully determined and is expressed in per cent. That which is received by the bottom pan is designated as " −270 mesh," or "No. 270 minus." The extremely fine quartz grains in the sand are frequently referred to as silt. The silt must not be confused with clay. If the sample being examined is a sand that contains clay, the clay is first removed by a washing process. The fineness test is then run on the dried quartz grains.

Grading Sand.—In order to provide a standard method for the classification of sands, the American Foundrymen's Association proposes to grade molding sands according to a grain-fineness number. The grain-fineness number is defined as approximately the number of the mesh of that screen (the number of wires per linear inch) that would just pass the sample if the grains of the sand were averaged in size. The grain fineness number is calculated from the percentages obtained in the fineness test according to a specified method.[1] Ten grain classes have been established, and to each has been assigned a grain-fineness range.

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[1] See "A Tentative Method for Grading Foundry Sands," adopted by Amer. Foundrymen's Assoc., December, 1926.

The Degree of Fineness Required.—The fineness of the sand selected by the foundryman is determined by the kind of castings to be made. For light castings with smooth surfaces, the sand should be fine; for heavy ones, an open, coarse-grained sand is best. If sand suited for heavy castings is used for light work, the casting will have a rough skin; the indentations caused by the larger grains are more noticeable on the smaller casting. Fine sand will take a sharper impression of the pattern, and by the use of such sand, a casting with a finer surface finish can be made.

If fine sand suitable for light castings were employed in making heavy ones, there is a great likelihood that gas flaws would be formed in the casting. With large castings, because of the greater mass of metal, a much larger volume of gases and vapors is formed when the melted metal comes into contact with the mold. A fine sand is insufficiently permeable to allow these gases and vapors to escape.

Further, if fine sand be employed for a heavy casting, there is danger that the sand will be fused and form a coating of scale on the casting. Although the heat is quickly disseminated when making small castings, with large masses of melted metal the temperature may be kept elevated sufficiently long to cause a vitreous coating to form. This coating is removable from the casting only with difficulty, as with hammer and chisel, sand blast or "pickling," which adds considerably to the cost.

For very large castings, the sand employed should show in the fineness test approximately 75 per cent on sieves 12, 20, and 40.[1] For small castings, where a fine-surface finish is required, approximately 75 per cent should remain on sieves 70, 100, and 140. The percentage of silt ("minus 270") in no foundry sand should exceed 10 per cent. It greatly lowers the permeability and decreases the strength of the bond as well.

Permeability.—The permeability of a sand may be defined as that property which allows liquids and gases to filter through it. This property must not be confused with porosity. The latter term is employed to denote the pore space between the grains. Two sands may possess the same total porosity, but if the pores in one are larger than in the other, and if other factors

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[1] EARNILL, "Methods of Testing the Various Physical Properties of Molding Sand," p. 5, University of Illinois.

are equal, the sand with the larger pores will have the greater permeability. This fact may be illustrated by the use of pipes or tubes. Because the frictional resistance is less, a gas or liquid under the same pressure will flow more freely through a large tube than it will through a bundle of small tubes that together possess a total area of opening equal to that of the large tube. Thus, with the same total porosity, a coarse-grained sand will be more permeable than a fine-grained sand.

The most important factor in determining the total porosity is the uniformity in size of the grains. This may be shown by placing marbles in a tray. When one views a layer of marbles, all of the same size, laying closely together in a tray, it is obvious that the openings between them cannot be filled by the marbles themselves. If, however, a quantity of small-sized shot were poured into the tray, the openings between the marbles would, to a large extent, be closed. By the use of some third substance with still finer grains, the mass would become even more compact. Although a gas could readily enough pass through a mass of uniformly-sized marbles, its passage would be greatly impeded if the interstices were closed in the manner suggested. Likewise, sand for foundry use is more permeable to gases if it is composed of grains nearly of the same size, rather than of grains of graded sizes. An admixture of fine sand very noticeably lessens the permeability of a coarser sand, and the decrease is the more marked, the finer the admixture. Silt (less than 270-mesh) is especially objectionable.

In this connection it should be pointed out that, if other factors are equal, a sand is also more permeable if the grains are rounded rather than sharp. By considering again the marbles in the tray, it is evident that when objects are spherical they can pack less closely together than when they are angular.

With respect to permeability, the best sand would be one with rounded grains, which in the fineness test would all be retained on the same sieve. With nearly all sands, however, in this test some of the sample is found on every sieve. But if 75 per cent of the sample is found on three successive sieves, the sand is said to be even grained.

The clay content of sands also affects their permeability. Other factors being equal, the sand with the less clay will be the more permeable. Clay is necessary, of course, for bond strength, but if the clay is well distributed over the sand grains, sufficient bond strength may be obtained without employing enough clay to greatly affect the permeability. Some sands have an unnecessarily high bond strength. In such cases, permeability could be increased by an admixture of a sand with approximately the same size grade distribution, but less clay. On the other hand, a sand that is weak but very permeable may be milled until the clay is evenly distributed with the result that it will acquire satisfactory strength and still retain sufficient permeability.

The permeability of a sand is also affected by the amount of water used to moisten it. Although it would seem on first thought that the addition of water to sand would lessen its permeability to gases, just the opposite has been found to be true up to a certain point. In the following tables[1] the rates of air flow through two samples of sand containing known percentages of moisture are shown:

Sample A		Sample B	
Per cent of moisture	Time required to draw 1 liter of air, seconds	Per cent of moisture	Time required to draw 1 liter of air, seconds
Air dry	3,300	Air dry	840
5	2,880	5	560
7	1,080	8	240
9	640	10	280
11	240	12	320
13	305	15	375
15	560	20	3,000
25	4,200		

The moist sand was rammed as nearly alike as possible in both cases. The results indicate that for each sand there is a comparatively narrow range of moisture within the limits of which the permeability is greatest. This amount of moisture is called the *optimum* water content.

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[1] Ries and Rosen, *loc. cit.*, p. 59.

The increased permeability that is possessed by the moistened sand is due to the bonding effect of the water. When the sand is dry, the grains move over one another with comparative freedom. The particles adjust themselves so that the finer ones fit between the coarser ones. The result is that the pore spaces are largely eliminated. When the right amount of water is added, the surface tension of the water films between the grains binds the grains together in such a way that minute bridges or arches are formed. Thus a spongy mass is produced.

The fact that sands become more open and porous when properly moistened can be readily observed. If equal weights of dry sand are tempered with increasing percentages of water, say 4, 6, 8, and 10 per cent, and are then placed in glass cylinders of equal dimensions, it will be apparent even to the eye that the specimens show different degrees of openness of texture and fill the cylinders to different levels. Moreover, when moistened with the right amount of water, the moistened sand as dumped will weigh less than an equal volume of dry sand. Again, the amount of diminution in volume that can be effected by ramming the sand is found to be more or less proportional to the amount of water used to moisten it. In sand-testing laboratories, when running daily tests on the same sand, the lessening in volume on ramming has been used to gage the percentage of moisture.

When water sufficient to saturate the sand is added, the spongy masses fall apart and the grains again pack closely together. In experiments with clay-free sands it has been shown that if sand is poured into water under suitable conditions, the particles so adjust themselves that they occupy the same space as that occupied by the sand when dry.

In evaluating the permeability of a new sand, the degree of ramming is an important consideration. With a given amount of ramming, one sand may exhibit a permeability that is highly satisfactory, while with the same amount of ramming, another sand may appear so unsuitable that it may be rejected. With more or less ramming, however, the rejected sand may yield good results.

Cohesiveness.—The cohesiveness of molding sand depends (1) upon the amount, kind, and condition of the clay in the sand; (2) upon the presence or absence of hydrated ferric oxide; (3)

upon the size of the grains, the relative proportion of the sizes, and the character of the grain surfaces; and (4) upon the amount and uniformity of the distribution of the water in the sand. There are probably other factors also that have a bearing on cohesiveness, but those mentioned are among the important ones.

In a natural-bonded molding sand, clay is the bonding agent. Without clay (or some other adhesive substance such as ferric hydroxide) a sand would be useless for molding. It does not necessarily follow, however, that a high percentage of clay will produce a proportionately high bond strength. Two sands that contain the same percentage of clay, and are alike in all other respects, may vary considerably in cohesiveness. Clays, when moist, differ in plasticity and adhesive quality, and this in turn causes the strength of the bond to vary. The adhesiveness of the clay is largely a function of the colloidal condition. Clays that are largely non-colloidal are low in plasticity and adhesiveness. As has been stated, the adhesiveness varies also with the moisture content, but this factor can be controlled.

It has been shown recently that the presence of limonite (hydrated ferric oxide) contributes greatly to the strength of the bond that clay can produce. As a ferric hydrogel, it forms an envelope about the sand grains that clings tenaciously. Clay does not adhere well to the clean surfaces of grains of chert or quartz, but the adhesion between the clay and the ferric hydrogel is very great.

When attempts were first made to produce synthetic molding sands by preparing artificial mixtures of clean sand and clay, the product was not very satisfactory. After the effect of the ferric hydrogel was discovered, and a suitable amount of this material was added to the mixture, synthetic molding sands were produced that were able to compete with the natural product.

Although ferric hydrogel is adhesive, and molding sands in which it forms the only bond can be used, its bonding qualities when used alone are imperfect; it serves much better when used in conjunction with clay. It must be remembered also that ferric oxide is a flux, and if it is present in too great a quantity, it may become objectionable due to this fact.

Other factors being equal, the adhesiveness of a molding sand in general decreases with the size of the quartz grains; the finer the sand, the less is the strength of the bond. A large percentage of silt is very detrimental to strength. It is fortunate that the bond strength tends to increase with grain size because in molding practice greater strength is needed in molds for which the coarser sands are required. On account of their greater permeability, and because the washing or scouring effect of the melted metal that the walls of the mold must resist is greater when large volumes of melted metal are poured, for heavy castings, coarse sands must be used.

If the grains of sand are angular and have rough surfaces, the bond will be greater than if the surfaces are smooth and the grains are rounded.

Durability or Life of Molding Sands.—When water is added to a molding sand, the bonding material swells, becomes sticky, and binds the grains of sand together. After the sand has been exposed to the heat of the melted metal, and then is moistened again, it does not develop the same degree of cohesiveness it formerly possessed. With repeated use, the sand will eventually become so depleted in bonding strength that, unless fresh molding sand or fresh clay is added, it will be no longer suitable for molds. Sands vary a great deal with respect to the rate at which cohesiveness is lost, and among foundrymen it is common practice to speak of long-lived and short-lived sands.

The length of life of the sand, as it is called, is important because it is a factor in determining the cost of producing castings. Some sands may be used a great many times without the addition of new material, while others are easily "burned." On an average, less than 1 lb. of new sand should be required for each 25 lb. of metal cast.

It has been explained that the cohesiveness of a molding sand depends more on the amount of clay in the colloidal state than it does on the total quantity of clay present. This is true also of the hydrated iron oxide. Even some of the silica may exist in the colloidal condition and contribute to the strength of the bond. When these colloidal materials are heated, they become dehydrated, and then are no longer adhesive.

After having been dehydrated, a substance in the colloidal condition may or may not be able to rehydrate and to become sticky again. With hydrated colloidal silica, for example, the reversible property is entirely lost; after dehydration it cannot readsorb water. The hydrated ferric oxide, on the other hand, although it dehydrates easily, readily becomes hydrated again. According to the researches of Paneth and Vorwerk[1] ferric hydroxide is apparently the only metallic hydroxide that will adsorb water and regain its original condition after being heated to 320°C. With regard to its ability to rehydrate after being dehydrated, clay occupies a position between the silica hydrogel and the ferric hydrogel. Baked clay will rehydrate only incompletely. The rehydratability of the bond in a molding sand, upon which the length of its life to a large degree depends, is, therefore, a variable function.

Although the durability or life of a molding sand is a property entirely distinct from its refractoriness or resistance to fusion, the former is to some degree affected by the latter. The sand that is most strongly dehydrated, of course, is that which lies closest to the metal. If the sand has a low refractoriness, a large part of its dehydrated material may be fused and may be removed because it adheres to the casting. As a result the heap sand may not become contaminated to so great a degree with dehydrated material, and may have a longer life than if its refractoriness were greater.

With regard to the changes that occur in the sand adjacent to the casting the following analyses[2] are of interest. Number I is an unused sand, known as Redford sand, from Richmond, Va. Number II is a sample of the same sand taken after casting from the layer next to the metal.

An examination of the grain-size distribution in the two analyses shows that, due to the fusing together of particles, there has been a marked increase in the coarseness of the sand. Ries says that, because some of the coarse grains were screened out, there was even a greater agglomeration than the analyses show.

The difference in chemical composition between the new and the used sand is due mainly to the loss of water and to the reduction of the ferric to ferrous oxide. As a result of iron oxide being received by the sand from the surface of the casting, there is also an increase in the total iron-oxide content.

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[1] *Z. physik. Chem.*, **101**, 445, 1922.

[2] Ries and Rosen, *loc. cit.*, p. 61.

MECHANICAL ANALYSIS

Number of mesh	Per cent, retained on mesh	
	I	II
20	1.51	5.34
40	1.26	14.73
60	1.27	10.41
80	0.56	1.28
100	6.27	14.61
250	71.69	59.37
Clay	16.52	3.52

CHEMICAL ANALYSIS

	Per cent	
Silica (SiO_2)	83.49	82.32
Alumina (Al_2O_3)	7.25	7.80
Ferric oxide (Fe_2O_3)	4.74	3.98
Ferrous oxide (FeO)	.....	2.38
Lime (CaO)	0.36	0.54
Magnesia (MgO)	0.35	0.41
Potash (K_2O)	1.30	1.64
Soda (Na_2O)	0.41	0.80
Titanium oxide (TiO_2)	0.30	0.22
Water (H_2O)	1.66	0.19
Total	99.85	100.28

High permeability of the sand tends to lessen the deterioration that results from repeated use. With high permeability the heated gases can escape more freely. Because the gases carry away the heat, the layer of sand lying next to the metal is kept at a lower temperature. If a fine sand were used for making heavy castings, there would be a tendency toward rapid deterioration because the heat would not be conducted away as rapidly as it should be.

Tempering sand with a slight excess of water tends to increase its durability or length of life above that which the sand will exhibit when tempered with the normal amount of water. The water will, of course, be converted into vapor, and heat will be carried away as the latent heat of steam. In this connection it must be remembered, of course, that sufficient permeability is the first consideration and that if too much water is used, flaws in the casting may be caused by steam that cannot escape with sufficient rapidity.

Loam Sand.—A loam sand is a high-bonded molding sand that may be employed in fabricating a mold on a fire-brick structure. The clay content exceeds that found in ordinary molding sands; it may be as high as 40 per cent. The cohesiveness and plasticity of a loam sand are such that the mold may be formed by a building-up process. Because this method of molding is employed for large castings, loam sands usually must have a fairly coarse texture. To lessen the shrinkage that results from the drying of the high percentage of clay, when loam sand is prepared for use, it is common practice to mix with it some clay-free sand. Because of its high clay content, loam sand is used a great deal in reconditioning "burned" sand in gray iron foundries.

Molding Sand for Non-ferrous Castings.—The molding sand employed for making castings of non-ferrous metals and alloys is a fine grained sand with a comparatively low clay content. Fineness of texture is necessary because brass, bronze, and aluminum castings are required to have a smooth finish. Inasmuch as fine sands are not very permeable, and the presence of clay decreases permeability, the clay content is kept as low as is practicable; it generally varies between 10 and 15 per cent. Fortunately the melting points and casting temperatures of the non-ferrous metals and alloys are comparatively low; if it were necessary to employ temperatures such as are required for casting iron and steel, the fine-grained sand would probably be fused. Because of the low temperatures, also, sands in the non-ferrous foundries tend to have a longer life than those employed for ferrous metals. As a result, less new sand must be added. In the United States much of the sand employed for non-ferrous work is obtained from the Hudson River basin, and is marketed under the name of "Albany Sand."

Core Sands

Although core sands contain much less clayey matter, they resemble as a rule, medium- or coarse-grained molding sands.

The clay content of core sands varies according to the size of the cores to be made. For small cores, sand with no clay is used; even crushed quartz rock may be employed very satisfactorily here. For large cores, the mixture may contain up to an approximate maximum of one-third of molding sand, which will introduce 6 or 7 per cent of clay into the core. The presence of much clay in core sand is objectionable because it lessens permeability, and causes the core to bake to a hard mass that will not disintegrate in the desired manner when the casting is cleaned. The necessary bond is obtained chiefly by the use of adhesives such as starch, dextrin, resins, oils, and other organic substances called core binders.

Because a great deal of gaseous matter is evolved from the binder, the greatest possible permeability is desired in core sands. Coarse sands require less binder than finer sands, and with a given amount of binder will produce stronger cores. With coarse-grained cores, therefore, a smaller quantity of gases will be formed, and, because of the greater permeability, the gases will have a better chance to escape. On account of its lower permeability, a fine sand should not be used for large cores. As a rule, small castings are required to have a smoother surface than large ones; consequently, fine sands are more desirable for small cores. In general, then, the sand that should be selected is the coarsest that is compatible with the finish the casting must have, and the finest that is compatible with the required permeability.

Owing to the expense of the binder, it is profitable to use a sand that requires the least binder. This is another reason for using the coarser sands. Besides, sands with clean spherical grains require less binder than those with angular grains.

Because of the relatively low temperatures needed in casting non-ferrous castings, fine sands, which have lower refractoriness, may be used. In steel foundries, on the other hand, core sands having the greatest possible resistance to fusion must be employed.

CORE BINDERS

The Necessity for Core Binders.—A core sand is required to possess two properties that are naturally somewhat incompatible. It must have both high permeability and high cohesiveness; in fact, it must be more open and permeable to gases, and at the same time possess greater strength than the sand for the mold itself. Clay contributes strength, but because clay lessens permeability, only a relatively small amount of clay can be allowed in a core mixture. Obviously, then, some other material having high adhesive qualities must be added to core sand. The adhesives employed for cementing the sand grains together are called core binders.

Requirements and Classes.—The ideal core binder is one that will hold the sand grains firmly together when green, will produce a strong, solid mass when the core is baked, and after the metal is poured will allow the core to disintegrate so that the sand may run readily from the interior of the casting. The binder, moreover, must be cheap. The materials most frequently employed as core binders may be divided into the following classes:

Clay.
Water-soluble binders.
Paste binders.
Resins and pitches.
Oils.

Clay.—A plastic clay mixed with sand produces an excellent bond and it is cheap, but if much is used it interferes with the venting of the core. Moreover, when the hot metal is poured against it, a clay bond becomes very hard, which makes the core difficult to remove from the casting. Usually no clay at all is used in small cores, and in the larger ones it does not amount to more than 6 or 7 per cent. Large cores are made of coarse sand, which, being more permeable to gases than fine sand, can carry a small amount of clay without the permeability being diminished unduly.

Water-soluble Binders.—Although the water-soluble binders are excellent adhesives, they possess two objectionable features that are typical of the class.

1. They have a tendency, during drying, to be carried to the exterior of the core and to be deposited there by the evaporating water. When this happens, a hard impenetrable surface is presented to the hot metal. As a result, gases cannot escape readily through the core and gas flaws are almost certain to be

formed in the casting. The concentration of the binder in the exterior also leaves the interior of the core in a loosely coherent condition. The segregation of the binder is more likely to be encountered in cores with thick sections, but for cores of large size, molding sand may be employed in the mixture, and the clay thus introduced will retard the diffusion of the binder.

2. The water-soluble adhesives have a tendency to absorb moisture and to allow the core to soften when it is stored in a damp place or is left in a green-sand mold for more than 12 hr. Moldenke says[1] that the remedy for softening is the proper baking of the core. He recommends that the process be carried out in two steps: drying at a temperature not lower than 250°F., followed by baking at about 375°F. Baking at this temperature, however, must not be too greatly prolonged, because, whereas underbaking yields cores that will soften, overbaking produces burnt and weak cores.

The most widely used binders of the water-soluble class are *molasses*, derived from cane sugar; "*hydrol*," a syrup produced during the manufacture of corn sugar; and "*glutrin*," a concentrate obtained from the sulfite liquor employed in the preparation of wood pulp for the manufacture of paper. These binders are diluted with water for use. They are generally employed with clay and other binders. If allowed to stand too long in solution in water, the molasses and hydrol have a tendency to ferment, which weakens their adhesive qualities. The original sulfite liquor, employed for treating the paper pulp, consists of an aqueous solution of calcium and magnesium acid sulfites. For use as a core binder, the "spent" liquor is evaporated to the consistency of a thick syrup, having a density of about 35°Bé. Its adhesive qualities depend upon the calcium and magnesium resinates formed during the "digesting" of the wood pulp.

Paste Binders.—These binders are among the most widely used of all classes. Although they have no tendency to concentrate in the exterior of the core during drying, unless they are evenly distributed by thoroughly working the core mixture, minute lumps of the binder, drying in the spaces between the sand grains, will interfere with the venting of the core. Accord-

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[1] "Coremaking," p. 7.

ing to Moldenke,[1] to secure best results, the mixture of binder and sand should be tempered with water during the afternoon preceding the day it is to be used. On standing over night, the binder will become suitably softened, so that when the mixture is reworked on the following morning, each grain of sand will become covered with a film of the binder. In this way a distribution comparable to that obtained with the water-soluble binders may be secured. The baking of cores with paste binders should be conducted in the same manner as described for the preceding class. Unless properly baked they absorb moisture, although to a lesser degree than those of the water-soluble type. The two most common paste binders are flour and dextrin.

Flour.—Although frequently flour of a poorer grade, really a fine grade of bran, is used as a core binder, it is only the starch and gluten of the flour that possess any adhesive quality, so that in reality it is more economical to use flour of a better grade, consisting almost wholly of starch and gluten. The bran has no value as a binder. The bran, moreover, adds to the organic matter, subject to destructive distillation during the baking of the cores and during casting. The stifling gases that result from the decomposition that takes place during these processes constitute one of the objections to flour as a core binder. Another objection is that cores containing flour, unless only the minimum quantity actually necessary is used, are subject to swelling when allowed to stand in the mold or any other place where moisture prevails.

Dextrin.—Dextrin is a colorless, uncrystallizable substance having strong adhesive properties. It has the same ultimate composition as starch and can be made from starch without much difficulty. Although employed in the manner of a paste binder, it is in reality readily soluble in water. It is employed on postage stamps and the flaps of envelopes. Being an excellent adhesive, a smaller quantity is required than is necessary with flour, and the gases that result from its decomposition are, therefore, less objectionable.

Resins and Pitches.—The best representative of this class is common *rosin.* Although rosin is one of the cheapest of the

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[1] *Loc. cit.*, p. 8.

large class of resins, it is really too expensive to be extensively employed as a core binder.[1] Rosin makes a strong, solid core, and burns out readily during casting. In the green core, however, it does not act as a bonding ingredient at all; it is necessary to use it with some other material. Sometimes clay may be used to supply the green strength, but usually flour or dextrin are employed for this purpose. Rosin melts at a low temperature, from 100 to 140°C. (212 to 284°F.), and, during baking, is drawn to the contact points of the sand grains by capillarity. On cooling, it binds the grains together. Because rosin remains soft at temperatures well below its melting point, cores bound with it cannot be handled until comparatively cold. Rosin has no tendency to absorb moisture. It preserves the sharp corners of cores, and is said to allow a free escape of gases in cores that are difficult to vent. For use it must be ground very fine.

Pitches and tar are used chiefly for large cores. Moldenke says[2] that although they are particularly good for the larger cores, they carbonize or char during casting, and cause difficulty in the cleaning room.

Oils.—Among the oils that may be employed in the core room are linseed, tung, soya-bean, cottonseed, corn, fish, and rosin oils (pages 494 to 503). Linseed oil is by far the best of this group. It can be used in the proportion of 1 part of oil to 75 or 80 parts of sand. Linseed oil cores are baked at about 475°F.[3] a higher temperature than is permissible when other binders are used. Because of the difference in the baking temperatures, linseed oil should not be used with paste binders. It should be remembered that linseed oil dries by oxidation (page 497), and that an abundant supply of oxygen, such as is supplied by a free circulation of air in the core oven, is of great advantage when baking the cores.

Linseed oil is very suitable for making thin, intricate cores, as for radiators and gas engines, where the core must be able to be cleaned out with exceptional ease. The cost of linseed-oil core making can be lessened by using a little finer sand to close

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[1] For the method of preparation, grades, and properties of rosin, see pp. 533 and 534.

[2] *Loc. cit.*, p. 9.

[3] Moldenke, *loc. cit.*, p. 8.

partially the voids between the coarser grains, which allows a core, equally good, to be made with less oil. Finely ground quartz rock is useful here. The use of the finer sand is not so objectionable with linseed oil as it would be with a paste binder, such as flour. The oil is drawn to the points of contact of the sand grains, which leaves the intergranular spaces open for the passing of gases. For the same reason, strong cores can be made with less binder than with those substances that do not collect in this way. Because of its high price, linseed oil is likely to be found adulterated with other oils, such as rosin oil, fish oil, and cottonseed oil. As a matter of fact, pure linseed oil hardly ever finds its way into a core room.

Parting Sand.—Parting sand is fine silica sand, fine burned sand, or other fine unbonded material used to prevent two surfaces from adhering. It may be employed to part the cope from the drag, or to prevent the sand from sticking to the pattern.

An artificially prepared product consisting of *tripolite*[1] impregnated with lard, stearic acid (page 490), or other fatty substance, has recently been used extensively as a parting material. In order that the former may absorb the latter, the tripolite and fatty substance are heated together, and then the material is ground.

If the cost is not prohibitive, *lycopodium powder* may be employed. This powder is a fine, impalpable dust consisting of the spores of a moss-like plant, of the genus *Lycopodia.* It is very inflammable.

Sometimes, instead of using a parting sand or powder, the surface of the mold may be covered with soot from a smoking torch. This practice serves the purpose also of drying the mold somewhat.

FOUNDRY FACINGS

With the exception of sea coal the substances included under the head of foundry facings are those that are used to line the mold to prevent the formation of a scale by a reaction between the silica of the sand and the ferrous oxide developed at the

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[1] Tripolite, known also as Tripoli powder, kieselguhr and diatomaceous earth, consists of the skeletons of microscopic plants called *diatoms.*

surface of the molten metal. The materials used as surface coatings must spread easily, have great heat-resisting power, and give the casting a fine blue surface. Sea coal is not a facing in the true sense but is used to mix with the sand to make the mold more porous or open. It serves as a vent and so prevents the formation of blow holes; indirectly it prevents the formation of the ferrous silicate mentioned previously. Because of this latter effect, which will be explained in the following paragraph, it is usually classed among the facings.

Sea Coal or Bituminous Facing.—Sea coal derives its name from the fact that in England it was shipped from Newcastle-on-Tyne, by the sea, to London, and was so named to distinguish it from charcoal. In the eastern United States, the coal used in this manner as a so-called facing comes from the Westmoreland region in Pennsylvania. It is crushed, screened to remove slate, and then is ground. It is a high-grade gas coal. It should never contain less than 35 per cent of volatile matter, never more than 8 per cent of ash, and 1.5 per cent of sulfur. The reason for the need of the high volatile matter is that when the molten metal is introduced into the mold, the heat drives off that portion of the coal that is volatile, which leaves the mold sufficiently porous to allow the escape of the heated gases. If the gases escape freely, blow holes are prevented. Furthermore, these gases in escaping carry away a considerable amount of heat from the surface where the metal is in contact with the mold. Thus, the heat intensity at this point is sufficiently lowered that the ferrous oxide formed at the surface of the molten metal is prevented from fusing with the sand. In other words, it prevents the formation of "scabs," which consist of ferrous silicate and entangled sand. Sand itself is not a good conductor of heat.

For heavy castings, the coal dust is mixed in about the proportion of 1 part of dust to 8 or 10 parts of sand; for light castings, about 1 of dust to 12 or 14 of sand is used. The fineness of the dust for heavy work is about 10-mesh, for light work about 20- to 40-mesh. For very light work and where extreme smoothness of surface is desired, the dust is bolted, *i.e.*, sifted through fine cloth. If the coal dust were not of proper fineness, upon burning away it would leave a pit-marked casting.

Graphite.—Apparently the best of the foundry facings is graphite, the finest grade of which is obtained from the island of Ceylon. The composition and general properties of graphite have been given on page 79, which see. As a facing it spreads easily and has a high heat-resisting power. To the foundry trade, graphite is known by several names which are really synonymous. According to custom, however, the highest quality is designated as "graphite," the second grade or blends as "plumbago," and the very cheapest grade as "black lead" or sometimes also as plumbago. Plumbago is often mixed with talc and can be sold at any price.

Coke Blacking.—This is made from the best grades of 72-hr. coke, finely ground. It can be used only with dry sand work, or as a wet blacking since it will not slick with a tool. It is used as a roll or ingot mold blacking.

Soapstone or talc makes a very satisfactory facing for gray-iron castings. It can be used on either dry or green sand molds since it "slicks" easily. It is said that there is objection to it in that it causes the casting to have a reddish color, which is often mistaken for burnt iron. Finely ground mica can also be used as a facing.

Molding Sand for Steel Castings

As is shown by the melting-point curves in Fig. 48 (page 290), the melting points of the steels become lower as the carbon content increases. Even with a high carbon content, however, the melting point of steel is considerably above that of ordinary foundry iron. Because of the high temperature it must withstand, the sands employed in making steel castings must be very refractory. Those that are used for this purpose consist almost entirely of silica with the least possible amount of clay that will form a bond. The clay content must be kept at the lowest possible point because of its comparatively low resistance to fusion. Generally the amount allowed to be present is not above 3 per cent, and this should be as nearly pure kaolin as possible. Because they produce fusible silicates, lime, magnesia, ferrous oxide, and especially the alkalies are very objectionable.

Inasmuch as so little clay is allowed in steel-foundry sands, it must be distributed evenly over the surfaces of the quartz grains.

This can be accomplished only by rolling the sand and the clay together. While absolutely dry, the clay, which is usually a good grade of fire clay, is first ground to a fineness such that 95 to 98 per cent will pass through a 200-mesh sieve. Then it is moistened and is mixed with the sand grains in a mechanical mixing device of the muller type. Pressure great enough to crush the sand must be avoided.

All steel-foundry sands are not prepared artificially. Some sands are found which contain 97 or 98 per cent of silica and which have a natural-clay bond that is very refractory. Such sand, which is called crude sand, is cheaper than the prepared sand.

In making molds for steel castings the layer of sand that lies next to the metal must have a bond strength above that which the slight amount of clay can give it. If insufficiently bonded, the sand would be washed away during the pouring of the melted steel. To supply this additional bond, some organic adhesive such as is used for cores is employed. Typical materials are molasses, dextrin, and glutrin (pages 385 to 387). The sand, clay, and organic adhesive are moistened with 3 or 4 per cent of water, and are thoroughly mixed. In some instances, in order to form a smooth refractory surface, the face of the mold is coated with silica flour mixed with molasses or dextrin.

CHAPTER IX

BUILDING STONES

Although practically all rocks are suitable for building construction from the point of view of their mechanical strength, there are other requirements which they may not be able to fill, and which may cause the stone to be rejected as a material unfit for building purposes. Among the important properties that must be taken into account are the durability of the stone, its tendency toward discoloration, and its resistance to the effects of fires. In the present chapter it is proposed to discuss building stones with special reference to these three factors.

Durability.—Baker,[1] in commenting upon this subject, says:

> Rock is supposed to be the type of all that is unchanging and lasting; but the truth is that, unless the stone is suited to the conditions in which it is placed, there are few substances more liable to decay and utter failure. The cities of northern Europe are full of failures of stones of important structures. The most costly building erected in modern times, perhaps the most costly edifice reared since the Great Pyramid—the Parliament House in London—was built of stone taken on the recommendation of a committee representing the best scientific and technical skill of Great Britain. The stone selected was submitted to various tests, but the corroding influence of a London atmosphere was overlooked. The great structure was built and now it seems questionable whether it can be made to endure as long as a timber building would stand, so great is the effect of the atmosphere upon the stone. This is only one of the numerous instances that might be cited in which a neglect to consider the climatic conditions of a particular locality in selecting a building material has proved disastrous.

Merril[2] in referring to instances of a similar sort makes the following statement:

> The Executive Mansion and portions of the Capitol buildings in Washington are of a sandstone so poor in enduring qualities that it has

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[1] "Treatise on Masonry Construction," p. 4.

[2] "Stones for Building and Decoration," p. 419.

been found necessary to paint them periodically in order to keep them in a condition in any way presentable.

The failure of building stones is caused by two types of agencies, mechanical and chemical. The former breaks down the structure of the stone by disintegration, the latter by decomposition.

Disintegration.—In this process, the mineral constituents of the stone are separated into granules with practically no alteration in their composition. Disintegration is due mainly to temperature variations. Changes in temperature operate in two ways: first, through the unequal changes in the volume of the component minerals that result from their different coefficients of expansion; and, second, through the action of frost. (Read the discussion under Mechanical Processes on page 366.)

The susceptibility to the action of frost is dependent upon the porosity and friability of the stone. Assuming composition and other characteristics to be equal, a porous stone is less resistant to freezing than a dense stone. Rocks with winding pores and tubes are more likely to be injured by freezing than those with straight pores and tubes.

If the stone is to be used in a location where friction is great, as for stair treads, resistance to abrasion must be considered as a factor in the choice of the stone. There is a wide variation in the ability of stones to withstand abrasive action.

Decomposition.—In the process of decomposition, the mineral constituents of the stone are changed into new compounds. Hydration, oxidation, and the attack of carbonic acid are the chief types of reactions involved. (Read the discussion under Chemical Processes on page 366.)

The carbonate stones, namely, the limestones, dolomites, and marbles, as well as the calcareous sandstones, *i.e.*, sandstones in which the quartz grains are cemented together with calcium carbonate, are often badly affected by atmospheres containing much carbon dioxide and sulfur dioxide. These gases are especially prevalent where smelters, furnaces, or factories exist. The carbonates are converted into soluble compounds and carried away by the rains. Stones consisting principally of silica are practically unaffected by such acid action. It should be observed in this connection, however, that chemical composition is not always determinative as regards the weathering of stones. Structure and density are also strongly influential. Thus, a dense, fine-grained carbonate rock may weather well; while a coarse-grained, porous stone, even though composed almost entirely of silica, may weather very poorly.

Life of Stones.—Ries[1] says that the life of a building stone may be considered as the length of time it will stand exposure to the weather without showing signs of disintegration or decay. To indicate the life of various stones, he quotes the following table compiled by Dr. A. A. Julien of New York City:

Kind of Stone	Life in Years
Coarse brownstone	5 to 15
Fine-laminated brownstone	20 to 25
Compact brownstone	100 to 200
Bluestone (sandstone), untried, perhaps centuries.	
Ohio sandstone (best siliceous variety) perhaps from one to many centuries.	
Coarse fossiliferous limestone	20 to 40
Fine oölitic (French) limestone	30 to 40
Marble, coarse dolomitic	40
Marble, fine dolomitic	60 to 80
Marble, fine	50 to 100
Granite	75 to 200
Gneiss, 50 years to many centuries.	

Discoloration.—Certain stones after having been placed in the building show changes in color. The pink granites often change to a much lighter shade because of the weathering of their feldspar; green stones sometimes have a tendency to fade. These changes do not, however, necessarily indicate a weakening of the stone.

Sandstones, granites, and others containing iron compounds are often changed in color due to the oxidation of the iron. Iron pyrite, which occurs quite commonly, is especially susceptible to oxidation. The stone may in this way be changed from a light color to a brownish yellow or a deep brown. The pyrite FeS_2 is oxidized to the basic ferric sulfate, as shown by the equation on page 367. If the pyrite was present in large lumps or grains, the reddish product of the reaction may spread over the stone in exceedingly unsightly blotches or streaks. The decom-

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[1] "Building Stones and Clay Products," p. 86.

position of the stone that results from the attack of the acid, formed at the same time, may cause a discolored saucer-shaped depression. In the older type of sidewalks formed of milled slabs of sandstone, such depressions may be frequently observed.

Fire Resistance.—Judging from experience there is no stone that can withstand the extreme heat developed by the burning of large buildings. Granites seem to be the least resistant and sandstones most. Granites are particularly likely to crack and spall if they are suddenly cooled from a highly heated state, as by the application of water. Limestones show good resistance at temperatures below 600°C., but at about this point the stone begins to dissociate into quicklime and carbon dioxide.

Kinds of Rocks

Classified according to origin, rocks are divisible into two major groups, igneous and sedimentary.

Igneous rocks are those that have been produced by the cooling of fused material. It is supposed, of course, that the total solid portion of the earth was so formed originally and hence was igneous, but it is doubtful if any of this original formation still exists. The igneous rocks here discussed are those produced later by the cooling of fused material forced up through outer layers of rock. In most cases this fused material cooled before it reached the surface and is now exposed only by the removal of overlying strata. Igneous rocks formed in this way are called *plutonic.* Those that cooled on the surface of the earth are called *volcanic.*

Sedimentary rocks are those that resulted from the decomposition of other strata. The decomposed material was carried by water usually, and deposited as a bed of sand, clay, or limestone. These loosely deposited layers when hardened formed rock.

Metamorphism of Rocks.—Frequently the structure and in some cases the chemical composition of both igneous and sedimentary rocks have been changed by heat, pressure, and other agencies. Sometimes the alteration has been so great that it is difficult to determine whether the original rock was of igneous or sedimentary origin. Rocks that have been altered in this way are known as *metamorphic rocks.*

IGNEOUS ROCKS

Structure.—Depending upon whether or not they have been metamorphosed, igneous rocks are divided into two classes. Those that solidified quietly from a state of fusion and were not later subjected to severe external stresses, are made up of crystals irregularly arranged and are called *massive* igneous rocks. On the other hand, when rock of the same composition was subjected to pressure, either during or after cooling, a banded structure was often developed. In some cases, the constituent minerals are found in more or less definite alternating bands; in others the mixed crystals are merely arranged with their long axes in the same direction. In either case the rock is called a *gneiss.*

Chemical Composition.—The igneous rocks range from 35 to 80 per cent silica with alumina as the second most abundant constituent. The following is an average by F. W. Clarke of analyses of 830 American igneous rocks:[1]

	Per Cent
Silica	59.71
Alumina	16.01
Ferric oxide	2.63
Ferrous oxide	3.52
Lime	4.90
Magnesia	4.36
Potash	2.80
Soda	3.55
Water	1.52

The term *acid igneous* is applied to those igneous rocks high in silica and relatively low in lime, magnesia, iron oxide, etc. *Basic igneous* signifies that the rock is high in lime, magnesia, etc., and low in silica.

Commercial Classification.—The scientific classification of igneous rocks is highly detailed and too complex to be introduced here. The following simple classification is used by quarrymen and builders:[2]

1. Granites.
2. Traps.
3. Serpentines.

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[1] Quoted from Eckel, "Building Stones and Clays," p. 23.

[2] ECKEL, *loc. cit.*, p. 30.

Granites.—The granites are crystalline, plutonic, igneous rocks, composed largely of quartz and feldspar, with usually some mica and occasionally hornblende. Because of the excess of silica, granites are designated as acid rocks.

Quartz is native silicon dioxide, or silica (SiO_2). Depending upon the impurities contained, its crystals, which occur in the hexagonal system, vary in luster and color. Quartz is the hardest of all the common minerals. It has a specific gravity of 2.6, is infusible in the blow-pipe flame, and resists all acids except hydrofluoric. It is very resistant to weathering.

Feldspar is essentially a silicate of alumina combined with the oxide of some other metal. Its color is light, usually whitish, gray, pink, or light green. The common or potash feldspar, known as orthoclase, is pink. It has the composition indicated by the formula $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$. Albite is a soda-alumina feldspar; some albite is usually found in granites. By the process of weathering, which takes place very readily, feldspar is converted into clay (page 368). When granites weather, because of the presence of the unweatherable quartz grains, a sandy clay is formed.

Mica in granite may be of two kinds, either the white called muscovite, or the black known as biotite. The former is a silicate of alumina and potash; the latter is a silicate of iron, magnesia, alumina, and potash. Mica occurs in granite in the form of smooth, shining scales, which cleave readily into thin, elastic leaves. It weathers rather readily but unless present in the granite in large quantity it is not considered injurious.

Hornblende is a silicate of iron, lime, magnesia, and alumina. Its color is usually dark green to greenish black. It occurs in compact crystals and is more resistant to the weather than mica.

Good granites are usually either gray or reddish in color; granites of such colors are composed of the minerals that are more resistant to weathering. The black or greenish granites are usually less durable for the opposite reason. Whitish and yellowish granites should be examined carefully to see that the feldspar and mica are fresh, since such colors are often produced by the weathering of these constituents.

Trap Rock.—The word trap, as here used, is derived from the Swedish *trapp*, meaning stairs; the term has reference to the occurrence of the rock in the quarry. Trap rock consists mainly of feldspar of the soda or lime (not potash) variety, and hornblende. The rock is basic in composition; the content of silica is notably low. It is fine-grained, compact, and dense, and may occur either in the massive or gneiss formation. Because of the way the rock is usually cracked, it is difficult to obtain large blocks of specified dimensions for building purposes. Because of the low silica content and the presence of a considerable amount of iron compounds, the color is usually dark—from dark gray and green to black.

Like all basic rocks, trap rock is likely to weather considerably with the production of a chalky or clay-like product.

The strength and density of trap rock exceed that of granite; hence, when considered from this standpoint only, it is very suitable for use as a building stone. Because of the great toughness of the blocks, however, it is difficult to dress them; and as they have a tendency to split into irregular masses, they are seldom used as a dimension stone for building. On the other hand, these very properties, *i.e.*, their density, strength, and toughness, make them exceptionally suitable for paving blocks, railway ballast, and concrete aggregate.

Serpentines are generally igneous in origin, but not directly so. Because they have been produced by the hydration of basic silicates, they may be classed as metamorphic rocks. Pure serpentine is a hydrated silicate of magnesia ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$); it contains about 13 per cent of combined water. It has a soapy feel and is soft enough to be easily cut with a knife. It is not much used as a building stone since in nearly all serpentine quarries, irregular joints occur which make it extremely difficult to obtain large-sized blocks. It is quite suitable for interior use. It is usually green or greenish yellow (although it may be other colors if impure) and is susceptible to a fine polish, unless, as is sometimes the case, it should contain hard crystals of pyrite, chromite, or magnetite. For exterior use it is defective, because it weathers irregularly, cracks, and fades.

Soapstone is closely allied to serpentine; it also is a hydrated magnesian silicate, $3MgO{\cdot}4SiO_2{\cdot}H_2O$. It differs from serpentine in that it is both less basic and less hydrous; it contains only about 5 per cent of combined water. Under the trade name of

"Alberine Stone," it is used frequently for sinks, washtubs, laboratory table tops, etc.

SEDIMENTARY ROCKS

Sedimentary rocks are those that have been formed of material usually carried by and deposited from water in the form of clays, sands, etc. Having been formed as sediments, these rocks possess a characteristic bedded or layer formation; the layers vary in composition, color, etc., depending upon the conditions prevailing at the time of deposition. In using these rocks for building purposes it is necessary to take account of this layer formation, since they split more readily along the bedding planes than in other directions; because of this fact, they are less suitable for massive structures than the igneous rocks. They should never be set in the wall on edge, since thin layers may split or scale off where exposed to the weather. Sedimentary rocks, like those of igneous origin, may be found greatly modified by metamorphism.

The sedimentary rocks considered in this discussion will be taken up in the following order: slates, sandstones, limestones, and marbles.

Slates.—With but few exceptions, roofing slates are the hardened, and more or less metamorphosed, siliceous clays that collected as fine silt on ancient sea bottoms.[1] In a few cases they are derived from rocks of igneous origin. By long-continued pressure a plane of cleavage has been formed. Although this cleavage plane may be parallel to the original bedding plane, it more usually diverges at some angle from the bedding plane, not infrequently at a right angle. Eckel says:[2]

> It has been proven experimentally that a distinct *slaty cleavage* can be produced in any fine-grained, homogeneous mass by long-continued heavy pressure, so that we may fairly assume that the cleavage of roofing slate was produced in this way.

The original bedding planes are discernible in the form of bands on the cleavage surface and are known as ribbons. Slates differ from clay rocks and shales in that the clays and shales break into more irregular masses; the easiest breaking occurs in planes

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[1] MERRILL, "Stones for Building and Decoration," p. 75.

[2] *Loc. cit.*, p. 96.

that run either parallel to the bedding, or parallel to joint systems.

Composition.—Since slates are derived from clayey rocks, they consist essentially of the silicates of alumina, lime, magnesia, potash, and soda; they contain also 3 or 4 per cent of combined water. In some varieties, mica scales, which add considerably to the elasticity and toughness of the slate, are abundant.

Color.—The commonest color of slate is some shade of gray or bluish gray; then follow in order, the black, green, and purple slates. In most cases these colors are dependent upon the amount and condition of two substances—organic matter and the iron oxides. If the slate contains considerable finely divided carbonaceous matter, it will probably show a glossy black color; if high in ferric iron, it will probably be a red or purple slate; if high in ferrous iron, it will probably be green in color, unless this is obscured by organic matter, in which case the color will likely be black. The glossy black slates are, as a rule, finer and more even-grained, softer and considerably smoother than slates of other colors. The gray slates, on the other hand, are coarser in grain and much harder; the reds and greens are intermediate.

Discoloration of Slates.—The discoloration of slates is due to the presence of the very unstable ferrous carbonate in a finely divided form, which gradually oxidizes to the brown, hydrated ferric oxide. Although the original ferrous carbonate is green, this color is not necessarily imparted to the slate since the green may be masked by graphitic or carbonaceous matter, in which case the slate will be black. Hence, some black slates may discolor or fade and others may not. This difference is exhibited by two grayish-black slates from Pennsylvania. The slates from the Peachbottom district have excellent weathering qualities and are permanent in color. Some slates from Lehigh and Northampton counties have a tendency to fade because of the oxidation of the ferrous-iron content. Since the amount of this ferrous iron often varies in the different beds of the same quarry, it may happen that patches of slate on the same roof may fade while others may not. In this way a very undesirable blotched appearance is presented.

Sandstones.—These stones are made up essentially of grains of quartz bound together by some cementing material. The cementing material may be silica, iron oxide, calcium carbonate, or clay; upon this basis the sandstones are divided in the same order into siliceous, ferruginous, calcareous, and argillaceous stones, although it not infrequently happens that more than one kind of cementing material may be present in the same stone. Beside the quartz grains and cementing material, other minerals are often found, as mica, pyrite, etc. Upon the nature and amount of the cementing material depends in a large measure the color, strength, and durability of the stone.

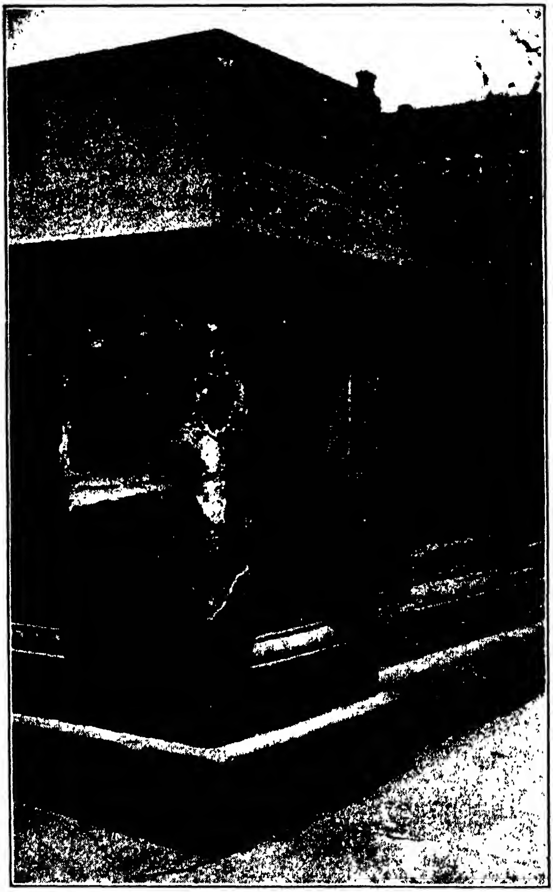

FIG. 75.—Weathered sandstone. Guard wall of bridge after 18 years' exposure

Colors.—The red and reddish-brown colors are due to the presence of ferric oxide, the yellow and yellowish brown to the presence of the same oxide in the hydrated condition. The faint-bluish or greenish tints are due to iron sulfide, iron carbonate, or more rarely to iron silicate in finely divided form. Carbonaceous material may cause a gray or black appearance.

Durability.—The durability of sandstones varies considerably. Stones with clay seams are liable to split with repeated thawing and freezing. Those containing mica scales along the bedding planes are liable to flake off, especially if the stone is set in the wall on edge.

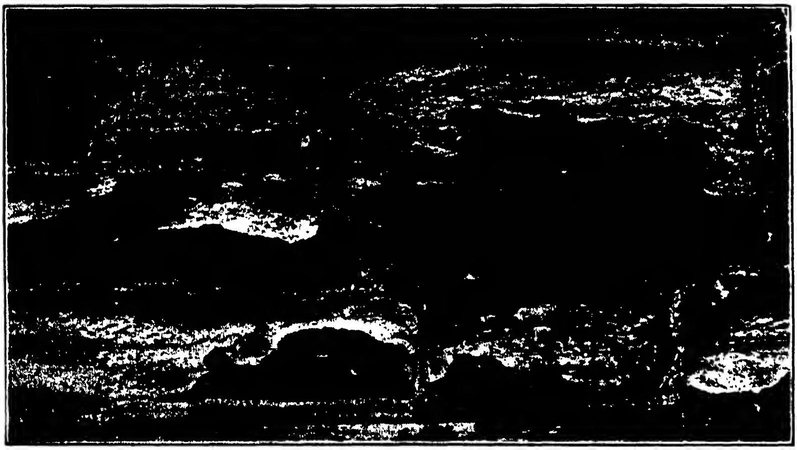

Fig. 76.—Weathered sandstone.

Of all varieties, the siliceous sandstone is most resistant to the action of the weather. If silica alone is present, however, they are frequently so hard that it is difficult to dress them. A good example of the siliceous type is the Berea sandstone of Ohio.

The ferruginous stones stand second in respect to durability. The "brownstones" of the eastern states are generally sandstones of this sort. They are of granitic origin and contain feldspar and mica in addition to the quartz and iron oxide. They are easy to dress but are not nearly so durable as the siliceous stones. In many cases they have shown very early failures. The early failure may have been due, however, to the presence of calcium carbonate in the cementing material.

The calcareous sandstones are generally light colored or gray and, although strong, are soft and easily worked. Because the calcium carbonate is leached out by the action of the carbon dioxide in the presence of water, they resist the action of the atmosphere very poorly.

The argillaceous sandstones are the least durable of all. They absorb water readily; thus they are susceptible to the action of frost. Being comparatively soft they are easily dressed.

Fig. 77.—Weathered sandstone. A corner of the same wall shown in Fig. 76. The stone has been softened to such an extent by weathering that a knife blade may be readily thrust into it.

Some sandstones contain little if any cementing material, but owe the strength they possess merely to the pressure to which they were subjected during formation. Certain varieties of such stones are used in the manufacture of grindstones and whetstones.[1] Since they do not contain much cementing material, they crumble slowly away, always presenting fresh sharp sur-

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[1] Merrill, *loc. cit.*, p. 125.

faces to be acted upon. In some cases, they possess sufficient cohesion to be used as building stones.

"Quarry Water."[1]—All sandstones, when freshly quarried, contain a certain amount of water. Although the presence of water causes them to be soft and easily worked, it renders them, on the other hand, very susceptible to injury if allowed to freeze when freshly quarried. Some quarries cannot be worked during the winter on this account. As the "quarry water" evaporates, the stone gains considerably in hardness and becomes more difficult to work. This has been explained on the basis of the assumption that in the freshly quarried stone a certain amount of the material exists in the dissolved state, which, as the water is evaporated, is deposited. The deposited material binds the grains more firmly together.

Limestones.—Limestones are stratified rocks consisting essentially of calcium carbonate ($CaCO_3$). They have been produced largely from deep-sea deposits of the calcareous remains of animal organisms. In some cases the shell formation of the individual organism is distinguishable. The different particles are cemented together by calcium carbonate deposited from solution. Pure calcium carbonate, as a mineral, is known as *calcite.* Limestone is not pure calcite, however. It contains usually iron oxide, silica, clay, and carbonaceous matter in varying quantities. With a sufficient quantity of silica, the limestone becomes a calcareous sandstone, with a sufficient quantity of clay, a calcareous shale. Magnesium carbonate is also usually present, replacing the calcium carbonate. The amount of this replacement may be considered to range from none at all to 100 per cent; in the latter case, the carbonate being entirely that of magnesium, the mineral is known as *magnesite.* When the two carbonates are present in molecular weight proportions ($CaCO_3 \cdot MgCO_3$) the rock is called *dolomite.* Formations of this sort contain 54.35 per cent of calcium carbonate and 45.65 per cent of magnesium carbonate. The term *limestone* is usually restricted to those rocks that contain less magnesium carbonate than the dolomite; those that contain more are known as impure magnesites.

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[1] *Ibid.*, p. 126.

Limestones may be white, gray, blue, or black, depending upon the impurities present. Their hardness is very variable. Some are so soft that they may be easily cut with a saw or knife; others are a great deal harder. Although both limestones and dolomites are moderately durable, they are not to be compared with good sandstones and granites in this respect. They are dissolved by the carbonic acid of natural waters, although dolomite does not yield so readily to this solvent action as the limestone.

Marbles.—In accordance with strict geologic definition, marbles are those highly crystalline formations that have been developed from limestones or dolomites by heat and pressure; they are, therefore, metamorphic rocks. The original limestone or dolomite, which was of ordinary type as far as composition or structure was concerned, was converted into a semifluid mass by the intense heat and pressure; during cooling, it assumed the crystalline state. The pressure in this case was sufficient to prevent the evolution of the carbon dioxide which would have occurred at this temperature under ordinary conditions.

According to the commercial conception, the term marble has a much broader meaning than the preceding definition shows. It includes any limestone, crystalline or not, that is capable of taking a high polish, and which when polished will show pleasing color effects. Eckel says[1] that according to the commercial classification there are three varieties of marble:

1. Highly crystalline marbles, showing distinct crystalline structure and fracture. These are usually white, though gray, black, or other markings may be present scattered over a white ground.
2. Subcrystalline or fossiliferous marbles, in which crystalline structure is rarely very noticeable, the value depending rather on color effect than upon texture.
3. Onyx marbles, translucent rocks, showing color banding, due to the fact that they were formed layer after layer by chemical deposition from cave or spring waters.

In chemical composition, marble differs in scarcely any respect from ordinary limestone. It is likely to contain the same impurities as limestone, two or three of which are objectionable. Mica, if abundant and present in bands or patches, interferes

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[1] "Building Stones and Clays," p. 166.

with the polishing of the stone; also since it weathers readily it may leave the surface pitted. This weathering is not likely to occur, of course, if the marble is used for interior work. Iron pyrite is quite objectionable. It oxidizes readily with the formation of the reddish, basic ferric sulfate and sulfuric acid (page 367). The latter, of course, exerts a solvent action on the stone.

Color of Marbles.—Marbles are exceedingly variable in color; some are snow white and others vary from gray to black. In addition, they may be colored red, pink, yellow, green, or brown; these shades are due chiefly to iron oxide. The gray and black colors are due to carbonaceous matter. The coloring matter may be uniformly distributed or present in patches which produces a mottled appearance.

Some ornamental marbles show that which is termed a *brecciated structure.* Such marbles are made up of angular pieces of crushed rock, with the spaces between filled with mineral matter afterward deposited.

Durability.—The weather-resisting properties of the marbles is about equal to that of the limestones, although those having the brecciated structure and those containing considerable mica are less durable.

CHAPTER X

LIME AND GYPSUM PRODUCTS

Lime Products

Lime is the oxide of calcium (CaO). Although in non-technical language the term "lime" is somewhat indiscriminately applied to a variety of calcium compounds, it properly refers to this one compound only. Frequently the terms "quicklime" and "caustic lime" are used to indicate more definitely this oxide. On a commercial scale, lime is obtained by calcining or "burning" limestone ($CaCO_3$). At the temperatures employed, the calcium carbonate dissociates into lime and carbon dioxide, which gas escapes. If the stone be pure calcium carbonate, the loss in weight resulting from the separation of the gas is equal to 44 per cent of the weight of the original stone. Commercial limes are not pure calcium oxide because limestones are not pure calcium carbonate.

Limestones.—Limestones belong to the class of sedimentary rocks. Such rocks are formed usually by deposition from water of material that has resulted from the decomposition of other formations. Limestones have been produced largely by deep-sea deposits of the calcareous remains of animal organisms. In some cases the individual organisms are plainly visible; they are merely cemented together by calcium carbonate deposited from solution. Although a pure limestone corresponds to the white mineral calcite $CaCO_3$, in ordinary limestones there are usually present varying amounts of magnesium carbonate, silica, iron oxide, clay, and carbonaceous matter. Frequently it happens that the calcium carbonate and magnesium carbonate are present in molecular weight proportions ($CaCO_3 \cdot MgCO_3$), which is equivalent to 54.35 per cent of the former and 45.65 per cent of the latter. Such rocks are called *dolomite.* Limestones are found that contain magnesium carbonate in any amount from

0.0 per cent to 45.65 per cent, but usually the amount is near either the upper or lower limit; the intermediate grades are comparatively rare.

Manufacture of Lime.—Lime is produced by calcining limestone in kilns. The temperatures employed may vary from 900 to 1200°C.; the resulting reaction is essentially:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$$

There are various types of kilns in use, but that which is generally employed is some form of shaft kiln. Rotary kilns, like those used in the Portland-cement industry, are used to some extent, but for such kilns the stone must be crushed. The shaft kilns are chiefly of the continuous type; the lime is drawn periodically from the bottom, while the charge is continuously introduced at the top. An older type is the intermittent kiln in which a charge is burned, allowed to cool, and then is drawn. This is, of course, less economical because of the heat wasted by cooling the kiln each time.

The shaft kilns differ in respect to the manner of heat application. In some of them the fuel is mixed with the charge, first a layer of coal or coke and then a layer of stone; these layers are then repeated until the kiln is filled. Fire is started at the bottom and works its way up. In this type the lime always contains the ashes of the fuel. In another type there is a separate fire box where the fuel is burned and the hot products of combustion only pass into the kiln. Lime produced in this type is, of course, not contaminated by the ashes. There are various modifications of these general types.

Physical Properties of Lime.—Lime is a non-crystalline substance; if pure, it is snow white. Often it may have a grayish, yellowish, or brownish color, due to the oxides of iron or manganese contained in the clay or other impurities in the stone.

Lime produced by burning a pure limestone has a specific gravity ranging from about 3.08 to 3.30. The density depends somewhat upon the kiln temperature. It approaches the higher limit as the kiln or calcining temperature increases. It is, of course, always more porous than the rock before it was calcined. Lime, as packed, weighs about 60 lb. per cubic foot.

Kinds of Lime.—As has been indicated elsewhere, aside from the 5 to 10 per cent of impurities, such as silica, alumina and iron oxide, commercial limes may contain from a trace to 44 per cent of magnesia. On the basis of the quantity of magnesia present, limes are divided into two classes: Those containing less than 5 per cent of magnesia are known as pure or high-calcium limes; those containing more than 5 per cent of magnesia are known as magnesian limes. The magnesian limes on the market, however, usually contain above 30 per cent of magnesia.[1] Because the properties of the two classes vary considerably, they will be discussed separately.

High-calcium limes contain generally from 90 to 95 per cent calcium oxide; the remainder consists of magnesia, alumina, iron oxide, silica, and a little carbon dioxide and water. High-calcium limes are generally desired for preparing building mortar because they slake readily, and because they swell considerably during slaking and thus produce a larger volume of paste.

A lime that contains less than 5 per cent of impurities such as silica, alumina, iron oxide, etc., is often called a "fat" or "rich" lime. Such limes slake exceptionally rapidly and produce more plastic mortars, and they are said to be "smoother" under the trowel than limes containing greater amounts of impurities, which are known as "lean" or "poor" limes.

Magnesian Limes.—By definition,[2] magnesian limes contain above 5 per cent of magnesia, but usually the commercial varieties contain above 30 per cent. The magnesian limes slake less rapidly than the high-calcium limes, develop less heat, and expand less in slaking. In mortars they do not possess as great early strength but develop greater ultimate strength than the high-calcium lime.[3] They are often considered superior to the high-calcium limes for finishing, but opinions vary as to this, and both kinds are used.

Slaking of Lime.—The slaking of lime is a process of hydration; the calcium oxide enters into chemical combination with water to form calcium hydroxide, as:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

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[1] Eckel, "Cements, Limes, and Plasters," p. 98.

[2] Eckel, *loc. cit.*, pp. 97 and 98.

[3] *Munic. Eng.*, **28**, 4–7, January, 1905.

This reaction is accompanied by the evolution of a great amount of heat, so that some of the water added may be converted into steam; the formation of steam is especially noticeable in the slaking of fat limes. It is important to consider this heat evolution with reference to the *fire danger*. According to the work of the Royal Saxon Mechanical-Technical Experiment Station,[1] it is easily possible for wood to be ignited by the heat evolved in slaking even poor or lean limes, for such limes, although poor in calcium oxide, may reach a temperature of 270 to 300°C.; at this point wood chars in air. High-grade or fat limes are still more dangerous, because in slaking, they can produce a temperature of 400° or over. It is not safe to ship or store lime in contact with wood, since water may accidentally come into contact with it.

Assuming the lime to be pure calcium oxide, during slaking the weight of water that must unite with it in order to convert it into the hydrated form is 32.1 per cent of the weight of the lime. Because the lime practically always contains inert impurities, however, somewhat less than this amount is theoretically required. On the other hand, some water is lost as steam; the amount varies with conditions. In mortar work, for which a stiff paste is required, about twice the theoretical quantity of water is employed. For best results, it is important that the proper amount of water be added at once, not in portions, and that it be distributed uniformly and quickly.

If the lime is wetted with enough water to start the hydration but not enough to complete it, the unhydrated portion becomes inert;[2] it is then described as "burnt." This condition may be brought about accidentally when partially slaked lumps of lime are pushed out of the water by the swelling of the mass beneath. The reason for the inertness produced by these conditions is that the lime is heated until it approaches the temperature at which it becomes dehydrated while it is still only partially hydrated. The reaction then runs very slowly because the lime must lose heat before the hydration can continue.[3] In the mean-

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[1] *Jour. Ind. Eng. Chem.*, **7**, 542, June, 1915.

[2] *U. S. Bur. Standards Tech. Paper* 16, p. 77.

[3] WHITMAN and DAVIS, "The Hydration of Lime," *Jour. Ind. Eng. Chem.*, **18**, 120, February, 1926.

time, the particles grow in size and the product is coarse and inferior.

If an insufficient amount of water is added in the beginning and then a further addition is made during the process, the slaked lime will be granular and lumpy. When properly slaked, the steam evolved by the heat of the reaction bursts the lumps and aids in the slaking. If water is added during the process, the evolution of steam is checked. Further, the added water causes a pasty coating of slaked lime to be formed on the surface of the lumps, which renders the entrance of water to the interior of the lumps difficult, if not impossible.[1]

The bulk of the lime increases from 2½ to 3½ times during slaking; the more rapid the slaking the more the volume increases. Impure calcium limes, magnesian, and dolomitic limes slake only about half as fast as the high-calcium limes and expand far less.

It has been observed, also, that the degree of plasticity is much increased by rapid slaking; this is due to the fact that rapid slaking produces a *colloidal hydrate,* whereas slow slaking tends to produce the crystalline condition. The colloidal hydrate is produced very rapidly, but crystals require much more time to form. When the hydrated product is crystalline, the volume is less, the mass is granular and gritty, and the sand-carrying capacity is much reduced. The slaking reaction may be hastened by using warm water or by covering the slaking lime with a tarpaulin.

From the results of their researches, Whitman and Davis conclude[2] that the best results in slaking lime are obtained with a moderate excess of water and a reasonably high temperature, because under these conditions the rate of hydration is rapid as compared to the rate of growth of the particles. They found that hydration with only a slight excess of water, or with steam, yielded a relatively coarse product. Agitation was found to be beneficial because it prevents the formation of tight clusters of crystals.

Magnesian limes are slow in slaking, and as has just been explained, slow slaking tends to produce a less plastic product. On this account magnesian limes can be mixed with less sand for

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[1] Baker, "A Treatise on Masonry Construction," p. 105.

[2] *Op. cit.*

use. Aside from its effect in lowering plasticity, magnesia is said to have a very marked effect in increasing the ease and smoothness with which the paste may be spread with a trowel. Magnesian limes will slake readily only if especial care is taken to burn them at low temperatures.

The *porosity* of the lime, which results largely from the evolution of the carbon-dioxide gas from the stone, is of importance in respect to the rate of slaking, since it allows the water to enter more readily and the slaking to proceed more rapidly. All limes are not equally porous. High burning temperatures make denser limes. This is at least partly due to the fact that high temperatures cause some of the lime to unite chemically with the impurities present; the reaction produces silicates and aluminates of lime. These compounds are much more readily fusible than the lime and, as they soften, close the pores of the stone. The fusion is especially noticeable on the outside of the lumps, where a more or less vitreous coating may form, particularly if the temperature exceeds 1200°C. to any extent. Limes in which the calcium oxide has reacted with the impurities are said to be "overburned." This overburning is, of course, more likely to occur if the impurities are high. It is very difficult to overburn a pure lime because calcium oxide is a very refractory substance.

If mortar is made of lime that for any reason has been incompletely slaked, it is very likely to be defective, because the lime is almost certain to slake eventually and then blisters, or more serious faults will show in the wall or other structure where the mortar is used.

Common Method of Slaking Lime.—In the ordinary practice of slaking, the lumps of lime are placed, usually in a water-tight box, in a layer from 6 to 8 in. deep. A quantity of water equal to 2, or 2½ times the actual volume of the lime (which is an amount a little greater than two-thirds the weight) is then poured on. Although this amount of water is about twice that theoretically required, the excess tends to insure thorough slaking. If the slaking is properly carried out, the slaked product will be in the form of a stiff paste. One barrel of lime (230 lb.) will make about 8 cu. ft. of such paste, which is frequently known as "lime putty." The paste may be kept almost indefinitely if it is kept from drying out. It is sometimes stored in casks or in the wide shallow boxes in which it is slaked. It cannot harden under water. The lime should be slaked at least 1 day prior to its use, in order that it may be more certain that the slaking is complete.

Fine Lime and Lump Lime.—If the lime has been made from broken rock it will generally be in lump form; the occurrence of powder or dust in this case indicates that the lime is old and has been poorly stored. It has already partly slaked by absorbing moisture from the air. Moreover, when thus slaked due to long exposure, it takes up carbon dioxide from the atmosphere and becomes more or less inert depending upon the extent to which this reaction has proceeded. Such lime is known as *air-slaked lime.* When completely air slaked it is useless for the purposes to which lime is usually put in construction work.

On the other hand, limes that are made from shells, soft chalk, marl, highly crystalline marbles, shelly limestones or limestones that contain much water or organic matter will usually come from the kiln in a more or less finely divided state. Fineness is no indication of air slaking in such cases. The product of the rotary kiln also is fine. Moreover, some manufacturers grind their product because it will keep better. Because air has such ready access to all parts of it, to preserve lump lime for any extended period, especially if it is in loose bulk, is very difficult. If it is contained in casks or barrels, stored in a dry place, and kept covered with tarred paper, canvas, or a tarpaulin, it may be preserved for some time. In the case of ground lime, by the slaking of the top layer, a coating is formed that protects the lime underneath.

When properly burned and fresh from the kiln, lime should be free from water and should not contain more than 0.5 per cent of carbon dioxide.

Hydrated Lime.—This lime is a somewhat recent commercial product prepared to avoid the unsatisfactory results that attend the old method of slaking lime in the mortar box by unskilled labor. It is essentially calcium hydroxide, *i.e.,* quicklime that has been slaked; it is usually prepared by the manufacturer of the lime. The process consists of first crushing the lime, if it is in lumps, to pieces not greater than 1 in. in diameter; then this crushed lime is agitated in one way or another with the proper amount of water. After slaking, the now hydrated lime is sieved and the coarse particles discarded, or in some cases ground and mixed with the hydrated lime, which is a fine, dry, white powder. Its specific gravity varies from about 2.15 to 2.24. It may be used for practically any purpose in place of lump lime.

If properly made and stored, hydrated lime will contain less than 1 per cent of carbon dioxide; this is equivalent to 2.27 per cent of carbonated lime. The determination of the carbon dioxide may be used as a test for the quality of the hydrated lime.

Emley[1] says that the chief advantages to the consumer of hydrated lime are as follows: It can be handled more easily because it is in powder form. It will keep better than lump lime for the reasons explained in the preceding discussion of fine lime and lump lime, although there is no evidence to show that it will keep better than quicklime of an equal degree of fineness. It is necessary only to soak it with water to prepare it for use, which saves time and labor, and eliminates any danger of loss of lime due to unskilled slaking. The hydrated lime should contain less refuse than lump lime because the inert material, such as produced by over- or underburning, can be screened out after hydrating. On the other hand, hydrated lime contains from 15 to 25 per cent water on which the consumer must pay the freight.

There is another objection, according to Mills,[2] who states that paste made of hydrated lime is very noticeably non-plastic, and low in sand-carrying capacity. Mills says further that some hydrates are so lacking in colloidal properties that they are absolutely gritty, and on this account are not generally suitable for plastering or finishing.

"Alca" Lime.[3]—The term "Alca" is derived by combining the symbols for aluminum and calcium; this term is used as a trade name to apply to a hydrated lime that has been specially prepared in order that it may be more plastic and suitable for wall plaster. It is made by incorporating with the hydrated lime about 15 per cent of calcium aluminate derived from a special blast-furnace slag. The product prepared in this way has been

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[1] *U. S. Bur. Standards Tech. Paper* 16, p. 18.

[2] "Materials of Construction," p. 55.

[3] *Ibid.*, p. 56.

found to have increased sand-carrying capacity, to be more easily applied with a trowel, and to set more rapidly than the ordinary limes. It is thought that the initial setting is dependent upon the hydration of the calcium aluminate, which will be described later in the discussion of the setting of Portland cement. In using the Alca lime, Mills says that best results are obtained if the sand and lime are first thoroughly mixed dry and then wet with about 16 per cent of water and allowed to stand for not less than 1 hr. before being used. If it can be allowed to stand for a longer time, overnight for example, it will be improved in plasticity and working qualities.

Hydraulic Limes.—As was stated in the discussion of overburned lean limes, if some of the calcium oxide reacts with the silica and alumina during burning, then the lime will have more or less well-defined hydraulic properties. The reaction mentioned produces calcium silicates and aluminates similar to those found in Portland cement.

In the manufacture of hydraulic limes proper, limestones are used that contain from about 10 to 17 per cent of impurities, chiefly silica, alumina, and iron oxide; sometimes the limestone may be of the magnesian variety. Higher burning temperatures are employed than in the manufacture of ordinary lime in order that the calcium oxide may react with the silica and alumina. Although hydraulic limes are not manufactured in the United States, considerable quantities are imported, especially from France.

Hydraulic limes contain enough free lime that they still slake in a manner similar to ordinary lime, only much more slowly. In slaking, care must be taken to use just the right amount of water; if an excess is employed, the lime will harden. Although some hydraulic limes have only slight hydraulic properties, others harden very satisfactorily under water. They are, however, not much used for under-water work. They set too slowly to be substituted for Portland cement in ordinary construction.

Grappier cements are obtained by grinding the unhydrated cores left when slaking hydraulic limes. These cores may consist of either under- or overburned material. The value of the product depends upon the quantity of calcium silicate or aluminate contained in it. Like the hydraulic limes, grappier cements are not manufactured to any great extent in the United States but are imported from Europe.

Hydraulic limes and grappier cements are very white and do not stain the stone, for example, in marble work, as does Portland cement. Their non-staining quality is due to their low content of iron oxide and soluble salts.

Lime-sand Mortar.—The lime paste alone is not suitable for use as a mortar. If the paste is allowed to dry it shrinks greatly and cracks. In practice, sand is always added to it; the proportions are about 2½ or 3 of sand to 1 of paste. The addition of this inert material almost eliminates shrinking and prevents the cracking. Also, the addition of sand makes the mass more porous, so that the penetration of the carbon dioxide, necessary for the hardening of the mortar, is facilitated. It is important that the sand and paste should be mixed in about the proportions indicated, since with these amounts the paste will just fill the voids in the sand. If much more sand than this is used the mortar will be weak because it will be too porous. If less is used, the resultant excess of paste will cause a shrinkage when drying. It is better to have too much rather than too little sand; a slight sacrifice of strength is immaterial, but shrinkage will cause cracks that are immediately noticeable.

If sands of different degrees of coarseness are mixed, the voids between the sand grains will be lessened; then a smaller proportion of paste may be used without the mortar becoming too porous.

The working qualities also are affected by the amount of sand. If too much sand is used, the mortar will be "short"; if too little, it will be sticky.

Hardening of Lime-sand Mortar.—Compared to the hardening of Portland cement, the hardening of lime-sand mortar is a very simple process. The initial "set" is due to the evaporation of the water. If used with porous bricks it may set very quickly because much of the water is taken up by the brick.

Not until after the mortar has become practically dry does the real hardening begin. The hardening is due to the absorption of carbon dioxide from the air; the following reaction occurs:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The calcium carbonate so produced crystallizes about the grains of sand and holds them together. The depth of the carbonate formed is from 0.10 to 0.12 in. the first year, but it is slower after that. The surface layer becomes more impervious to the passage of the necessary carbon dioxide gas as the crystals of the carbonate form in the pores. The inner portions of thick walls often show the presence of calcium hydroxide after a century or two. On this account lime-sand mortar is not suitable for use in extremely thick walls. After about 25 years, however, the hardening has been completed in ordinary walls.

Because it cannot set when air is excluded, lime-sand mortar cannot be used for structures under water, nor in soil that is constantly wet. And because it never acquires any great amount of strength it should not be used where great strength is required.

GYPSUM PRODUCTS

Gypsum.—The mineral gypsum, from which various kinds of commercial plasters are prepared, is the hydrated calcium sulfate $CaSO_4 \cdot 2H_2O$. It frequently occurs in the massive form known as *rock gypsum*, or it may be found as a granular variety known as *gypsum sand.* Sometimes it occurs relatively pure, but generally it contains a few per cent of impurities such as silica, alumina, iron oxide, and the carbonates of calcium and magnesium. An earthy variety known as *gypsum earth* or *gypsite* may contain 50 per cent or more of such impurities, especially silica and the carbonates mentioned. Pure gypsum is white; when crystalline, it is more or less translucent. It is so soft that it can be readily scratched with the thumbnail. *Alabaster* is a pure variety of gypsum used to some extent for statuary. A crystalline variety, practically colorless and transparent, is known as *selenite.* The selenite crystals are frequently laminated, splitting into thin leaves like mica, but unlike mica the leaves are inelastic.

Preparation of Gypsum Plasters.—The manufacture of gypsum plasters from native gypsum is based on a process of dehydration. As described by Stone,[1] when the dihydrate is stirred and heated

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[1] "Gypsum Products," *U. S. Bur. Mines Tech. Paper* 155, p. 17, July, 1917.

with a gradually increasing temperature, the water of crystallization begins to be evolved rapidly at about 110°C. The escape of the resulting steam causes an appearance of "boiling" in the powdered mass. This agitation continues until a temperature of about 130°C. is reached, when the boiling largely ceases and the mass settles down to about 86 to 90 per cent of its original volume. This quiet stage is called the first settle, and indicates that most of the dihydrate has been converted into the hemihydrate.

If the heating is continued beyond this point, the dehydration is resumed and a second boiling, more vigorous than the first, is noted. When the mass quiets down again, the second settle is said to have been reached. Stone says that at this stage all of the dihydrate has been converted into the hemihydrate, and some of it has been completely dehydrated to form the soluble anhydrite. This degree of dehydration reduces the bulk of the plaster to about 82 to 85 per cent of the original volume of the gypsum.

Depending upon the variety of plaster desired, dehydration is discontinued either before or after the second settle. In making wall plaster, for example, it is the common practice according to Stone, to stop the calcination after the first settle at temperatures ranging between about 155 and 175°C. Depending upon the extent of the calcination, plaster of Paris, which is commonly called stucco in the trade, is spoken of as first- or second-settle stucco.

Setting and Hardening of Gypsum Plasters.—The setting of the gypsum plasters depends upon the fact that the hemihydrate and the soluble form of the anhydrite are more soluble in water than the dihydrate. The hemihydrate dissolves and combines with water to form the dihydrate, which precipitates from the solution to form a solid mass of fine, interlaced crystals. The equation for the hydration may be represented as follows:

$$CaSO_4 \cdot \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

As a result of the hydration and crystallization, the plaster sets and hardens.

In speaking of relationship between the calcination of gypsum and the setting properties of the plaster, Eckel says[1] that about

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[1] "Mineral Resources of the United States," p. 1111, 1905.

205°C. is a critical temperature in the calcining process. If heated much above this temperature, practically all of the combined water is driven off; the product is then known as "hard-burned" or "dead-burned" plaster. Although the plaster is called "dead-burned" and sometimes even "anhydrous," it is generally understood that it is not absolutely so; slight traces of hydrated crystals still remain which serve as nuclei about which other crystals of hydrated sulfate may form. All plasters that result from calcination at these elevated temperatures are very slow in hydrating; the rate is dependent upon the intensity and prolongation of the heating during manufacture and upon the degree of fineness of the gypsum. For practical purposes, however, the gypsum is calcined under such conditions that the setting and hardening are not prohibited altogether, but only greatly prolonged; hydration then requires hours or days, instead of minutes as with plaster of Paris. When finally formed, the hydrated product resulting from these slowly setting plasters is both harder and stronger than that produced by the ordinary plaster of Paris.

Control of Rate of Set.—Because plasters that consist chiefly of the hemihydrate set so quickly that sufficient time is not allowed for mixing and placing, a retarder must be added to delay the set. Materials employed for this purpose are such as flour, glue, and similar organic, colloidal substances. The added organic materials act as protective colloids. They form a film about the calcium-sulfate particles and impede the hydration, with the result that the crystals do not so readily grow together and cohere. According to Stone[1] the retarder usually employed in the United States and Canada is made by treating low grades of hair with caustic soda and lime. The caustic soda converts the hair into a glue-like mass, and the lime acts as a drier of the solution. Native impurities, such as clay, present in the gypsite from which some plasters are made, also act as protective colloids and, therefore, as retarding agents.

Classification of Plasters.—On the basis of the degree of dehydration, the gypsum products may be divided into two major classes; these two classes, in turn, may be subdivided into two subclasses on the basis of whether or not the product is pure or

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[1] *Loc. cit.*, p. 27.

impure. The following classification is essentially as given by Eckel:[1]

A. Produced by the *incomplete* dehydration of gypsum, the temperature employed not exceeding 205°C.

1. Produced by calcining a *pure* gypsum; no foreign material is added either before or after calcining. *Plaster of Paris.*

2. Produced by calcining a gypsum containing certain natural *impurities*, or by adding to a calcined, pure gypsum certain materials that serve to retard the setting of the product. *Cement Plaster.*

B. Produced by the *complete* dehydration of gypsum, the calcination being carried out at temperatures exceeding 205°C.

1. Produced by calcining a *pure* gypsum. *Flooring Plaster.*

2. Produced by calcining at red heat, or above, gypsum to which certain substances (usually alum or borax) have been added. *Hard-finish Plaster.*

In commercial classification, the term *calcined plaster* is used to designate a burned plaster to which nothing has been added. Calcined plaster may include both plaster of Paris and cement plaster; it is the latter if the original gypsum used was impure.

Plaster of Paris.—As has been indicated in the preceding classification, plaster of Paris is prepared by calcining a pure gypsum to the half-hydrate, without the addition of foreign material. It is usually ground to a fineness such that 80 to 90 per cent will pass a 100-mesh sieve. It sets very rapidly, generally in 5 to 15 min.

Stucco is practically the same as plaster of Paris, since it is made from fairly pure gypsum, but usually it is not so finely ground as plaster of Paris.[2]

Cement plasters are made in a manner similar to plaster of Paris but they set more slowly because of the presence of retarding agents. The plaster contains a small amount of hair, from 3 to 5 lb. per ton, which has been added to increase its strength and cohesiveness. By some manufacturers, sisal, or manila fiber, is

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[1] "Mineral Resources of the United States," p. 1112, U. S. Geol. Survey, 1905.

[2] The term "stucco" is used also in a somewhat different sense to indicate a mortar finish on walls. The material used for such work consists essentially of a mortar made of calcined plaster and sand to which usually has been added a certain amount of lime, fiber, and sometimes coloring matter.

employed instead of hair. Cement plaster is used commonly for the base coat, and the hair or other fiber prevents wastage that excessive dropping of plaster, back of the lath, would cause.

Since the advent of metal lath, the use of calcined gypsum in wall plasters has met with some objection. Calcium sulfate is a compound that results from the reaction of a strong acid with a relatively weak base; in the presence of water, it dissolves slightly and ionizes to produce an acid reaction. On this account, with damp walls, it causes the lath on which it is used to corrode. On the other hand, Portland cement and calcium aluminate, which also set rather rapidly by hydration, have an alkaline reaction and inhibit the corrosion of the metal.

Unless the plaster is made from the earthy variety of gypsum, and therefore already contains clay, it is necessary to add clay or hydrated lime to increase the plasticity and sand-carrying capacity. For this purpose about 15 per cent of hydrated lime is usually added, which, besides increasing the working qualities of the mass, corrects its tendency to bring about corrosion.

Cement plaster, as marketed, contains no sand, and 2 or 3 parts of sand must be added in preparing it for use. The setting time varies from 1 to 2 hr.

Staff.—For temporary buildings, such as are erected for exhibitions, a gypsum plaster called "staff" is employed. It has the same general character as plaster of Paris, but contains fiber of some sort to reinforce and toughen it when set.

Wood-fiber Plaster.—Like cement plaster, wood-fiber plaster also contains an agent to retard the set, but instead of hair, about 50 lb. of wood fiber per ton of plaster is employed as a binder. It is designed to be used generally without sand, and finds application where lightness of weight, and heat or sound insulation are important. The wood fiber used in the plaster is obtained from non-staining woods, such as cottonwood or basswood.

Gypsum Plaster Board.—Plaster board is a composite material made up of alternate layers of fibrous material, such as wool felt or tough paper, and gypsum plaster. The number of plys varies according to the type of construction for which it is used. During the setting and hardening of the plaster between the sheets of paper or felt, the crystals of the dihydrate that are formed, penetrate and interlock with the fibrous layers and bind them together.

Flooring plasters differ from the preceding forms in that they are calcined at such temperatures that they are practically anhydrous. They set very slowly and require very fine grinding, but ultimately they develop great strength and hardness. Eckel[1] says that these plasters are manufactured and used on a fairly large scale in certain European countries, but have not been used in the United States.

Hard-finish Plasters.—Like the flooring plasters, these plasters are practically anhydrous. They have, however, been given additional treatment to that received by the flooring plasters. After a preliminary burning at a red heat, the calcined product is dipped into a solution of alum or other salt, as borax, and then is burned again. This salt treatment aids in increasing the hardness. After the final burning, the product is very finely ground. It is necessary to use a very pure gypsum, since even a trace of iron oxide would detract from the necessary whiteness. Representatives of these plasters are known as "Keene's Cement" and "Parian Cement." They are manufactured in the United States and a considerable amount is imported.

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[1] "Cements, Limes, and Plasters," p. 75.

CHAPTER XI

PORTLAND AND OTHER CEMENTS; CONCRETE

PORTLAND CEMENT

Portland cement is a finely ground mixture of calcium compounds capable of setting and hardening by chemical combination with water; the main essential ingredients are lime, silica, and alumina, which are combined to form the silicates and aluminates of lime.

Historical.—Some knowledge of cements similar to Portland, at least in respect to the fact that they possessed the property of setting under water, was possessed by the Romans and recorded in their literature, but the wide usefulness of such materials seems not to have been appreciated for a great many centuries. Perhaps the first great impetus given to the development of the hydraulic cements was that contributed by Smeaton, who in 1756 was assigned the task of erecting a new lighthouse on Eddystone Rock after the old wooden structure had been destroyed. By experimenting he found that the best mortar for work under water consisted of that made from lime produced by burning limestone that contained considerable clayey matter. In taking the stone from the quarry, however, Smeaton selected only those layers that had been shown by test to burn to a lime that would slake with water. It did not, apparently, occur to him to grind the unslakable portions. Had he done so, he would have produced a cementing material of much more highly developed hydraulic properties than that which he used.

About 50 years after Smeaton's contribution, Vicat, a French chemist, showed that it was not necessary to depend upon rock in which the lime and clay occurred coincidently, but that suitable mixtures could be prepared artificially. Vicat produced a hydraulic cement by burning finely pulverized chalk and clay after he had mixed them in the form of a paste.

The first patent taken out for the making of a Portland cement was that issued in 1824 to Aspdin, a Yorkshire bricklayer, who heated finely pulverized chalk, or road dust from limestone roads, with the clayey mud of the River Medway. Because of a certain resemblance, which in reality was slight,[1] between his product when set and a well-known limestone quarried near Portland in Dorsetshire on the southern coast of England and extensively used for building under the name of Portland stone, he named his product "Portland cement." This name has been almost universally adopted.

Although patented in 1824, Portland cement was not used in England to any extent until 1859. In the United States, it was first manufactured in the year 1875 at Coplay, Pa.

Materials.—Portland cement is made by fusing together two materials, one rich in lime, as limestone, marl, or chalk, and one rich in silica and alumina, as clay, shale, slate, or blast-furnace slag; the former are known generically as calcareous and the latter as argillaceous materials. In the Lehigh district of Pennsylvania is found a certain clayey limestone that contains the calcareous and argillaceous materials in almost the right proportion; it is technically known as "cement rock." If it contains too much lime, clay is added; if too much clay, lime is added. A large proportion of the cement produced in the United States is made from this rock. A considerable quantity also is made from a mixture of pure limestone and clay or shale. In some of the central states cement is made by combining clay with marl, an amorphous calcium carbonate containing much water and organic matter. Portland cement is produced also from a mixture of blast-furnace slag and limestone.

Manufacture.—Portland cement may be manufactured by either the wet or the dry process. The differences between these methods are mainly in the treatment of the raw materials.

In the dry process, the calcareous and argillaceous materials are coarsely crushed and are dried in inclined rotating cylinders, after which they are held in storage bins until analyzed. From these bins, the materials are drawn and mixed in proportions indicated by the analyses. The mixture is then ground in suitable mills to such a degree of fineness that at least 90 per

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[1] Eckel, "Cements, Limes, and Plasters," p. 294.

cent will pass through a 100-mesh sieve. The grinding also produces an intimate mixing of the materials. The mixture is now ready for the kiln in which it is burned.

In the wet process, the materials are crushed and are mixed in the presence of water, and are ground in the wet condition to a sludge or slurry. After grinding, the slurry, which contains 35 to 40 per cent of water, is stored in tanks. This practice allows corrections to be made in the mixture before burning, with the result that a more uniform product may be obtained. The slurry is fed directly, without drying, into the kiln where it is burned. This saves the cost of the equipment and fuel required for the separate drying operation, but the wet condition of the charge lessens the output of the kiln. With very long kilns (200 ft. or more), the diminution of output becomes less apparent; the charge is dried by the hot gases at the upper end of the kiln.

Eckel[1] says that the wet process is indicated in localities where the raw materials are either irregular in composition, or are naturally wet or are difficult to dry, as marls, chalks, and some clays; but that where the raw materials are naturally dry, or are easy to dry, and are at the same time regular in composition, the dry process is the more economical of the two. About 60 per cent of the cement now manufactured in the United States is made by the dry process, but the wet process has been gaining gradually and may ultimately pass the dry process in tonnage production.

In both the wet and dry processes, the finely ground mixture is burned in a rotary kiln. A rotary kiln is a sheet-steel, brick-lined cylinder, which may vary from 60 to 250 ft. or more in length, and from 5 to 15 ft. in diameter. It is inclined at an angle of about 15 deg. to the horizontal, and is caused to rotate at the rate of one turn or half-turn per minute. The material to be burned is fed in at the upper end, and gradually works through the kiln. The temperature within the kiln may range from 1450 to 1600°C. The heat is generated usually by burning powdered coal, which is blown in at the lower end. Also oil and gas are sometimes used. In passing through the kiln the mixture is heated to the point of incipient fusion and leaves the lower end in the form of small lumps known as "clinker." After cooling,

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[1] "Cements, Limes, and Plasters," 3d ed., p. 391.

which may be accomplished by allowing it to lie in piles or by passing it through mechanical cooling devices, the clinker is hard, glassy, and of a blackish color. When cooled it is ground so that at least 78 per cent will pass a 200-mesh sieve.

Since ground clinker alone would set too rapidly, it is necessary to add a retarding agent. This may consist of gypsum, plaster of Paris, or anhydrous calcium sulfate, but because it is cheaper, gypsum is the form usually employed. The quantity added amounts to 2 or 3 per cent of the weight of the clinker. Since the grinding process brings about thorough mixing, the addition is usually made before the clinker is ground. After grinding, the cement is prepared for shipment.

Composition.—As has been said before, Portland cements consist chiefly of lime, silica, and alumina. As given by Meade[1] the cements of good quality usually fall within the following limits of composition:

	Limits, Per Cent	Average, Per Cent
Lime	60.0 to 64 5	62.0
Silica	20.0 to 24.0	22.0
Alumina	5 0 to 9.0	7.5
Magnesia	1.0 to 4.0	2.5
Iron oxide	2.0 to 4 0	2.5
Sulfur trioxide	1 0 to 1.75	1.5

Since iron oxide occurs in nearly all clays and shales, it is found in all ordinary Portland cements. Cements that contain no iron oxide are usually white.

Experience has shown that the ratio between the percentage of lime and the combined percentages of silica, alumina, and iron oxide should fall within rather well-defined limits. Michaelis[2] says that the ratio of lime to the three acid anhydrides mentioned should be about 2 on an average, or should not fall below 1.8 or go above 2.2, as:

$$\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} = 1.8 \text{ to } 2.2$$

Objection has been raised to this statement on the ground that it is not correct to assume that lime manifests a tendency to combine with silica, alumina, and iron oxide equally.

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[1] ROGERS AND AUBERT, "Industrial Chemistry," p. 269.

[2] *Cement Eng. News*, August, 1900.

Le Chatelier and others[1] have shown that in ordinary practice the most basic silicate of constant volume contains 2.8 parts by weight of lime to 1 of silica, and that the most basic aluminate contains 1.1 part of lime to 1 of alumina. On this basis, the following formula has been suggested:

$$CaO = 2.8SiO_2 + 1.1Al_2O_3$$

Others who have studied the subject, offer other expressions to indicate the ratios that should be maintained. Although the suggested values differ somewhat, this fact does not detract from the truth of the statement that in order to secure a satisfactory cement, it is important to control very carefully the relative amounts of these anhydrides in the mixture.

The ratio between the percentages of silica and alumina should be as follows:

$$\frac{SiO_2}{Al_2O_3} = 2.5 \text{ to } 4$$

If too much lime is present, the cement will expand and crack during setting; it is then described as "unsound." If too little lime is present, the cement may "set" too quickly. Cements containing high percentages of alumina also set rapidly. High-silica cements harden very slowly and have, therefore, a low strength at first, because of this fact. Magnesia is generally considered harmful if the amount exceeds 5 per cent. Its effect is not exactly understood, but it is thought to produce disintegration by the expansion resulting from the formation of magnesium hydroxide [$Mg(OH)_2$]. Cements should not contain more than 2.00 per cent of SO_3; this is the equivalent of 3.4 per cent of calcium sulfate.

Components.—Aluminum oxide is an amphoteric substance; that is to say, it may act as either an acid or basic anhydride. In clay, it takes the part of a base, but when the clay is mixed with lime, and the mixture is heated to incipient fusion in the cement kiln, the alumina functions as an acid. Investigations have shown that at high temperatures lime can combine with alumina only in the molecular-weight proportions[2] shown by the

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[1] BOGUE, "A Digest of the Literature on the Constitution of Portland Cement Clinker," p. 22.

[2] *U. S. Bur. Standards Res. Paper* 34, p. 952.

four following formulas, which have been arranged in the order of decreasing basicity:

$$(CaO)_3{\cdot}Al_2O_3,\ (CaO)_5{\cdot}(Al_2O_3)_3,$$
$$CaO{\cdot}Al_2O_3,\ (CaO)_3{\cdot}(Al_2O_3)_5$$

The first member of this series, the tricalcium aluminate, appears to be the only aluminate that occurs in ordinary Portland cement, of which it comprises from 15 to 20 per cent. The monocalcium and 3:5 aluminates are found in the early-hardening, high-alumina cements, which will be described later. The other important components of cement of the usual Portland type are tricalcium silicate [$(CaO)_3{\cdot}SiO_2$], and the beta form of dicalcium silicate [$(CaO)_2{\cdot}SiO_2$]. The last-named is the chief constituent.[1] In brief, then, disregarding the magnesia, iron oxide, and sulfur trioxide, the first two of which are accidental and unnecessary, it may be said that the essential components of a normal Portland cement are tricalcium aluminate, and the tri- and di-calcium silicates.

By employing petrographic methods, Tornebohm[2] identified four crystalline constituents and an isotropic, colorless glass, which he stated practically always occurred in Portland-cement clinker. The crystalline substances he named *alite*, *belite*, *celite*, and *felite*. About 7 years later, Richardson,[3] in working on the constitution of Portland-cement clinker, concluded that alite was a solid solution composed of 1 part of tricalcium aluminate dissolved in 6 parts of tricalcium silicate, and that celite consisted of the dicalcium aluminate dissolved in the dicalcium silicate in the 1:6 ratio. He concluded, further, that the relative proportions of the alite and celite in a cement depended upon the basicity of the mixture and the ratio of silica to alumina. Campbell and White[4] also offer evidence in favor of the solid-solution theory of Portland-cement clinker, but from their work they conclude that alite consists of a solid solution of lime and some calcium aluminate and ferrite in dicalcium silicate, while celite consists essentially of a calcium aluminate.

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[1] *U. S. Bur. Standards Tech. Paper* 43, p. 63.

[2] *Tonind.-Ztg.*, p. 1148, 1897.

[3] *Cement*, **4**, 276, 1903; and **5**, 40, 1904.

[4] *Jour. Amer. Chem. Soc.*, **28**, 1273, 1906.

A great many other investigators have worked upon the problem of the constitution of Portland-cement clinker, but because of lack of space, the results of their studies cannot be mentioned here. For a bibliography and summary of the work that has been done, the student is referred to Bogue's "Digest of the Literature on the Constitution of Portland Cement Clinker."[1]

The Setting and Hardening of Portland Cement.—Although the subject has been carefully studied, the changes that take place during the setting and hardening of Portland cement are only imperfectly known. It is understood, of course, that the setting and hardening depend upon the hydration of the cement compounds, and the processes of hydration and the composition of the hydrated products have, in general, been determined.

The explanation of the changes taking place during hydration is based on the early work of Le Chatelier,[2] who observed that when a cement is gaged with water, its tricalcium silicate is not hydrolyzed, but is hydrated in a manner similar to plaster of Paris, or in accordance with the following equation:

$$(CaO)_3{\cdot}Al_2O_3 + \text{water} \rightarrow (CaO)_3{\cdot}Al_2O_3{\cdot}12H_2O$$

Since the tricalcium aluminate is more readily active with water than the other components of the cement, it is generally considered that upon its hydration the initial setting of the cement depends. The evidence seems to show that the hydrated product appears first in the amorphous form, but very soon begins to crystallize with the formation of hexagonal needles and plates.[3]

The tricalcium silicate, which reacts next, undergoes hydrolysis as well as hydration. It splits up into amorphous hydrated monocalcium silicate, and hydrated lime, thus:

$$(CaO)_3{\cdot}SiO_2 + \text{water} \rightarrow CaO{\cdot}SiO_2{\cdot}2\tfrac{1}{2}H_2O + 2Ca(OH)_2$$

To the reaction represented by this equation is ascribed the hardening of the cement that takes place during about the first week. The amount of combined water taken up by these compounds seems to depend somewhat upon conditions, since other investigators who have examined the hydration products have

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[1] Portland Cement Association Fellowship, *U. S. Bur. Standards, Paper* 3.

[2] "Experimental Study on the Constitution of Hydraulic Mortars," 1887.

[3] KLEIN and PHILLIPS, *U. S. Bur. Standards Tech. Paper* 43, p. 10.

reported various numbers of molecules. Still this variation may be due to the differing degrees of drying to which the hydrated substances were subjected in preparing them for examination.[1]

The Colloidal Theory of Cement Hardening.[2]—The colloidal theory is but one of the theories that have been advanced to explain the setting and hardening of cements, but since colloidal chemistry has become more familiar, it has been quite generally accepted.

Before proceeding with the colloidal theory, it will be necessary to consider a few points concerning colloids in general. For this purpose the student is referred to page 579 of this text, where a brief discussion is given.

In discussing the colloidal theory of cement *hardening* it will be assumed that the processes of *hydration* are essentially as shown in the equations given by Le Chatelier. Further, according to this theory, the hydrated substances are produced in the colloidal condition. And it does not seem unreasonable to assume that such is the case. The microscope shows that the freshly hydrated aluminates and silicates are definitely noncrystalline, and that these amorphous substances do not commence to crystallize until 10 to 20 days have passed—long after the cement has become quite hard. Then, proceeding upon the assumption that the hydrated products are colloidal, the hardening can be explained in the following manner.

Since the hydration must begin at the surface, the grains become covered with a coating of colloidal gel, which possesses adhesive properties, and causes the grains to stick together. Because the gel is not very permeable to water, the centers of the grains may not become hydrated. They can become hydrated only as water can slowly diffuse through the colloidal coating.

At this stage, the cement is not hard. The thin coating of colloid that surrounds the grains contains absorbed water, *i.e.*,

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[1] Klein and Phillips, "The Hydration of Portland Cement," *U. S. Bur. Standards Tech. Paper* 43, pp. 17 and 51.

[2] For a more complete discussion of this theory, see Michaelis, "The Hardening Process of Hydraulic Cements," 1907; for general colloidal chemistry, see Taylor, "Chemistry of Colloids," Bancroft, "Applied Colloid Chemistry; General Theory," or Bogue, "The Theory and Application of Colloidal Behavior."

it is wet, soft, and jelly-like. The hardening of the cement depends upon the drying of this gel, just as in the familiar case of the glue jelly, which becomes very hard and strong as it dries out. In order that the cement gel may dry out, it is not necessary for the water to evaporate, although some water is usually lost in this way, when the cement hardens in air. Its *free* water may be taken up by the unhydrated centers of the grains and converted into *combined* water, in which condition it can no longer manifest itself as water, just as water of crystallization does not cause crystals containing it to appear wet, even though they may be more than half water by weight. The cement gel can dry out in this way even when under water. Water cannot pass between the grains (this does not refer to the pore spaces) since the colloidal coatings cohere, and it cannot readily pass through the colloid itself because it is not sufficiently permeable. Then, the centers of the grains, by continued hydration, use up the free water in the gel faster than it can be supplied from the outside, and the gel becomes dry and hard. Moreover, the cement gel is an irreversible colloid; it cannot be softened again by water absorption after it has become hard.

In accounting for the fact that the cement in hydrating does not become increased in volume, like a glue jelly for example, Michaelis[1] says that as the grains of the pulverized cement begin to hydrate they acquire the colloidal state and immediately stick together; this interferes with their individual expansion. Further, he has demonstrated[2] that if the cement is continuously agitated in water so that the particles are kept separated, they do swell and a flocculent, voluminous mass is produced. In the case cited by him, the swelled colloid formed by the agitation of equal parts by weight of Portland cement and slag cement with 40 times as much water, was allowed to harden under water for 5 years, and although it had contracted somewhat during hardening, it still possessed a volume from 15 to 20 times that of the original cement. In a similar manner, the author has obtained the increase shown in Fig. 78. Portland cement was gaged with sufficient water to make a paste of medium consistency. One portion was at once pressed into a small porcelain crucible of 6-cc.

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[1] *Loc. cit.*, p. 14.

[2] *Ibid.*, p. 21.

capacity, and allowed to harden, which produced the small block shown in the center of the illustration. Two other equal portions were continuously agitated for 6 hr. with 200 cc. of distilled water and were then filtered into Gooch crucibles. The filtering was carried out with suction, in order that the material might be compacted as much as possible. In this way the larger blocks were formed. When hardened and dried the bulk was equal to about 24 cc., which was four times the volume of the original paste.

Michaelis says further that a dough may be prepared by agitating cement in water, which may be handled like paper; slabs are formed of it by pressure, which when hardened resemble slate.

Fig. 78.—Showing increase in volume due to the swelling of the colloidal gel in Portland cement.

Rate of Hydration and Development of Strength.—The following summary of the hydration of Portland-cement compounds is given by Klein and Phillips of the U. S. Bureau of Standards.[1] A short time after the cement is gaged with water, hydrated tricalcium aluminate is produced in amorphous form and later crystallizes. At the same time sulfo-aluminate crystals ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot xH_2O$) are formed; these are produced by the reaction of the aluminate with the gypsum added to retard the setting. At this time also the low-burned and finely-ground lime is hydrated.

The next compound to react is the tricalcium silicate. Its hydration may begin within 24 hr. and generally is completed within 7 days.

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[1] "Hydration of Portland Cements," *Tech. Paper* 43, p. 63.

Between 7 and 28 days the amorphous aluminate commences to crystallize and the beta orthosilicate (dicalcium silicate) begins to hydrate. Although the latter is the chief constituent of American Portland cements it is the least reactive compound. The early strength (24 hr.) of cements is probably due to the hydration of free lime and the aluminates. The increase of strength between 24 hr. and 7 days depends upon the hydration of the tricalcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between 7 and 28 days is due to the hydration of the beta-calcium orthosilicate (dicalcium silicate), but here are encountered opposing forces in the hydration of any high-burned free lime present and in the crystallization of the aluminate. It is to this hydration that the falling off in strength between 7 and 28 days of very high-burned, high-limed cements is due, whereas the decrease shown by the high-alumina cements is due to the crystallization of the aluminate.

Retardation of Set by Gypsum.—The exact manner in which gypsum retards the initial set of cement is not known. For reasons that are pointed out by Klein and Phillips,[1] the usual explanation that the retardation is due to the formation of the sulfo-aluminate crystals having a selective action for water is insufficient. From their observations it appears that the retarding effect of the gypsum is due to its action as an electrolyte on a colloid solution, *i.e.*, in this case, it prevents the hydrated aluminate from precipitating from its sol to form a gel.[2] They found that with 2 per cent plaster of Paris, the hydrated substance could coagulate and separate as a solid least readily, while with other concentrations of plaster, the separation of the solid occurs in a shorter time; the set takes place more readily, therefore. Because the gypsum retards the coagulation, the hydration of the tricalcium aluminate becomes more nearly complete since the impervious coating about the cement grains is not formed so readily.

Retardation of Set Due to Aeration.—The time required for the initial set of the cement is lengthened by the exposure to the air. The aluminate grains absorb a small amount of water from the moisture of the air and become coated with a thin layer of more or less impermeable colloid. Then, when the cement is gaged with water, this layer retards the passage of

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[1] *Loc. cit.*, pp. 29 and 61.

[2] See Liquid glues, p. 589.

the water to the unhydrated center of the grains, so that a longer time is required for hydration and coagulation to take place. On this account an old cement is likely to set more slowly than a fresh one.

Effect of Regaging the Cement.—The following explanation of the effect of regaging is quoted from Klein and Phillips:[1]

> The effect of regaging is merely to hydrate a greater amount of aluminate than would be done by one mixing, but a very important factor is the amount of gypsum present. From this work it is very evident that the early strengths in cement are due not to the crystallization of the aluminates but to the formation of a dense, hard, amorphous mass of hydrated aluminate. Then it follows that the greater the amount of hydrated aluminate formed in 24 hr., the greater the early strength, and for this reason the high-alumina cements always show high early strengths. It has already been noted that aluminates without gypsum set up almost instantaneously with water, but that a very small amount is hydrated. In other words, the grains hydrate along the edges and adhere, so that the addition of large amounts of water has little effect since it can but slowly permeate through the amorphous material which is formed. The addition of gypsum, however, allows a greater amount of water to penetrate toward the center of the grains before there is coagulation with the formation of the impermeable wall through which the water penetrates very slowly.
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> Manifestly, therefore, the slower setting the cement, the less it will be benefited by remixing, as the effect of the latter is to remove mechanically the hydrated material from the surface of the grains, thus exposing a fresh surface to be hydrated. Conversely, a quick-setting cement will be benefited by remixing or continuous mixing, until a point is reached at which the cohesion between the hydrated particles is reduced. A cement takes up water very slowly, and if 20 per cent of the water be used in mixing, this is not combined even after the cement has hardened, but part of it is combined and part is mechanically held between the grains, where it slowly penetrates from the outside to the center of each grain. It is evident, therefore, that an excess of water is necessary for complete hydration. However, the greater the excess, the less the cohesion between the particles of the hydrated material and the lower the resulting strength tests. Therefore, additions of gypsum to the cement and the remixing of the cement play the same rôle in allowing the access of water to the aluminate grains.

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[1] *Loc. cit.*, p. 54.

Effect of Fineness on Setting and Hardening.—Generally the American specifications for Portland cements require that the degree of fineness be sufficient that 78 per cent will pass a 200-mesh sieve. And it is very important that the cement be fine. It has been shown[1] that in a cement of normal fineness, only about half the particles have been hydrated when the cement has hardened. The reaction with water is always very incomplete because of the impervious coating formed about the grains; the larger the grains, of course, the greater will be the amount of the material unhydrated in the center. Desch[2] says that if a cement which has once hardened be reground to the specified fineness and then regaged with water, it will develop a very considerable degree of strength due to the hydration of the previously unchanged material. And this is well known. The unhydrated centers of the grains have no function other than could be fulfilled more cheaply by sand. Thus it is evident that the finer cements allow the use of more sand in the mixture.

Other Factors Affecting Setting and Hardening.—A thin mixture with water sets more slowly than a stiff mixture. The greater amount of water does not retard the hydration, but does lessen the setting because it lessens the cohesion between the hydrated particles.

Heat hastens and cold retards hardening. The effect becomes noticeable when the temperature falls to below 50°F.; it is more marked at lower temperatures. Benson[3] says that the temperature of the water used has also a modifiying effect; that cold water retards, while warm water hastens the setting and also increases the ultimate hardness. Because hardening depends upon the drying of the gel, which in turn depends upon the diffusion of water from the gel coating to the center of the grain, higher temperatures would be expected to accelerate hardening on account of the lower viscosity of water at the higher temperature. Hence it would appear that cements which are put into service in warm weather would develop greater hardness than during cold weather.

The Effect of Freezing during Setting.—If freezing occurs during the setting of the cement, the colloidal mass is to some

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[1] DESCH, "Chemistry and Testing of Cement," p. 117.

[2] *Ibid.*, p. 119.

[3] "Industrial Chemistry," p. 281.

degree prevented from consolidating. During the time prior to the completion of the set, a certain amount of free water exists in the interstices between the hydrating grains of cement. Under normal conditions, this water diffuses through the colloidal coating of the grains and is used up by continued hydration. Then as the grains continue swelling they stick together and the mass consolidates. But since freezing retards diffusion and hydration, these processes may be delayed to such an extent that the water will evaporate from the mortar and not leave enough for sufficient hydration when the temperature rises. This evaporation of water may occur even though the temperature remains below the freezing point. As an illustration, it is necessary only to be reminded that wet clothes on the line dry in zero weather. The effect of the drying of the cement is most noticeable on exposed surfaces, and is very similar to that produced by using a cement mortar with a dry porous brick.

Further detriment results from the expansion that attends the freezing of the uncombined water. The expansion forces the grains apart, and although the dehydration should continue after thawing, the consolidation would be imperfect and the structure lacking in strength.

Effect of Salt Solutions Used to Lower the Freezing Point.—Small percentages of sodium or calcium chlorides lower the freezing point of the water and thus allow hardening to proceed at temperatures below 32°F. These additions, however, always lower the ultimate strength of the hardened mortar or concrete, in some cases as much as 25 to 30 per cent. The use of such salts in reinforced concrete should be prohibited, because they are almost certain to produce corrosion of the reinforcing rods, especially in damp locations. Corrosion is more likely to occur with the calcium than with the sodium chloride because it is more hygroscopic.

The Cause of "Hair Cracks."—When a cement sets and hardens in air, there is a slight contraction due to the drying out of the colloidal gel. This contraction is, of course, lessened by the sand or other inert substances. On the other hand, in mixtures that are too rich, *i.e.*, contain too little inert material, the contraction is manifested by the development of fine hair cracks. It is noticeable especially in rich facing mortars. The remedy is, of course, to use a mortar containing less cement, the whiteness being secured, if this is especially desired, by the use of marble dust.

Hair cracks may be produced also when the mixture is too wet, since the volume is then partly dependent upon water; shrinkage occurs when the water dries out.

Action of Destructive Agents. *Heat.*—Concrete begins to disintegrate under heat when a temperature of about 300°C. is reached, because then the combined water is expelled. In a concrete that is made of proper aggregate and is suitably proportioned, however, the conductivity is so low that this disintegration is likely to occur in only a thin surface layer.

In reinforced concrete the coefficient of expansion of the concrete is practically the same as that of the steel,[1] and the value of reinforced concrete in fire resistance is due largely to this fact. But the *heat conductivity* of the steel is much greater than that of the concrete. Consequently, if the steel is covered with only a thin layer of concrete at any point it will, in case of fire, become heated more rapidly, expand at a greater rate, and so set up internal stresses that may be disastrous.

Frost.—If cracks or "voids" due to improper proportioning exist in the cement or concrete, frost may prove destructive. The enormous expansive force manifested by the freezing of the water contained in these cracks and voids causes the mass to disintegrate.

Carbonic and Other Acids.—A water solution of carbon dioxide exerts a destructive action on cement and concrete because of the formation of the soluble bicarbonate of calcium. Marsh waters are active in this way. For a similar reason, contact with sewage is detrimental. By the bacterial fermentation of the organic matter, carbon dioxide is formed. Moreover, the hydrogen sulfide that is always given off from decaying sewage may become partly oxidized to sulfuric acid; this acid, of course, is also destructive.

Action of Sea Water.—If not well made, concrete structures are subject to destruction by the action of sea water. The action seems to be due, however, more to mechanical than to chemical forces. It generally occurs when a porous concrete structure is

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[1] Desch, *loc. cit.*, p. 201.

alternately exposed to the water and then to the air by the tides. Crystallization of the dissolved salts in the pores is brought about by evaporation of the water, and the expansion resulting from this crystallization causes disintegration. Porous stone, brick, and other substances are affected in the same way. If it is required to resist sea water, therefore, it is very essential that the concrete be dense.

In respect to the chemical action of sea water, the report of Bates, Phillips and Wig of the U. S. Bureau of Standards[1] says that although in laboratory tests it is found that various sulfate and chloride solutions have a chemical action on cements, in service this action is much retarded if not entirely suspended in most cases, due probably to the carbonization of the lime of the cement near the surface, or to the formation of a protective coating by deposits of salts. The report states further that properly made Portland-cement concrete, when totally immersed, is apparently not subject to decomposition by the chemical action of sea water, and that the metal reinforcement is not subject to corrosion if imbedded to a depth of 2 in. or more from the surface of well-made concrete.[2]

HIGH-ALUMINA CEMENTS

Development.—The development of high-alumina cements resulted from researches conducted independently by different workers who were aiming at entirely dissimilar objects. One of the objects was the production of a cement capable of yielding a high early strength, and the other was the manufacture of a product that would be more resistant than ordinary Portland cement to waters that carry soluble sulfates, such as sea water and ground waters of "alkali" regions. Structures made by the use of ordinary Portland cement are subject to early failure in the presence of sulfate waters, especially those carrying sodium sulfate, largely because of the expansion that results from the formation of crystals (page 458) when the water dries out. The present commercial cements of the new, high-alumina type com-

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[1] "Action of Salts in Alkali Water and Sea Water on Cements," *Tech. Paper* 12, p. 100, 1912.

[2] For a general discussion of the protection afforded the reinforcement by concrete see Corrosion, p. 361.

bine both features; they develop high early strength and resist the attack of sulfate-bearing waters.

Composition and Manufacture.—The usual Portland cement is made from the two classes of materials represented by limestone and clay, but the raw materials needed for the production of the high-alumina cements are typified by limestone and bauxite (page 84). Clay cannot be employed to furnish the alumina for the latter because too much silica would thereby be introduced into the mixture. The composition of a typical high-alumina cement is shown by the following analysis:[1]

	Per Cent
Silica	5.0
Alumina	42.0
Ferric oxide	10 0
Lime	42.0
Impurities	1.0

According to Eckel,[2] the fact that the high-alumina cements contain lime and alumina in equal, or substantially equal, amounts is determined merely by furnace practice. In the lime-alumina series, the eutectic (page 167) contains equal percentages of the constituents, and this composition is preferred because it is easy to fuse.

The preceding analysis should be compared with the analysis of a representative Portland cement on page 427. From this comparison, it will be readily apparent that the newer cements are distinctly higher in alumina and correspondingly lower in lime and silica than those of the Portland type.

The manner of burning the two cements is also different. Portland cements are burned, generally, in a rotary kiln, to a clinker only, *i.e.*, to incipient vitrification, but the high-alumina cements are actually melted. The fusion may be brought about in a cupola or in an electric-arc furnace, and the product is tapped as a slag. Because of the liquid, or semi-liquid, nature of the product, in France the high-alumina cements are frequently spoken of as *ciment fondu*, or fused cement.

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[1] Bates, "High-alumina Hydraulic Cements," *Ind. Eng. Chem.*, **18, 554,** June, 1926.

[2] "Cements, Limes, and Plasters," 3d ed., p. 645.

Another difference between the two cements is that it is not necessary to add a retarding agent to the high-alumina cement to delay its setting. Before grinding the Portland-cement clinker, about 3 per cent of gypsum is added to overcome its tendency to set quickly. Although Portland cements harden slowly if the gypsum is not added, they acquire an early initial set; but the fused cements naturally set relatively slowly and then gain hardness in a comparatively short time.

Components.—The chief components[1] of the high-alumina cements are the monocalcium aluminate $CaO \cdot Al_2O_3$, and the 3:5 aluminate $(CaO)_3 \cdot (Al_2O_3)_5$. Small quantities of the dicalcium silicate $(CaO)_2 \cdot SiO_2$, and the dicalcium aluminosilicate $(CaO)_2 \cdot Al_2O_3 \cdot SiO_2$ are also present.[2] If the lime content of the mixture is somewhat high, the 3:5 aluminate may be replaced by the 5:3 aluminate $(CaO)_5 \cdot (Al_2O_3)_3$. Iron and magnesia compounds will, of course, be present as minor components. It may be noted that the dicalcium silicate is the only compound present in both high-alumina and Portland cements, but whereas the latter contains above 40 per cent of this compound, in the former only a little is present.

Hydration, Setting, and Hardening of High-alumina Cements. Although the activity of the monocalcium and 3:5 aluminates is distinctly less than that of the tricalcium aluminate found in Portland cement, they begin to hydrate very soon after the addition of water. Both the monocalcium and 3:5 aluminate react with water to form supersaturated and metastable solutions of the calcium salt of the fairly strong, monobasic, aluminic acid.[3] The amphoteric aluminum hydroxide, when acting as an acid, is assumed[4] to ionize as follows:

$$Al(OH)_3 = H_3AlO_3 \rightleftharpoons H^+H_2AlO_3^-,$$

or

$$H_3AlO_3 \rightleftharpoons H_2O + H^+AlO_2^-$$

The calcium-aluminate solutions formed of this acid have a molar ratio of approximately 1, $CaO:Al_2O_3$. If the dissolved salt were

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[1] *U. S. Bur. Standards Res. Paper* 34, p. 972, 1928.

[2] *U. S. Bur. Standards Tech. Paper* 197, 1921.

[3] WELLS, "Reaction of Water on Calcium Aluminates," *U. S. Bur. Standards Res.* Paper 34, p. 967, 1928.

[4] WASHBURN, "Principles of Physical Chemistry," 1st ed., p. 311.

considered to be the product of the neutralization of the acid by the lime of the aluminate, the reaction would be represented as follows:

$$CaO + 2H_3AlO_3 \rightarrow CaAl_2O_4 + 3H_2O,$$

or

$$CaO + 2HAlO_2 \rightarrow CaAl_2O_4 + H_2O$$

The solution of the aluminate thus formed is metastable and soon precipitates gelatinous hydrated alumina and hydrated tricalcium aluminate,[1] thus:

$$3CaAl_2O_4 + \text{water} \rightarrow 4Al(OH)_3 + (CaO)_3{\cdot}Al_2O_3{\cdot}12H_2O$$

To the formation and coagulation of these solids, the setting of the cement is due.

The hardening of the aluminate cement is apparently due to the same process that brings about the hardening of ordinary Portland cement. The unhydrated cores of the particles absorb the free water from the gelatinous material about them, which is thus caused to dry to a dense, hard mass. The absorbed water taken up by the cores is consumed in the formation of additional hydrated material.

Although the high-alumina cements harden and gain strength in much less time than the usual Portland cements, the setting of the former is naturally much slower than the setting of the latter. In the alumina cement, no retarding agent, such as the gypsum used in Portland cement, is needed. The setting time of the alumina cement, unretarded, is equivalent to the setting time of Portland cement when properly retarded with gypsum, but after a normal setting interval, the high-alumina cement hardens rapidly. The hydration of the aluminates in a high-alumina cement seems to proceed in a few hours much farther than the hydration of the silicates in Portland cement.

Due to the rapidity with which the process takes place, the heat liberated by the reactions incident to hardening of the high-alumina cements, particularly in large masses of concrete, cannot be dissipated as quickly as it is generated. As a result, temperatures sufficiently high permanently to injure the concrete

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[1] WELLS, *loc. cit.*, pp. 962 and 967.

may be developed. Bates says[1] that this is likely to happen especially if the practice of covering the concrete with wet burlap to prevent evaporation is followed. On this account it is advisable to spray the concrete with water at about the time that the final set occurs, which will vary from 3 to 12 hr. after the material is placed. According to Bates, the time for wetting can be determined by noting the first rise of temperature as indicated by the feeling of warmth when the hand is placed on the mass.

HIGH EARLY-STRENGTH PORTLAND CEMENTS

The hardening rate of cement of the Portland type may be greatly accelerated through care in its manufacture. By taking special precautions, a cement is produced that is capable of developing in 2 or 3 days the same mortar strength as is attained in 28 days by the usual Portlands. In producing the accelerated Portland, the mixture is more finely ground and blended, the amount of lime is kept at the upper limit, and the temperature at which the clinker is burned is higher than usual as is required by the higher lime-to-silica ratio.[2] The clinker is ground much finer also; only from 5 to 10 per cent is retained on a 200-mesh sieve. Portland cements prepared in this manner acquire a final set in from 2 to 6 hr., and at the end of 24 hr. acquire a strength in compression approximately 2½ times as great as the ordinary Portlands. At the present time, in America, the high early-strength Portlands are used more extensively than the high-alumina cements.

TESTING AND STORING OF CEMENTS

Testing.—Cements are tested chiefly by mechanical means, the tests usually applied being the test for soundness (constancy of volume), the compression test, fineness, time of setting, and specific gravity. The first two of these are the most important.

The test for soundness is applied to determine whether or not the cement will cause mortars or concretes made of it to disintegrate in any way. The lack of soundness may be due to free

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[1] "High-alumina Hydraulic Cements," *Ind. Eng. Chem.*, **18**, 558, June, 1926.

[2] BATES, *loc. cit.*, p. 557

or slakable lime, or to coarse grinding. Free lime, in slaking, expands and may cause crumbling. If the quantity present is not too great, it may be rendered inert by air slaking, which may be accomplished by storing the cement for 2 or 3 weeks. Thoroughly slaked lime, such as is sometimes added to Portland-cement mixtures for waterproofing, or for the purpose of increasing its plasticity or smoothness under the trowel does not have this undesirable effect on soundness. Coarseness of grinding tends to lessen soundness because the hydration of the larger particles is deferred; when it does occur a disintegrating action may be manifested.

The degree of fineness is determined by sieving. As has been said before, fineness is essential, because only the finer of the particles are actively hydraulic; the coarser ones fulfill merely the function of sand. The finer the cement, therefore, the greater is the proportion of sand that can be mixed with it.

The determination of the setting rate is important, since in some cements, the initial set may occur before sufficient time has elapsed to allow the mortar or concrete to be placed. On the other hand, after it has been placed, hardening must not be too long deferred, since the longer the time required for the development of hardness and strength, the greater is the chance that it may be injured by accidents.

Storing.—In order that cement may be kept in a condition fit for use it must be properly stored. It should be kept in an atmosphere as dry as possible, and on a raised floor. Moreover, it should be kept covered with canvas or roofing paper. It absorbs moisture from the air quite readily; hence, it should be shielded from moisture-laden currents of air as much as possible. When it has become wet it sets and then cannot be used. Lumps are sometimes formed by pressure during storing; such lumps must not be mistaken for lumps caused by dampness. Lumps caused by pressure are readily pulverized.

CONCRETE

Water.—In concrete, water is the most important ingredient; more important variations in the strength and other properties of the concrete are produced by slight changes in the water content than are produced by similar changes in the other ingredients. By changing the amount of mixing water, a variation of as much as 100 per cent in the strength may be produced in concretes alike in composition in all other respects.

Much valuable information on this subject has been contributed by Abrams[1] who has shown that in certain instances a concrete consisting of 1 volume of cement to 9 volumes of mixed aggregate is as strong as a mixture of 1 of cement to 2 of aggregate, depending only on the water content. In other instances, he shows that increasing the quantity of mixing water by 13 per cent lessens the strength of the concrete as much as if one-third of the cement has been omitted from the mixture. In all cases the quantity of mixing water used should be no more than is required to produce a workable concrete. If materials and conditions of test are equal, the strength of the concrete is determined by the quantity of mixing water employed.

Until Abrams' work focussed attention on the fact that an excess of water causes faulty concrete, the tendency had been to use entirely too much water; and, in spite of the educational work that has been done, in much of the concrete now being placed, too much water is still employed. Concrete that will flow through a chute as a thin sludge is too wet. Or, if water rises to the top when the concrete is spaded or tamped, too much has been employed. The watery layer, carrying cement and other fine particles, that rises to the top of the concrete under such conditions is called *laitance*. Laitance layers in a concrete that is exposed to the weather are always subject to early failure.

Excess of water greatly increases the porosity of the concrete; the space occupied by the water obviously cannot be filled by the solids of the concrete. Because of the pore spaces, the continuity of the mass is interrupted, and the concrete lacks strength. Besides, a porous concrete is more susceptible to the action of frost. If too much water is employed in their construction, concrete piers, walls, etc., that are alternately wet by sea water and then allowed to dry, as by the rise and fall of tides, are notably lacking in durability. Their destruction is caused by the crystallization of the dissolved salts in the pore spaces as the water evaporates.

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[1] "Design of Concrete Mixtures," *Bull.* 1, Structural Materials Research Laboratory, Lewis Institute, Chicago.

The consistency of the concrete, which depends largely upon the amount of water present, may be regulated by the slump test. Abrams[1] says that normal consistency (relative consistency = 1) requires the use of water in such quantity that a slump of ½ to 1 in. will occur in a concrete containing 1 of cement to about 4 of aggregate, freshly molded in a cylinder 6 by 12 in., when the form is withdrawn by a steady, upward pull. Although this consistency is somewhat dry for most work, it can be used where slight tamping is practicable.

With 10 per cent more water than is required for normal consistency (relative consistency = 1.10), when tested under the conditions stated in the previous paragraph, a slump of about 5 to 6 in. will be shown. This is about the driest concrete that can be used in concrete-road construction.

When tested under the conditions described, a concrete having a relative consistency of 1.25 will show a slump of 8 to 9 in. This is about the wettest consistency that should be used in reinforced-concrete building construction.

Instead of using the cylinder, a cone frustrum, 4 in. in diameter at the top, 8 in. at the bottom, and 12 in. high, is more frequently employed. With this form of mold, for any given consistency, the slump will be less than when the cylinder is used. With the cone frustrum, for example, a 4-in. slump will represent a relative consistency of about 1.15; a 6-in. slump, a relative consistency of about 1.25, etc. These figures vary somewhat, however, with the character of the aggregate employed and other factors.

With regard also to the quality of the water that may be used in mixing concrete, Abrams[2] has contributed some very valuable information. Sixty-eight samples were tested; among them were sea and alkali waters, bog waters, mine and mineral waters, waters containing sewage and industrial wastes, and solutions of common salt. Most of the samples gave good results; among those that were found unsatisfactory were acid waters, lime soak from a tannery, refuse from a paint factory, a mineral water from Colorado, and waters containing over 5 per cent of common salt.

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[1] *Loc. cit.*, p. 16.

[2] "Tests of Impure Waters for Mixing Concrete," *Bull.* 12, Structural Materials Research Laboratory, Lewis Institute, Chicago, 1924.

Most of the mineral waters were entirely satisfactory; the only one found unsuitable was a highly carbonated water. Common salt in solution proved to be particularly objectionable; 5 per cent was found to reduce the strength of the concrete about 30 per cent.

Sand.—To be suitable for the making of concrete, sand should be coarse grained, and reasonably clean—free from clay, loam, silt, and vegetable matter. It is not advisable to allow the use of sand containing more than 5 per cent of such material; when more than 10 per cent is present, the sand should be rejected, or else it should be washed. When the sand is not clean, no amount of cement will make strong concrete.

An idea of the amount of clay, loam, etc., present may be obtained in the following manner.[1] Put 4 in. of sand in a pint preserving jar, then fill to within 1 in. of the top with clean water, and close the lid tightly. Shake vigorously for 10 min., stand upright and allow to settle. If more than ½ in. of clay or loam shows as a layer on the top of the sand, the sand should be rejected or washed. The line of separation between the clay and sand is clearly indicated by the difference in color and fineness.

It is of considerable importance that the sand be not too fine. Tests have shown[1] that an exceedingly fine sand required seven times the amount of cement required by a coarser sand retained on a 20-mesh screen, without increasing the strength of the concrete. Also when the sand particles are about of uniform size, the strength of the concrete made from it is not nearly so great as when the particles are of different sizes. When the size of the particles vary, the voids, *i.e.*, the open spaces between the particles, are much less and the resultant concrete is more sound.

Since the quantity of sand, like the other materials in the concrete, is employed in proportions by volume, the amount of water in the sand becomes an important factor. Moist sand, containing about 5 per cent of water, will occupy about 25 per cent more space than the same sand when oven dry. When dry the grains of sand move easily and pack closely together, whereas, when the sand is damp, because of the surface tension of the films or droplets of water between the grains, the grains of sand cohere

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[1] U. S. Dept. Agr. *Farmers' Bull.* 461, p. 7.

and tend to bridge or arch, which increases the porosity and consequently the bulk of the sand. Incidentally, it follows that damp sand, as received from a hopper or thrown from a spade, will be considerably lighter per unit volume than the same sand when dry. The greater bulkiness of damp sand, as compared to dry sand, must be taken into account when proportioning concrete by volume.

Because the percentage of moisture in the sand fluctuates from day to day, it becomes difficult, by the usual volume-measuring device, to apportion to a batch of concrete a predetermined quantity of sand. The variation in the water content of the sand may be caused by the prevalence or absence of rains, the period of storage, and other factors; the sand at the base of the stock pile will likely contain more water than that at the top.

To overcome the difficulty due to the variable water content, a method, known as the inundation method, has been developed for measuring the sand and at the same time introducing water for mixing the concrete. It has been found that when sand is shaken into water, the sand grains become so arranged that the space occupied is the same as when the sand is oven dried. In the inundation method, a quantity of water is first placed in the measuring device, and then the sand is shaken in from a hopper above; the measuring vessel is entirely filled with sand so that the water overflows. The inundated sand is then dumped into the mixer. Regardless of the previous percentage of moisture in the sand, the quantity apportioned to each batch is thus made constant. The additional water required for mixing is measured by a separate device.

Stone and Gravel.—The best rocks for concrete are in general the traps,[1] granites, and some varieties of sandstone and limestone. The shale, slate, and very soft limestone and sandstone should not be used, because the strength of the concrete, of course, can never be greater than the strength of the material used in it.

If blast-furnace slag is employed, it should be free from iron shot. Since some of the pellets of iron would inevitably be exposed in the surface layer of the concrete, the structure would not only be unsightly when the iron corrodes, but the increased

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[1] See page 398.

volume of the rust as compared to the iron, would tend to rupture the mass.

The Theory of Concrete.—The theory of the concrete mixture is that the stone and sand are so proportioned that the sand will just fill the voids in the stone, while the cement will fill the voids in the sand. In this manner a solid mass is obtained. This is the ideal mixture, but it is rarely, if ever, exactly reached in practice. Due to varying-size particles, the voids in both the stone and sand vary. Hence, in order to be absolutely safe a little more sand and cement than will just fill the voids are used. Generally the mixture contains half as much sand as stone or gravel. For example, the following proportions make a very good concrete for walks and floors, although mixtures containing much less cement are often used: screened gravel or crushed rock, 5 parts; sand, 2½ parts; Portland cement, 1 part. Proportions vary greatly, of course, in accordance with the character of the work being done. They may range from 1, 2, and 4 to 1, 3½, and 7 or even more.

WATERPROOFING CONCRETE

The cement concrete, as it is ordinarily made, is more or less porous and permeable to moisture. In a great many of its uses it would be a great deal more efficient if it were not so, as for example, in constructing basement walls and floors, vaults, reservoirs, drains, etc., as well as in all of the reinforced work, the permanency of which would be less doubted if it were waterproof. The corrosion of the reinforcing rods would certainly be prevented if the moisture were excluded.

A great deal can be done toward making concrete waterproof by merely having the ingredients of the concrete *rightly proportioned,* so that the voids are eliminated. It is said that it can be made entirely waterproof in this manner.

In the methods that are commonly employed, however, some special waterproofing material is used. This material is either applied as an external coating, or mixed with concrete before it is placed in the forms. Searle[1] makes a distinction between dampproofing and waterproofing, and says that the term *dampproofing* should be used to denote the methods and appliances

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[1] "Cement, Concrete, and Bricks," p. 197.

employed to keep out the dampness from the superstructures of buildings, and the term *waterproofing* for the methods used for treating work subject to hydrostatic pressure, and for vessels intended to contain or retain water.

Dampproofing.—The materials employed in dampproofing are divided into three classes: transparent coatings, opaque cement coatings, and bituminous coatings.

Transparent coatings[1] consist of those materials that do not change the appearance of the surface treated. Perhaps the oldest coating of this class is that produced by alternate applications of solutions of soap and alum or other aluminum salt. As these materials react within the pores, an insoluble aluminum soap is formed, which in addition to being insoluble has a distinct water-repelling property. Because it is necessary to repeat the process a number of times to secure a sufficient amount of the insoluble soap, this method is not economical and is not much used at present.

Paraffine wax is another example of the transparent coatings; it may be applied either as melted wax after the exposed surface has been carefully heated, or it may be applied as a solution in petroleum naphtha.

Solutions of waterglass or sodium silicate are also employed. The silicate is decomposed by the action of carbonic acid, and gelatinous silica is set free in the pores. There is an objectionable feature accompanying this process, in that it is difficult to cause the silicate to penetrate sufficiently.

The aluminum, magnesium, and zinc silicofluorides or fluosilicates, known sometimes as fluates, are also used.

Opaque Coatings.—Paints are included under this head, but ordinarily paints cannot be safely applied to cement coatings, since the calcium hydroxide that is set free during the setting of the cement reacts with the oil and destroys the durability of the film. To prevent this destructive action on the oil, the cement surface is first treated with a solution of zinc sulfate which reacts with the calcium hydroxide to produce calcium sulfate and zinc hydroxide. Both of these compounds are quite stable and do not react with the oil. Sometimes a casein paint is used as a

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[1] For test data, see Kessler, "Exposure Tests on Colorless Waterproofing Materials," *U. S. Bur. Standards Tech. Paper* 248, 1924.

first coat before the application of the oil paint. Or the casein paint may be applied alone followed with a treatment with formaldehyde to render it waterproof and resistant to molds, etc. Casein is obtained from milk by precipitating it with dilute acids. (Read Casein Paints, page 527.)

If there is no objection to the color, tar makes a very serviceable coating. The tar is heated to expel moisture, is treated with lime to neutralize its acidity, and then is applied hot, or it may be applied as a paint after thinning it with petroleum naphtha or benzol.

Special bitumens[1] are not used as surface coatings; they are incorporated into the wall. The bitumen is applied before the finishing coat; then a coating of plaster, with which the bitumen forms a very good bond, is applied directly to the bituminous surface.

Waterproofing.—The methods of waterproofing are divided by Searle into two classes: the "integral" or rigid method, in which a waterproofing material is incorporated with the concrete mass; and the "membrane"or bituminous-shield method, in which the concrete is insulated from contact with water by the use of a continuous, waterproof, bituminous layer.

The Integral Method.—The materials employed here include hydrated lime and calcium soaps.

Hydrated lime may be used for waterproofing with fair success. It has been found that amounts not exceeding 15 per cent may be employed without decreasing the strength of the cement. Moreover, the plasticity and easy-working qualities of the cement are increased.

If soap is employed, it may be previously prepared and added in the dry state, in which case it is very difficult to mix uniformly, or it may be formed in the concrete by using a water solution of sodium soap in place of water only in mixing.

According to Page,[2] concrete may be made thoroughly waterproof by mixing with it a quantity of heavy mineral oil, equal to from 5 to 10 per cent of the weight of the cement used. He says:

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[1] SEARLE, *loc. cit.*, p. 200.

[2] U. S. Office Public Roads, *Bull.* 46.

The admixture of oil is not detrimental to the tensile strength of mortar composed of 1 part cement and 3 parts of sand when the oil added does not exceed 10 per cent of the weight of the cement used. The compressive strength of mortar and of concrete suffers slightly with the addition of oil, although when 10 per cent of oil is added the decrease in strength is not serious. Concrete mixed with oil requires a period of time about 50 per cent longer to set hard than does plain concrete, but the increase of strength is nearly as rapid in the oil-mixed material as in the plain concrete.

Desch[1] says, however, that from general experience it has been found that the oil decreases the strength of the concrete about 30 per cent.

The Membrane Method.—In this method, no effort is made to treat the concrete; the object is merely to insulate it from contact with water by the use of a waterproof shield. Coatings of felt and burlap, saturated and coated with bitumen, are extensively used. This method has the advantage over the preceding, in that it in no wise affects the strength of the concrete.

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[1] *Loc. cit.*, p. 213.

CHAPTER XII

CLAY AND CLAY PRODUCTS

Source and Composition of Clay.—Pure clay is a hydrated alumina silicate ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), technically known as kaolin; it is pure white. It is produced by the weathering of feldspars, a group of mineral substances that consist of the silicates of alumina, potash, soda, and lime. Potash feldspar, known as orthoclase, is $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. By the action that occurs during weathering of orthoclase, the potash, together with two-thirds of the silica, is dissolved out, water is combined with the residue, and kaolin is formed. Pure kaolin is produced only by the weathering of pure feldspar, but this occurs in nature very rarely.

The common clays are formed by the weathering of igneous rocks, shales, and clayey limestones; the composition of the clay depends upon the character of the rock from which it was formed. Iron oxide is present in most clays, and small quantities of lime, magnesia, and the alkalies are of frequent occurrence. Since the rock may also contain constituents that are not susceptible to the weathering action, unweathered substances may be found mechanically mixed with the clay. In the weathering of granite. which is a notable source of common clay, the feldspar constituent is weathered as described. Granites contain a great deal of quartz, however, and since quartz is practically unaffected by the weathering process, the clay that results will contain it, usually in a finely divided state. In this way a sandy clay is formed.

In the production of clay, chemical action is not always of fundamental importance, as it is in the weathering of feldspar. Sometimes it amounts to very little, as in the weathering of shales, where frequently the action is merely a physical disintegration. In such cases, the composition of the clay differs very little from that of the original rock. (For a more complete discussion of the formation of clays, read pages 366 to 368.)

Clays may or may not be found where first formed. Kaolin is very light and is easily washed away and deposited in some other place. Clays that have been carried in this manner are known as *transported* or *sedimentary* clays, while those that remain in place where formed are called *residual clays.* In transit, sedimentary clays may become contaminated with considerable amounts of other materials, and thus be very impure; the substance is called clay, however, as long as sufficient kaolin is present to form a plastic mass when properly mixed with water.

Properties of Clay.—Among the noteworthy properties of clay are its plasticity and imperviousness to water when moist, and the ease with which it can be converted into a stone-like mass when heated, or as it is technically known, "fired" or "burnt." Burnt clay is probably the most enduring of all materials, as is evidenced by the state of preservation of specimens found in the ruins of remotest antiquity. Clay is unique in respect to the property it has of being readily fashioned into any desired form, which form may then, without difficulty, be made permanent.

Clays for Bricks and Other Clay Products.—Although all clays can be molded when properly moistened, and can be converted into a hardened form by heat, they are not all suitable for making bricks. For this purpose, the clay must quite accurately retain its shape during burning, and not warp. When burned it must possess suitable hardness, porosity and color. It must be as free as possible from pebbles, especially of limestone. Limestone will be calcined during burning and after the brick has been placed in the wall will hydrate; rupture will be caused by the resulting expansion.

The clay must not be too plastic. Highly plastic clays often show an excessive shrinkage, both during the drying of the paste and during the subsequent burning. Pure kaolin becomes so cracked and distorted, due to shrinkage, that it cannot be used without admixture of sand, previously burned clay, or similar material. The shrinkage of brick clay is controlled in the same manner. The object is not to prevent shrinkage altogether. A certain amount—about a total of 8 or 9 per cent—is considered desirable, since it aids in producing a more compact product.

Highly plastic clays are also hard to work. This difficulty is corrected by the addition of the same material that is used to offset shrinkage. Too much of this material must not be used, however, for although the clay works easily, the resultant brick will be soft and porous.

Fluxing Constituents.—Because they combine with the silica during burning to produce fusible compounds, the soda, potash, lime, magnesia, and ferrous oxide present in the clay are known as the fluxing constituents. If the fluxes are almost entirely absent, the burnt clay is open and porous; if present in sufficient amount, the granules of clay become fused together so that a more or less vitrified product results.

Color of Clay and Clay Products.—Iron oxide is the coloring agent of both the burned and unburned clay. The oxide is generally ferric, but it is probable that it does not occur in the free state in the raw clay, but rather as an almost colorless hydrated silicate. Upon heating, the silicate is decomposed into ferric oxide, silica, and water. All clays, including those of a greenish or grayish color, will burn red if burned in an oxidizing flame. If burned in a reducing flame, ferrous silicate will be formed, which may impart a purplish color to the burned product. If present in sufficient amount, it will color the burned clay black. When iron pyrite is present, the sulfur content is oxidized leaving ferrous oxide, which readily combines with the silica and produces the black color as just described. If the pyrite is present in large-sized granules, a hole is left where the granule was. The sulfur escapes as sulfur dioxide, and the ferrous silicate is absorbed by the brick; a black-lined opening is thus produced. Openings of this sort are usually found in hard-burned building bricks. If considerable pyrite is present, the bricks may be rendered too porous for use. Carbonaceous matter in clay acts as a reducing agent and converts ferric iron into the ferrous condition. In this way ferrous silicate may be formed from ferric oxide during burning.

Clays free from iron oxide will likely burn white, since other oxides capable of producing color are not usually present. Buff and cream bricks are made by the burning of clays containing very little iron oxide. If a great quantity of lime is present, however, the coloring effect of the iron oxide is overcome, even though it may be present in considerable quantity. Hence, cream or buff bricks may be produced from clay either low in iron oxide or high in lime.

BUILDING BRICKS

Brick-making Methods.—The suitably prepared clay may be molded into shape by any one of three methods. These methods are designated as the soft-mud, stiff-mud, and dry-press processes.

In the *soft-mud process* the clay is mixed with water to the consistency of a soft paste and pressed into wooden molds. In order that the brick may be delivered from the mold the more easily the mold is usually sanded each time before being filled. It is not difficult to recognize soft-mud bricks since they will show five sanded surfaces with the sixth comparatively rough; it is made so by scraping off the excess clay from the top of the mold. Unless repressed, soft-mud bricks lack sharp corners and straight edges. The interior is likely to show more pebbly particles also, than bricks made by other processes.

In the *stiff-mud process* the clay is mixed with just sufficient water to make it plastic, but still quite stiff; then it is forced through a rectangular die in the form of a bar, upon a cutting table. This bar is cut into brick lengths by means of wires. Since the wire makes a somewhat tearing cut, the cut surfaces are always recognizable on a stiff-mud brick. Another characteristic of these bricks that makes recognition quite certain depends upon the manner of mixing the clay. The mixing is done by means of a rotary shaft supplied with blades; the clay is forced through the die by means of a tapering screw. The twisting action resulting from this treatment produces usually a laminated structure within the brick. A stiff-mud brick will have four smooth surfaces and two roughly cut surfaces. Upon the cut surfaces the laminations are sometimes visible.

In the *dry-press process* the clay is allowed to dry in the air until its moisture content is reduced to at least 12 or 15 per cent. The clay is then granulated and screened. After this, it is conveyed to the pressing machine where it is pressed in steel molds. The process produces bricks with sharp edges and smooth surfaces. Such bricks are usually employed for front or face bricks. If the dry-press bricks are not well vitrified in burning they are likely to show a granular structure; the grains of clay cannot coalesce nearly so well as when the clay is mixed in a more or less plastic state.

Repressing.—The soft-mud and stiff-mud bricks are sometimes repressed shortly after molding. The repressing straightens the edges and removes the surface roughness. Usually, also, during the repressing some design is stamped upon the surface of the bricks. Repressing makes the bricks denser and stronger and more resistant to weathering.

Burning.—Most of the common bricks are fired at about 1050°C., while the pressed bricks are heated to a temperature of about 1280°C.

Rejected Brick.—Because of overfiring or perhaps for some other reason, many bricks come from the kiln discolored, roughened, or twisted. Such bricks must be cast aside and are known as "culls." The brickmaker is rarely able to obtain more than 85 per cent of good bricks from the kiln, and often the percentage is not so great.

Comparison of Bricks Made by Different Processes.[1]—Soft-mud bricks are generally more homogeneous in structure than the bricks made by other processes, and they are less likely to be affected by frost action if properly burned. Unless repressed, however, they lack smooth surfaces and sharp edges.

Stiff-mud bricks also usually possess a good structure, but laminations may be pronounced and separations may occur between them.

The dry-pressed bricks present the most finely finished surfaces. On the other hand, because of the granular structure, which results from the manner in which they are made, if they are not well burned, they are likely to be softer, with less cohesion between the particles than bricks made by other processes.

Efflorescence on Bricks.—Efflorescence is a coating—usually white—which appears on stored bricks or upon bricks laid in the wall. It consists usually of the soluble sulfates of magnesium, sodium, and potassium. Sometimes it is due to calcium sulfate, less frequently to the sulfates of iron and aluminum. These

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[1] For a further discussion of bricks, especially for requisite qualities and methods of testing, see Ries, "Building Stone and Clay Products," pp. 284–319.

salts may have been present naturally in the clay or water used to make the bricks, or may have been produced by the oxidation of minerals during burning. Sometimes they are produced by the reactions of weathering, as by the action of atmospheric sulfur dioxide upon certain silicates existing in the brick. Or in a similar manner, pyrite left in the brick, by being oxidized to produce sulfuric acid, may cause salts to be formed. In rare cases, efflorescence may be due to mortar.

Regardless of the manner in which they are formed, the incrustation is produced by the leaching out of these salts from the bricks by water; the salts are then deposited upon the surface of the bricks as the water evaporates. The incrustation, or efflorescence, is most pronounced near the eaves and downspouts under windowsills, etc., where the water soaked into the bricks either through leakage from the eaves and spout or through being caught and drained from the sills.

Aside from being unsightly, efflorescence exerts a disintegrating effect upon the bricks. The salts producing it are somewhat hygroscopic, and even when not actually wetted by rains, they dissolve by taking up moisture from the atmosphere and saturate the bricks with their solutions. Then, when dry weather arrives, they bring about disintegration of the bricks by the expansive force of their crystallization. It may have been observed that during damp or wet weather the efflorescence often disappears; it returns, however, with the coming of dry weather.

The remedy for efflorescence lies chiefly with the maker of the bricks. Water should be used for mixing with the clay that is free from salts. Hard burning, which volatilizes the alkalies and increases the density of the bricks so that less water can find entrance for leaching, is also of great value. Treatment with barium salts is also effective, since the soluble sulfates are converted into the insoluble barium sulfate. The by-products of the reaction, being less stable, are decomposed during the burning of the bricks.

It is not an uncommon practice to remove efflorescence by the use of washes containing nitric or hydrochloric acids, but this is very objectionable. Although the incrustation is for a time removed, the real evil is only aggravated. By the action of the acid, the salts present are converted into more soluble forms, which means an increase in the quantity dissolved, and a consequent increase in the amount of incrustation left by the evaporated water. The only really successful way is to cut off the source of water supply to the wall. If the wall can be thoroughly dried, good results may be secured by removing the efflorescence with a scratch brush or similar device, and then applying a waterproof coating such as described for waterproofing cement and concrete (page 449).

TERRA-COTTA WARE

Terra cotta means baked earth. This name is applied to a variety of forms of burned clay used for structural purposes. The forms are molded usually from low-grade fire clays and are hard-burned but not vitrified. In this discussion, the terra-cotta products will be considered under three heads: (1) decorative terra cotta; (2) building blocks; and (3) fireproofing.

Decorative terra cotta is either molded in plaster casts or is modeled by skilled artisans. After drying, there is sprayed upon the surface a coating consisting of clay, quartz, feldspar, and other ingredients, ground in water to the consistency of a thin cream. This mixture is known as the "slip layer." In addition to this layer the ware may subsequently be glazed. The slip layer may be colored and the ware decorated to show various designs.

Building blocks are made usually from clays and shales, or a mixture of these with low-grade fire clays. They are generally hard-burned but not vitrified. No surface coating is applied, since they are used strictly for structural purposes and are then covered by other material as mortar or plaster. They are made in a variety of forms, for example, those known as hollow blocks, furring blocks, hollow bricks, book tiles, etc. They are widely used because of their light weight, and their non-conductivity of sound and heat.

Fireproofing is a general name applied to the hollow ware used for flat arches in floors, for partitions and for furring in fireproof buildings. It serves to protect the metallic members from the intense heat in case of fire, and so prevents warping and other injury. It serves also as a non-conductor of heat at all times.

Terra-cotta lumber is a name given to that sort of fireproofing that has been made soft and porous by the addition of straw, sawdust, etc., to the clay mixture. The straw and sawdust burn out in the kiln leaving the product in such condition that nails or screws may be readily driven into it.

OTHER CLAY PRODUCTS

Roofing Tile.[1]—The procedure in making roofing tile is very similar to that followed in the manufacture of pressed bricks. The pressed forms are carefully dried and burned. It is said that a softer-burned tile is a poorer conductor of heat and hence provides a cooler roof, but when all factors are considered there is much difference of opinion as to whether a porous or vitrified tile is best. Vitrified tiles have a greater frost resistance and are probably more enduring on this account.

Wall tiles are pressed tiles and may be made from either dry or plastic clay. Those made from dry clay are known as "dust-body" or "dry-press" tiles. The clay used in this process is not dust-dry, however, because after it has been dried and pulverized it is steamed to render it slightly moist. Most of the wall tiles are "dry-pressed." After pressing, the tiles are set in fire-clay boxes to protect them from direct contact with the flame and then are burned. When burned, the face of the tiles is dipped in a glazing preparation, consisting usually of the silicates of lead, potassium, calcium, and aluminum, ground with water to the consistency of a cream. In this way a transparent glaze is formed. If a colored glaze is desired, the coloring matter is introduced in the form of metallic oxides. By suitable employment of such oxides, almost any color or shade desired may be obtained. After dipping and drying, the tiles are again fired until the glaze is fused, producing in this way a lustrous surface. Matte or dull glazes also are much used, and these glazes, too, may be colored. The dulled appearance is produced by applying a thick coating of the surface material.

Floor tiles are made by the dry-press process; since they are rarely glazed, only one firing is necessary. Floor tiles may be divided into two kinds—plain and encaustic tiles.

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[1] For manufacture and properties of roofing tile see *Bull.* 11, 4th series, Ohio Geol. Survey.

The *plain tiles* are made of one clay throughout; they are burned sufficiently hard to be vitrified or semi-vitrified. Vitrification results from surface fusion of the component grains. Examples of the plain tiles are the *mosaics*.

The *encaustic tiles* have a facing of one kind of clay and a backing of another. The surface may have a design of several colors. It is first put down in the molding box by the aid of a brass cell frame. The various-colored clays are sifted into this frame, and then the frame is lifted out. When this is done the mold is filled with a clay backing. Encaustic tiles cannot be burned to vitrification, since the colors are largely dependent upon iron compounds in the clay and such clays burn to buff or red when vitrified.

Sewer pipes are formed from plastic clay in a special form of press. Odd-shaped sections, such as traps, sockets, etc., are usually made by hand in plaster molds. After careful drying the ware is fired. When the kiln has reached a temperature of about 1200°C., common salt ($NaCl$) is thrown into the fires. The salt volatilizes and as it comes into contact with the earthenware, reacts with the clay and produces a readily fusible sodium-aluminum silicate which covers the surface of the articles as a glaze. This glaze is known as the "salt glaze;" it is the usual form applied to sewer pipe in the United States. The clay of which the pipe is made must be chosen with this object in view, since all clays will not take a salt glaze. A glaze is sometimes secured by coating the article with an easily fusible "slip clay" consisting of a mixture of litharge (PbO) and clay, or finely ground feldspar, and subjecting the coated article to a white heat. This glaze is in no way superior to the salt glaze; besides, it is not so cheap.

Drainage tiles are made of red-burning clay by the stiff-mud process; the product issues upon the cutting table as a hollow cylinder, which is divided into lengths by wires. After drying, the tiles are fired, but are not vitrified or glazed since in this case porosity is desired.

SANITARY WARE

Sanitary ware may be divided into two main classes: (1) that produced by the application of a glaze to a clay-product body, and (2) that produced by enameling articles made of cast iron and steel. In both cases it is essential that the coating applied have the same coefficient of expansion as the material composing the body. This, of course, is presumably taken care of by the manufacturer, but sometimes within only certain ranges of temperature. Hence, cracking of the enamel may result from contact with boiling water, when atmospheric changes of temperature would have no effect. None of the ordinary glazes or enamels on sanitary ware are able to withstand the action of the strong acids, such as nitric, hydrochloric, and sulfuric, since they were not made with this object in view. The composition of the enamel is too high in basic oxides, especially of the heavy metals, and too low in silica. By suitably adjusting conditions, however, glazes and enamels can be made that are proof against at least the weaker acids, such as found in foods, etc.

Vitreous Ware.—That class of ware produced by the application of a glaze to a clay-product body is known as vitreous ware. The body of the ware is made of a mixture of pure, white-burning clay, ground flint, and feldspar. Since this mixture has a yellowish tint, a small amount of cobaltic oxide is added. During the firing of the ware, the cobaltic oxide reacts with silica in the mixture, producing blue cobaltic silicate, which changes the yellowish white of the mixture to a bluish white. The finely ground mixture is worked up into a cream-like fluid, called "slip;" is strained to remove coarse particles; is filtered to remove water; and the resulting putty is stored in cellars to "age." Aging increases the plastic character of the clay. When removed from storage, the clay is compressed in a pugging mill to remove air bubbles. From the clay thus prepared, the articles are made by various methods, as by the use of a potter's wheel, by pressing in a mold, or by casting. In many instances, the article is made in sections; the various pieces are then stuck together by means of a little slip and soft clay. The joints are smoothed to as perfect a seam as possible. In a syphon-jet water closet, for example, there may be as many as 16 pieces.

A process that is used for making small articles is known as the *dust process*. For this process, the clay is dried and ground to a fine dust, and then is pressed into shape in steel dies. The buttons used as index plates on faucets are thus made; the words "hot" and "cold" are stamped upon the button after the first firing.

Before the ware made by any process can be fired, it must be thoroughly dried, an operation that in some instances requires several weeks. When dried, it is placed in rough clay boxes or cases, called "saggers," which are sealed with clay wadding. This is done to prevent the flame in the kiln from coming into direct contact with the ware, for if this should happen the ware would be discolored. When fired, the ware is called "biscuit."

Printing.—If it desired to have the ware show any printing, it is placed upon it while in the biscuit condition. A clay paste containing an ingredient that will burn to the desired color is prepared and spread upon an engraved copper plate. The excess clay is then removed, leaving only that which lies in the lines of the engraving. Tissue paper is now spread upon the copper plate with even pressure; when the plate is withdrawn the clay adheres to the paper. The paper carrying the color-clay design is laid upon the ware and rubbed with a hard brush, which causes the design to be transferred to the ware. Afterward the paper is washed off.

Glazing.—The mixture for the glaze contains a variety of substances, such as feldspar, flint, kaolin, boric acid, and certain metallic oxides, such as those of zinc, tin, and lead; it is so proportioned that its fusing point is lower than that of the body of the ware or biscuit. The mixture is fused to a glass, ground in water to a cream-like consistency, and then the biscuit is dipped into it. After drying, the ware is fired in a kiln that is not so hot as that in which the biscuit was first fired, but it brings the glaze to its fusing point, so that it fills the pores of the ware with the result that the glaze and body become practically a single mass. Water closets, tanks, lavatories, drinking fountains, etc., are made in this manner.

Enameled Cast-iron and Steel Ware.—If the sanitary ware is made by enameling a metallic body, cast iron is the metal that is usually employed, although steel is used to some extent. If steel is employed, it is used in the form of sheets which are pressed or stamped into shape.

Preparation of the Cast-iron Body.—For making the casting, the iron must be of special composition. Grunwald[1] says that cast iron of the following composition is generally used:

	Per Cent
Carbon	3.5
Silicon	2.0
Phosphorus	1.4 to 1.8
Manganese	0.5 to 0.7

The very high phosphorus content is essential to the production of the thin sections of the castings, since phosphorus confers much increased fluidity upon the molten iron, and lessens its shrinkage.

The shape of the casting is important. It must be free from heavy spots and sharp edges. When poured, the iron must not be too hot, since scale or sand fused into the casting will make it impossible to produce a smooth enameled surface. The castings are not machined before enameling, because machining produces a surface that is too close grained. If it is necessary to do any finishing, they are pickled, and sand blasted. If the articles become rusted during storage before enameling, all traces of rust must be removed, since the enamel would be stained otherwise.

Preparation of Steel for Enameling.—After pressing or stamping into shape, the grease and oil are removed from the forms either by burning them off in a furnace or by immersion in an acid "pickling" bath. If the piece is to be burned, it is usually first sprinkled with hydrochloric acid and is then held in the furnace until red hot. If treated in a pickling bath, it is afterward rinsed in water and then sponged by hand to remove the carbon film left by the action of the acid. Next it is passed into a neutralizing tank containing a solution of soda ash and caustic soda, after which it is placed in a drying room, heated to about 120°C., and allowed to remain until dry.

Preparation of the Enamel.—The enamel applied to the iron or steel article is in some respects a glass, but it is not an ordinary glass. It consists essentially of the following: silica, derived

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[1] "Theory and Practice of Enameling on Iron and Steel."

from quartz, flint or sand; alumina, obtained by the use of feldspar and clay; and lime from fluorspar or calcite. In addition to these substances, cryolite (Na_3AlF_6) is introduced as an aid in imparting a water-white color and making the enamel nontransparent. About 3 per cent of tin oxide (SnO_2) is added for its whitening effect. Tin oxide is expensive and a satisfactory substitute has long been sought. Recently, zirconium oxide (ZrO_2)[1] has been employed for this purpose and it is said to yield a ware that is in no way inferior, perhaps superior, to that produced with tin oxide.[2] Borax is used to introduce the boric anhydride B_2O_3, which among other desirable features makes the enamel more ductile and elastic. Soda ash and pearl ash are used as fluxes. Sodium and potassium nitrates are used as oxidizing agents. If the enamel being made is designed for the ground coat, it almost always contains a certain amount of cobaltic oxide, which seems to possess a great power of causing the enamel to stick to the metal. The reason is not well understood. Because of the use of cobaltic oxide, the ground coat is usually colored blue, but color is no object in the ground coat. After the mixture is made and fused to a glass, it is cooled and then is finely ground.

Application of the Enamel.—When the metallic article, for example, a bath-tub casting, has been made, cleaned, and smoothed, a first coating of enamel is applied in the wet form. As has been said, this coating is of such composition that it possesses the quality of sticking very well to the iron. It is then able to form a strong bond between the iron and the white enamel later applied. After the wet or slush coat has dried, the article is placed in a furnace heated to a temperature of about 925°C., and the enamel is fused. When the first coat has been properly melted, the article is withdrawn from the furnace, and the first coat of white enamel is sifted on in the form of a powder. The article is then quickly returned to the furnace and reheated until the freshly deposited enamel has melted and combined with

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[1] The zirconium oxide is derived from zircon, a by-product obtained from ilmenite (p. 152) which is now mined extensively for the purpose of preparing titanium oxide to be used as a substitute for white lead.

[2] FURNESS, Tin in 1926, "Mineral Resources of the United States," p. 39, U. S. Geol. Survey.

the first. After this, a second, or more coatings, of the powdered enamel are applied in a like manner. After the last coating has been applied, the article is withdrawn from the furnace and allowed to cool in an atmosphere free from dust.

Bath tubs, sinks, lavatories, tanks, etc., are made of enameled cast iron.

CHAPTER XIII

PAINTS, VARNISHES, STAINS, AND FILLERS

Paint Materials

Paints are preparations designed to be applied as surface coatings for the purpose of decoration or protection, or both; they consist generally of mineral pigments ground in oil. The oil used must be of such character that upon exposure to the air in a thin layer it will oxidize, either spontaneously or by the aid of catalysts, and form a tough, rubbery film. Films produced in this way from oil alone, however, are more or less porous and permeable to water, and lack wearing qualities; hence mineral pigments are ground with the oil. It is the function of the pigments to close the pores, and supply hardness and strength to the film. Although linseed oil is the most widely used paint oil, there are several others that may be employed, especially for certain particular purposes. The number of pigments that may be used is very great; each pigment possesses certain characteristic properties upon which, in a large measure, depends the value of the paint in which it is employed. Because the properties of the paints are so largely determined by the constituents from which they are made, in the present chapter considerable attention will be devoted to raw materials.

Paint Pigments[1]

Definition of Terms.—In describing the various physical and chemical properties of paint pigments the following terms are commonly used:

Whiteness.—All white pigments when ground in oil do not produce white paints. For example, barytes, which is white,

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[1] The information given in this chapter on Paints and Paint Pigments has been derived largely from the Bulletins issued during 1909 and 1910, by the Scientific Section of the Paint Manufacturers Association of the United States.

becomes transparent when ground in oil. Lithopone (page 473), when ground in oil and painted out, produces a whiter surface than any other pigment but it has a tendency to darken upon exposure to sunlight. Zinc oxide is also very white when ground in oil and because its whiteness is more permanent, it is used as a standard for whiteness.

Opacity.—This term is used to designate the degree to which a pigment is able to hide the underlying surface.

Stable and Chemically Active Pigments.—Stable pigments are such as barytes, China clay, silica, etc., which neither react with the oil nor with atmospheric gases. Chemically active pigments are such as white lead, which reacts with the atmospheric gases and also either reacts with oil or causes its disintegration in some other manner so that chalking results.

Chalking.—This term is used to designate the development of a condition of the paint coat which allows the pigment to be removed after the manner of chalk dust by rubbing with a cloth or with the hands. It is due to the disintegration of the film.

Checking.—This has reference to the development on the paint surface of fine hair-like lines, usually interlaced and forked. It is the result of a lack of elasticity and is also sometimes an attendant of chalking.

"*Tooth.*"—This term applies to the manner in which the paint works under the brush. It implies a certain drag or resistance to spreading. The proper degree of tooth allows sufficient spreading without too much greasiness or excessive flow.

Spreading Values.—Some pigments cause the paint to spread out to an exceedingly thin surface, too thin to be durable, while others spread with difficulty.

Antisettlers and Reinforcing Pigments or Paint-coat Strengtheners.—Some pigments when ground in oil settle to the bottom and form a hardened mass on standing. When admixed with pigments of this sort, asbestine (page 476) and China clay have a certain ability to prevent the settling. Asbestine occurs in long needle-shaped crystals and China clay in flake form, and they form a web that tends to hold up the other pigments. In a paint coating they act in a manner similar to rods or webs in concrete, hair in plaster, or woven wire in fireproofed glass. They increase the abrasion resistance of the film.

Inhibiting, Accelerating, and Indeterminate Pigments.—These terms are used with reference to pigments applied to iron structures. Inhibiting signifies that the pigment has a tendency to retard rusting; accelerating, that it has a tendency to hasten the rusting; and indeterminate that it is neutral or has no pronounced tendency either way.

THE WHITE PIGMENTS

Basic-carbonate White Lead (*Corroded White Lead, Dutch-process White Lead*) [$(PbCO_3)_2 \cdot Pb(OH)_2$].—This pigment is made by supporting lead grids in clay pots in the bottoms of which is acetic acid about as strong as vinegar. The pots are stacked in tiers in tan bark, which, by fermenting, produces heat and carbon dioxide. The heat vaporizes the acetic acid; the vapors attack the lead and produce basic lead acetate. The carbon dioxide finds its way into the loosely covered pots and converts the basic acetate into the basic carbonate. The process is very slow; it requires from 100 to 130 days. When completed, the white lead is broken up, ground in water, and floated to separate the "blue" or uncorroded lead; then it is dried in copper pans. It is sold either dry or ground in oil.

Corroded white lead is about 75 per cent carbonate and 25 per cent hydroxide, or 85 per cent lead oxide and 15 per cent carbon dioxide and water by weight. Of all the pigments it has the greatest opacity or hiding power and is fairly white. It consists of particles of variable size; for this reason paints made of it are relatively free from unfilled spaces known as voids. Its particles are also fairly coarse; about 10 per cent of them are quite coarse and even its finer particles are coarse in comparison to the particles of basic-sulfate white lead or the still finer particles of zinc oxide. The gradation in the size of its particles explains its low oil-absorbing power, its opacity, and its denseness or compactness.

Its specific gravity is 6.8; it grinds in 9 per cent of oil to a stiff paste, 100 lb. of which can be prepared for use by mixing with 4 to 6 gal. of oil, a quart of turpentine, and a pint of drier. When applied to iron and steel structures it has good inhibitive qualities. The greatest defect chargeable to white lead as a pigment is that paints made of it are very much subject to chalking. There is some difference of opinion concerning the exact cause of the chalking. One explanation is that because of the basic nature of the pigment it reacts with the linseed oil, saponifying it to a certain degree, which brings about a disintegration of the linoxyn film; but zinc oxide reacts in a similar manner and does not produce chalking. Another explanation is that the chalking is due to the reaction of the pigment with the carbon dioxide of the air, whereby the lead hydroxide is converted into the carbonate. Besides, lead carbonate forms the soluble bicarbonate of lead in the presence of water containing carbon dioxide; perhaps this reaction is a factor in the chalking. Whatever may be the cause, the chalking is very characteristic of white lead. An attendant evil is that after the chalking has started, the paint holds very tenaciously the dust that settles upon it, so that it soon becomes unsightly due to this cause. Paint in this condition cannot be cleaned by sponging with water.

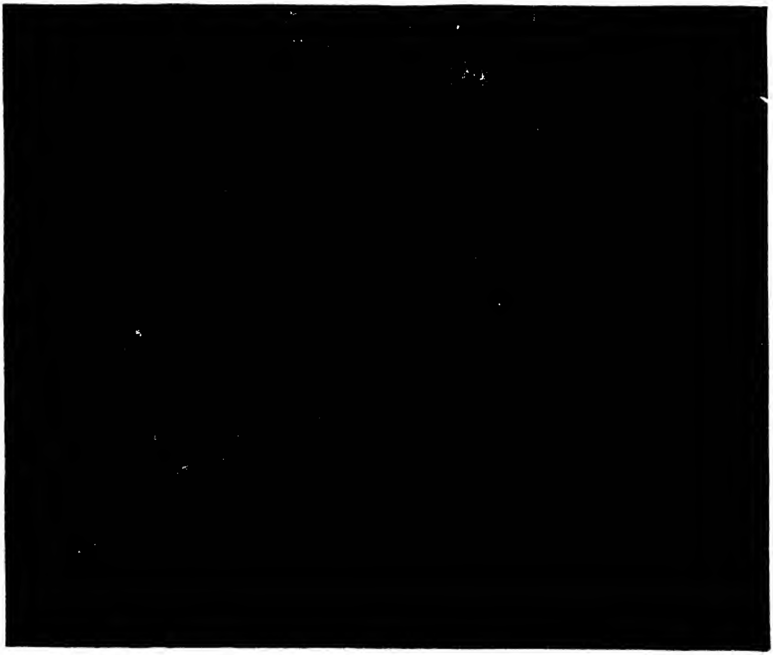

FIG. 79.—Type of paint decay known as chalking. Magnified view. (*Gardner.*)

Paint containing only the basic-carbonate white lead as a pigment is subject also to rapid checking. Because of its basic reaction the pigment damages delicate colors with which it may be tinted. Unless reinforced it settles badly; thereby non-uniformity is produced in painting. It is much damaged by atmospheric gases, turning dark in the presence of the very prevalent hydrogen sulphide, due to the formation of the black lead sulphide. For this reason it should not be used with a pigment containing free or sulfide sulfur. It is somewhat deficient in spreading power. In general it may be said that white lead is weak in those respects in which zinc oxide is strong, and *vice versa*.

As reported by "Mineral Resources of the United States," the use of white lead as a pigment in recent years has been gradually decreasing. The downward trend in its consumption has been occasioned by the increasing popularity of zinc white, titanium white, lithopone, barium pigments, and the cellulose lacquers.

Testing of White Lead.—The purity of white lead can in a measure be determined by its complete solubility in nitric acid. Barytes, sand, etc., will remain undissolved. If ground with oil, the oil must previously be removed by several washings with benzine.

Zinc Oxide (*Zinc White, Chinese White*) (ZnO).—The American-process zinc oxide is obtained by the roasting of zinc ores, as the sulfide, carbonate, etc. The French-process oxide is obtained by sublimation and oxidation of spelter or metallic zinc. There are various grades of each.

Because of its chemical stability and extreme whiteness, it is an excellent pigment to use as a base for delicate colors. It has good opacity and spreads well. Its particles are very fine and it has no tendency to chalk; hence it can be mixed to advantage with the basic-carbonate white lead, the particles of which are coarser and which has a tendency to chalk. It has good drying powers of itself, hence with it little added drier is needed. If very rapid drying is desired, litharge is the drier that should be used. Because of its continued oxidizing effect on the oil zinc oxide produces a very hard paint, but for the same reason one that is very inelastic. Although it reacts with the hydrogen sulfide of the atmosphere it does not darken on this account because the zinc sulfide is almost white.

It has a specific gravity of 5.2 and grinds in 16 per cent of oil to a stiff paste, 100 lb. of which can be thinned for use with 64 lb. of additional oil. The reason why so much more oil is required by zinc oxide than by white lead depends partly upon the fact that a certain weight of zinc oxide is much more voluminous than an equal weight of the basic-carbonate white lead. It is also partly due to the fact that the particles of zinc oxide are of approximately equal size and so do not make as dense a mass as do the graded particles of white lead; consequently, more space remains to be filled with oil.

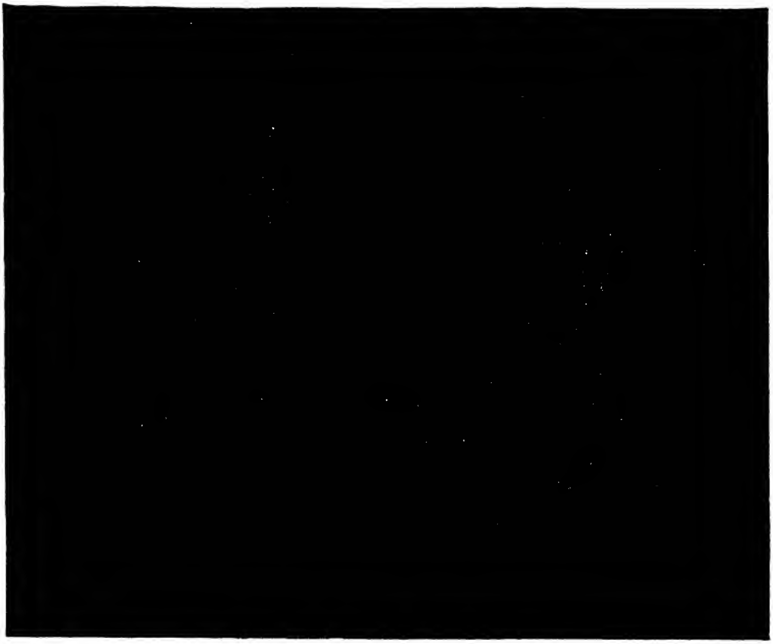

Fig. 80.—Type of paint decay known as checking. Magnified view. (*Gardner.*)

Zinc oxide is excellent for use in enamels, because of the gloss and whiteness it confers upon the paint. It has good inhibitive qualities.

Its greatest defect is that when used alone, because of the hardness and inelasticity of the film, it has a tendency to cause the paint to check, crack, and peel badly. Moreover, it reacts with the carbon dioxide of the air, increasing about twice in volume in so doing. The inelasticity coupled with the increase of bulk causes the paint to peel or flake off. The roughness so caused makes it impossible to produce a smooth surface in repainting without removing the old paint. When used alone, the paint possesses excessive flowing qualities and spreads out too thin. These defects can be eliminated by proper reinforcement, as, for example, with basic-carbonate white lead, calcium carbonate, etc.

Adulterations may be detected in samples of supposedly pure zinc oxide by determining its solubility when gently warmed with dilute sulfuric acid. If pure, it will dissolve to a clear solution without effervescence. Effervescence would point toward the presence of calcium carbonate or whiting. Of course, lead carbonate will effervesce also. Insoluble residues indicate the presence of silica, China clay, or some compound of calcium, barium, or lead, present either as the sulfate or converted into the sulfate by the action of the acid.

Sublimed White Lead (*Basic-sulfate White Lead*) [$(PbSO_4)_2 \cdot Pb(OH)_2$].—This pigment is obtained by oxidizing with air the fume produced by roasting and volatilizing galena ore (PbS).

It is a fine, white, amorphous pigment, composed of 75 per cent lead sulfate, 20 per cent lead oxide and 5 per cent zinc oxide. It is very dense, and is more permanent than the basic carbonate. It surpasses the basic carbonate for painting on wood, having most of its good properties and not its defects. It has a specific gravity of 6.2 and grinds to a stiff paste in about 10 per cent of oil. For 100 lb. of this paste 38 lb. of oil are needed to thin it for application. Because of its fineness it has a tendency to exhibit excessive flowing and spreading qualities.

Lithopone ($BaSO_4 \cdot ZnS$).—This pigment is made by the simultaneous precipitation of the insoluble barium sulfate and zinc sulfide by mixing solutions of the soluble salts, zinc sulfate and barium sulfide; the reaction is:

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4$$

The precipitate contains between 70 and 75 per cent of barium sulfate and the remainder consists of zinc sulfide. The mixed precipitates are not, however, suitable for use as a pigment without further treatment, but when the mass is heated to dull redness, suddenly plunged into water, ground in the pulp state, thoroughly washed and dried, its characteristics are totally changed and it makes a very effective and durable pigment for paint purposes.[1]

Lithopone, like zinc oxide, is composed of extremely fine particles, but it is much denser than the latter. It spreads well, forms durable films, and is not affected by atmospheric gases. It is probably the whitest of all pigments, and is much used for making enamels for interior use. Because of the presence of sulfide sulfur in lithopone, it must not be used with pigments or driers containing lead.

Lithopone possesses a very peculiar characteristic. It is darkened by ultra-violet light, especially in the presence of moisture, but whitens again if kept in the dark. Thus, lithopone paints employed for outside work have a tendency to darken in the daytime, but possess their original whiteness the following morning. This phenomenon has occasioned much research and discussion. It is now believed that the darkening is due to a partial conversion of the zinc sulfide to metallic zinc and probably free sulfur or hydrogen sulfide. The whitening is due to the oxidation of the zinc to zinc oxide, but when exposed to ultra-violet light, the pigment darkens again. The redarkening may be due in part to the influence of free sulfur, which causes the zinc oxide to darken, or to the photogenic decomposition of more zinc sulfide.[2] Lithopone manufacturers have succeeded in producing a pigment that exhibits a minimum darkening tendency by developing a protective film of zinc oxide about the particles of zinc sulfide. The zinc oxide content is kept between 3 and 5 per cent.[3]

Titanium White ("*Titanox*") ($BaSO_4 \cdot TiO_2$).—Titanium white is the most recent addition to the list of important white pigments. Although new, it is extensively used. The competition of this pigment, together with that of the pyroxylin lacquers, has caused a noticeable decline in the consumption of white lead.

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[1] TOCH in Rogers and Aubert's "Industrial Chemistry," p. 330.

[2] *Ind. Eng. Chem.*, **21**, 348, April, 1929.

[3] TOCH, "Chemistry and Technology of Paints," p. 46.

Titanium white is prepared from ilmenite (page 152), an iron titanium oxide ($FeTiO_3$), a lustrous, black mineral. In the process of manufacture, the ilmenite is ground and worked into a paste with sulfuric acid which, when heated, reacts. The product of the reaction is extracted with water, and the solution is separated from the residue by filtering. On heating the solution of sulfates of iron and titanium thus obtained, the titanium salt is hydrolyzed and basic titanium sulfate is precipitated. Prior to heating, precipitated barium sulfate is suspended in the clear solution, and this is carried down with the titanium compound to form an integral part of the pigment. The mixture is dried and calcined in a rotary kiln. By this process the basic sulfate is converted into titanium dioxide. The barium sulfate, which is employed to increase the opacity of the pigment, gives best results, for most purposes, when used in molecular-weight proportions. On this basis, the finished product consists of 25.5 per cent of titanium oxide, and 74.5 per cent of barium sulfate.[1] The barium sulfate is a necessary ingredient, and must not be considered as an adulterant.

The particles of titanium white are very fine; the specific gravity of the pigment is low, and its oil absorption is high. As a result of these properties its covering power is very great, approximately twice that of white lead. Its opacity is much superior to the other commonly used white pigments. On the other hand, if great care is not taken to control the temperature carefully during calcination, other pigments may excel the titanium product in whiteness. Unduly high temperatures cause yellowish crystals of rutile (page 152) to be formed. The commercial pigment as now manufactured, however, is very satisfactory with respect to its whiteness.

Titanium oxide is chemically inert. It reacts neither with the oil with which it is ground nor with atmospheric gases, and it is compatible with all other pigments. Being the oxide of a metal, it might be expected to be a basic anhydride, but its tendencies are more acidic than basic, and on this account it can be used with acid resins in lacquers without danger of forming gelatinous products, such as result from the use of zinc oxide under these conditions.

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[1] HEATON, "Outlines of Paint Technology," p. 96.

Titanium-oxide paints produce films of great elasticity, but being soft, the film lacks abrasion resistance. Better results are secured if some pigment such as zinc oxide, which tends to produce a hard inelastic paint, is employed in conjunction with it. In enamels for interior use, titanium white is an excellent pigment, but when exposed to the weather, paints containing it chalk rather badly. It is inferior to white lead for outside work.

Reinforcing Pigments.—In relatively small amounts, the pigments grouped under this head are useful in overcoming the defects of other pigments, but they must never be used in excess. The reinforcing pigments may be divided into two classes: (1) those that grind in oil to produce a white paste, and (2) those that are practically transparent in oil. The transparency of the latter class is due to the fact that the index of refraction of the pigment is almost identical with that of the oil, so that in passing through the mixture, the rays of light are not deflected. There is a marked difference, therefore, when these pigments are used with colors. Those that form white pastes dilute the color to produce a tint of that color. Because of this fact, they are called *diluents.* Those that do not produce white pastes, when used with colored pigments, allow the full strength of the colored pigment to be effective. Because they contribute the physical properties required, and serve as a foundation for the preparation of a colored paint with a relatively small amount of the more costly colored pigment, white pigments of this type are called *bases.*

a. Diluents.—In the class of white reinforcing pigments that produce white pastes when ground in oil are asbestine, talc, and China clay.

Asbestine (Magnesium Silicate).—Asbestine is prepared by grinding the native mineral, asbestos, which is very fibrous in character, and even upon grinding finely, retains a rod-like form. Hence it is an indispensable paint-coat strengthener; in mixed paints it will hold up the heavier pigments and retard settling. It is very stable and retards chalking of paints applied outside, but it lacks opacity in oil and does not spread well. It has a specific gravity of 2.7 and grinds with 32 per cent of oil to a stiff paste.

The *talcose* variety of magnesium silicate, instead of being fibrous, is platelike in structure. It has the same properties and is put to the same use as asbestine.

China Clay (Hydrated Aluminum Silicate, Kaolin, Pipe Clay). This material is produced by the weathering of pure feldspar (page 368). It is a very permanent, white, amorphous powder. It is very fine, is a good spreader, inhibits settling, and retards the chalking of white lead. Its particles are not all of the same size, hence it is high in density. It has a specific gravity of 2.6 and grinds to a paste in 28 per cent of oil.

b. Bases.—The chief pigments belonging in this class are silica, native and precipitated calcium carbonate, gypsum, and native and precipitated barium sulfate.

Silica (Silex, Quartz Silica, Siliceous Earth, Decomposed Silica) (SiO_2).—This pigment is obtained by grinding white sand. The particles are not of uniform size, but they have sharp angular edges and corners, which accounts for the excellent tooth the pigment possesses. It is very stable and resistant; when mixed with white lead and zinc oxide it produces an excellent wearing paint. It has good spreading qualities, but because of its crystalline structure and transparency in oil it lacks hiding power. Because of this transparency, it makes an excellent filler for natural hardwoods.

Whiting (Calcium Carbonate, Paris White, White Mineral Primer) ($CaCO_3$).—Whiting is prepared by grinding chalk. In small quantities it is very useful in neutralizing any free organic acid of the linseed oil or the free acid sometimes found in Venetian red. It does not settle much and is a good spreader. Its specific gravity is about 2.8, and it grinds in 20 per cent of oil to a stiff paste. It thickens the paint and increases its density; if used in large quantity, it thickens the paint too much. It possesses but little opacity.

Calcium Carbonate (Precipitated Form) ($CaCO_3$).—This pigment is prepared by treating lime water with carbon dioxide. It possesses more opacity, but otherwise is similar to whiting. It is much used in making putty. It is not a suitable pigment for use on iron structures, since it contains some soluble impurities gathered up during its manufacture, which stimulate corrosion. It has a considerable tendency to chalk.

Gypsum (Terra Alba, Hydrated Calcium Sulfate) ($CaSO_4 \cdot 2H_2O$).—This pigment is prepared by grinding the native mineral. It has excellent opacity when ground in water, and is therefore much used as a base for distemper colors (page 527). It is chemically stable and possesses good tooth. For painting upon wood it is very serviceable as a reinforcing pigment to overcome some of the defects of the fundamental pigments, such as the excessive spreading of zinc oxide, or the chalking of white lead. It is not suitable as a reinforcing pigment in paints to be applied to iron, since it is somewhat soluble in water, and dissociates into calcium and sulfate ions, which serve to accelerate corrosion. It lacks opacity in oil.

Barytes (Natural Barium Sulfate) ($BaSO_4$).—Barytes occurs as a native mineral; it is prepared for use as a pigment by grinding and washing in hydrochloric acid to free it from iron compounds so that its color may be white. It possesses good tooth and prevents excessive spreading of the paints in which it is used, but lacks opacity in oil. It is an excellent base on which to precipitate colors in the formation of "lake pigments" (page 488).

Blanc fixe is precipitated barium sulfate. It has practically the same properties and uses as barytes.

Influence on Corrosion.—Of the reinforcing pigments, gypsum, barytes, and blanc fixe have a stimulating effect upon corrosion when applied to iron; asbestine, talcose, China clay, silica, and whiting are indeterminate in their action.

THE COLORED PIGMENTS

Concerning the Use of Colored Pigments.—In using a colored paint, the *color* of the pigment is not the only point to be considered in choosing it. In addition to having the required tint or shade it must not be chemically active with any other material used in the paint. Ultramarine, for example, must not be mixed with white lead. The color of the pigment must be "fast" to light. That light induces chemical changes is true not only of direct sunlight but in a less degree also of diffused daylight.

At times paint is required to be applied directly to walls rather recently finished with lime or cement plaster, as in the case of decorative or fresco painting. In this event the pigment must be such that it is not affected by alkalies. Prussian blue is an example of a pigment thus affected. The alkalinity of freshly plastered walls can be corrected by washing them with a solution of zinc sulfate; the substances produced by the reaction of the zinc salt with the calcium hydroxide of the plaster are zinc hydroxide and calcium sulfate, both of which are insoluble. Whether or not a pigment is affected by alkalies may be determined by shaking it with lime water and allowing it to stand for several hours.

If the painted surface is to be varnished, the mineral colors should be used in the paint if possible, since the "lake" colors are often dissolved by the varnish solvents.

THE BLUE PIGMENTS

Prussian Blue (*Paris Blue, Chinese Blue, etc.*) [$Fe_4(FeC_6N_6)_3$]. The pigment is manufactured in a variety of slightly different ways; the depth of color varies somewhat with the method. It is usually made by treating a freshly prepared water solution of ferrous sulfate with a solution of potassium ferrocyanide. A white or greenish-white precipitate of the ferrous ferrocyanide is formed, which is oxidized with some oxidizing agent to the ferric compound. The oxidizing is usually done with bleaching powder.

The coloring powers of this pigment are very great; it is the best of the blues in this respect. One-half ounce will tint 20 lb. of zinc white a perceptible blue. It is quite permanent and resists the action of atmospheric agencies and light. It absorbs much linseed oil which it tends to preserve, presenting a glossy surface even after long exposure. Its particles vary much in size and are of an amorphous structure.

It cannot be used with whiting, basic-carbonate white lead, or other basic pigments since it reacts with these pigments and assumes a reddish tinge; ferric hydroxide is formed.

Ultramarine blue is made by fusing together silica, China clay, sodium carbonate, and sulfur in crucibles. The materials react chemically, but it is not known in exactly what manner. In the initial stages of fusion, the product is green; with further heating a very bright blue is developed. The final product is ground very fine and then is bolted.[1]

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[1] Sifted through fine-meshed cloth.

Formerly this pigment was gotten from the earth as a mineral; it was obtained from lapis lazuli, found in Persia, China, and Siberia.

There are two varieties of the manufactured ultramarine: (1) sulfate ultramarine (so named because in its manufacture sodium sulfate is substituted for a part of the sodium carbonate), of a pale greenish-blue color; (2) soda ultramarine, of a violet-blue color.

Ultramarine is not discolored by light, and is unaffected by alkalies. Sulfate ultramarine is the palest blue pigment made. Ultramarine is not affected by heat, hence can well be used where resistance to heat is essential.

Although ultramarine is an excellent pigment for painting on wood it is not a good pigment for painting on iron, because its sulfide-sulfur content is likely to hasten corrosion. It cannot be used with pigments containing lead, such as white lead or chrome yellow, because of the darkening that results from the lead sulfide formed. Its blue color is discharged by acids and acid vapors.

THE GREEN PIGMENTS

The green pigments may be divided into two classes: (1) those having an inherent or natural green color; (2) those prepared by an intimate mixture of blue and yellow. Guignet's green and emerald green are examples of the former class, and chrome green of the latter.

Chromium Oxide (*Permanent Green, Guignet's Green*) (Cr_2O_3).—By fusing 1 part of potassium dichromate with 3 parts of boric acid, then boiling with water, washing and filtering, a sesquioxide of chromium suitable for a pigment is formed. It is of a brilliant dark-green shade possessing unequaled permanence. It is not affected by atmospheric agencies and light, nor if pure, by acids or alkalies. Very frequently it is mixed with chrome yellow, and this component cannot withstand acids. It is very stable in respect to high temperatures; it is resistant up to 800°F., above which, however, it turns brown. When mixed with the chrome yellow it is resistant to only 300°F.

Pure chromium oxide can then be well used in painting motor parts. Because of its permanence it is used for signal work on railroads. It does not affect, nor is it affected chemically by other pigments. It has good body and covering power. In respect to corrosion it has an inhibitive action. The one objection to this green is its rather high cost.

Emerald Green (*Paris Green, Schweinfurt Green, Copper Acetoarsenite*) [$Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$].—In preparing this pigment, a sodium arsenite is first produced by treating white arsenic with washing soda; then the sodium arsenite is treated with a hot solution of copper sulfate which produces the olive-green copper arsenite. Dilute acetic acid or vinegar is added to the copper arsenite and the mixture is allowed to stand; from it crystallizes the emerald green.

It is an exceedingly beautiful, bright-green pigment. In oil it has moderate opacity and covering power. It dries well, is not affected by light, and has good spreading qualities.

It is exceedingly poisonous. It is darkened by hydrogen sulfide of the atmosphere, but is not affected by other gases. It cannot be mixed with cadmium yellow, ultramarine, and other pigments containing sulfide sulfur, due to the formation of the black copper sulfide. It is soluble in acids and alkalies, including ammonia.

Chrome Green (*Brunswick Green, Prussian Green, Green Vermilion*).—This pigment consists of an intimate mixture of Prussian blue and lead chromate. It can be made by the dry method by grinding together Prussian blue and chrome yellow, but it is more often made by precipitating together these two colors upon barytes.

Chrome green is produced in two tones, blue and yellow. The blue tone is the one made by the latter of the two methods; it contains from 75 to 85 per cent of the white pigment. The yellow tone contains no white pigment; hence it is much the stronger in coloring value.

Chrome green has good covering power, better than any other green pigment, and is comparatively low priced. It has a specific gravity of 4.4 and grinds in 25 per cent of oil to a stiff paste.

On iron it inhibits corrosion when pure, but it not infrequently contains water-soluble impurities, which detract from this property. Moreover, lead chromate itself is somewhat soluble in water. It cannot be used with pigments containing sulfide sulfur, because the sulfur would react with the chrome yellow and darken the green. It is likewise affected by hydrogen sulfide. It should not be used with the basic-carbonate white lead or with whiting, since the basicity of these pigments affects both the blue and yellow components; the green is turned into a red. It cannot be used with acids, which dissolve the chrome yellow and cause the green to turn blue.

THE YELLOW PIGMENTS

Chrome Yellow (*Neutral Chromate of Lead*) ($PbCrO_4$). (*a*) *Light Yellow Chrome* (Sulfur or Canary Chrome).—This pigment is obtained by precipitating lead chromate from a solution of lead salt by the use of potassium dichromate. By the addition of sulfuric acid, or some soluble sulfate, there is precipitated concurrently lead sulfate also, which serves to make the pigment light in color. Hence, the sulfur chrome yellow is really a mixture of lead chromate and lead sulfate; it may contain as much as 60 per cent of the latter. It is often adulterated by the addition of gypsum, China clay, and barytes, of which materials it is able to hold a great deal without the shade being sensibly affected.

(*b*) *Medium yellow chrome* is pure neutral chromate of lead and should contain no white pigment.

The chrome yellows are very brilliant and have the greatest covering power of all the yellow pigments. The particles are fine, the color is unaffected by light, and the pigment has an exceedingly high tinting power.

Although theoretically the chromates are good inhibitors, their practical value in this respect is not high, because they usually contain water-soluble impurities, which is generally true of all precipitated pigments.

Because of their lead content, they are darkened by hydrogen sulfide, by ultramarine, cadmium yellow, and other pigments containing sulfide sulfur. They are turned orange by basic pigments, as white lead, because the basic chromate of lead is formed. They have a tendency to cause the paints to dry slowly.

Zinc Chrome (*Citron Yellow*) ($ZnCrO_4$).—Zinc chrome is prepared by precipitating the pigment from zinc salt solutions by potassium dichromate, or by boiling zinc oxide with sulfuric acid and potassium dichromate.

Zinc chrome has a delicate, bright sulfur-yellow color, and has good body and covering power, but it is not equal in this respect to the lead chromes. It is not affected by light or atmospheric gases. Hydrogen sulfide does not affect it, nor is it affected by other pigments.

For metals it has a higher inhibitive value than any other pigment. The Scientific Section of the Paint Manufacturers Association of the United States recommends a 2 per cent addition of this pigment to all paints to be applied to iron or steel surfaces. It is somewhat soluble in water, however, and is dissolved by weak acids, both organic and mineral. Heat decomposes it, causing it to turn to a gray-violet color due to the formation of the zinc and chromium oxides. It is slow in drying, and it requires a considerable amount of added drier, therefore.

Cadmium Yellow (*Cadmium Sulfide*) (CdS).—In preparing cadmium yellow, an aqueous solution of a cadmium salt is treated with a solution of sodium sulfide or with hydrogen sulfide. The pigment has a brilliant, beautiful, yellow color, ranging from pale to deep orange. It has good covering power and is not affected by light and atmospheric gases. It cannot be mixed with white lead or emerald green because of its sulfide-sulfur content. In the presence of moisture it has a tendency to oxidize to cadmium sulfate and fade. It is rather high-priced.

Yellow ochers are pigments found native in many localities; they consist of either clay or calcium carbonate, colored with about 20 per cent of hydrated ferric oxide. They are prepared for use by grinding and levigating. This process consists of stirring the pigment in a gentle current of water which carries the fine particles into a settling tank, and leaves the coarser material behind. The fine material is used as the pigment; after drying it is ready for use. Sometimes the ochers are calcined (strongly heated); the color is thereby changed to a reddish tone, due to the formation of the dehydrated ferric oxide.

The ochers are usually of a golden-yellow color. They have a moderate opacity usually, although this varies much according to the source of the pigment; some varieties are almost transparent in oil. They have a moderate spreading power. Other pigments are not affected by them nor are they affected by any other pigments. They are not affected by atmospheric gases.

Sienna is also an earthy pigment. It belongs to the ocher class, and is of similar composition, but it contains more iron oxide and a considerable amount of brown manganic oxide; hence it is darker in color. The name sienna is taken from the name of the town in Italy where this pigment was first obtained. The pigment upon being burnt or calcined becomes, according to its composition, brown or reddish orange to dark red.

It has properties similar to the ochers. It is almost transparent in oil; it is, therefore, used almost exclusively as a glaze[1] or tinting color.

THE RED PIGMENTS

Red Lead (*Minium*) (Pb_3O_4).—This pigment is prepared by heating metallic lead in furnaces in the presence of air, whereby litharge (PbO) is first formed. The litharge is then further oxidized into red lead by heating to about 375°C. in a muffle furnace.

The pigment has a bright-red color and is permanent when exposed to light. Its particles vary in size, hence it makes a very compact coat. It has very strong drying properties; it rapidly oxidizes the oil with which it is mixed. On this account it is usually mixed with the oil at the time of application; 30 lb. of the red lead to a gallon of oil is the proportion most generally used. This is a very small amount of oil as compared with the amounts taken up by other pigments. Because of the small amount of oil and also its strong oxidizing power, paints made of red lead have a marked tendency to dry to very hard and brittle films and not infrequently scale off. No added drier is needed with red-lead paints. Red lead is largely used mixed with more inert pigments. It cannot be mixed with sulfide

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[1] To *glaze*, in this sense, means to cover thinly with a transparent color in order to modify the tone.

sulfur-bearing pigments and is turned brown by the action of atmospheric hydrogen sulfide. It has long been used in paints for the protection of iron and steel and is considered very valuable for this purpose.

Venetian red consists of a mixture of ferric oxide (Fe_2O_3) and calcium sulfate ($CaSO_4$). It is prepared by heating a mixture of ferrous sulfate ($FeSO_4$) and quicklime (CaO). The amount of calcium sulfate varies, but may make up as much as half of the mixture. The color of the pigment depends somewhat upon the temperature of the furnace; the lower temperatures produce the brighter colors.

Venetian red is a very permanent red pigment. It does not affect other pigments nor is it affected by them. It forms excellent protective paints for wood, is especially good as a priming coat, but is not a good paint for metal. The calcium sulfate which it contains, dissolves and ionizes slightly in water; the resulting sulfate ions are active in stimulating corrosion. Also it may contain some sulfur trioxide not properly neutralized by lime during the calcination. It does not exert a drying action on the oil as does the red lead, and the longer it stands in the full amount of oil it is to receive, the better paint films it seems to produce.

Natural Iron Oxides (*Indian Red, Colcothar*).—These iron-oxide pigments are obtained by grinding red-hematite-iron ores, levigating with water, and then drying. Although they vary much in composition, they contain usually from 88 to 95 per cent iron oxide and the remainder clay and silica.

Their properties are very similar to those of the Venetian reds, but for metals the natural oxides are much better, since they contain no ionizing calcium sulfate nor any free acid.

Chrome Red (*American Vermilion, Basic Lead Chromate*) [$Pb_2(OH)_2CrO_4$].—This is the most highly basic of the lead-chromate pigments. It is obtained by boiling white lead with a solution of potassium dichromate and then treating the mass with a small quantity of sulfuric acid to brighten the shade.

Its particles are granular and coarse. Its general properties resemble those of chrome yellow (which see). For painting on metal it has very excellent inhibiting powers; it is among the best of pigments for this purpose.

THE BROWN PIGMENTS

Prince's Metallic Brown (*Prince's Mineral*).—This is an oxide of iron pigment mined as an ore. It occurs both as the hydrated oxide and as the carbonate, which are roasted at a red heat and then are ground. The pigment contains a high percentage of alumina and silica.

It has a good brown color and is very permanent. Its particles are generally fine but of varying sizes. It forms compact paint coats that are very good for both wood and metal.

Umber is also a natural pigment consisting of a clay base containing iron oxide. It belongs to the same general class as the ochers but differs from them in that it contains considerable amounts of the brown manganic oxide. The raw umber is of a dull grayish-brown color, but upon burning (calcining) it turns to a reddish brown, which color is very permanent. Its properties in general very much resemble the properties of the ochers.

Vandyke brown consists of a mixture of red iron oxide and yellow ocher, darkened with lampblack or some bituminous compound. It is very permanent upon exposure, and works well in oil, but it seems to cause the paint to dry poorly.

THE BLACK PIGMENTS

Lampblack is made by burning heavy refuse oils in a limited supply of air. It is in reality a soot, averaging about 98 per cent pure carbon. There are various grades. The soot from the flame is received into different chambers arranged in a series. The black that collects in the first chamber contains a certain amount of oily matter which has passed off unburned. On this account it has a brownish or grayish tint. That in the farther chambers is freer from the oily deposit. Lampblack in general possesses a grayer tone than many of the other carbon pigments so that it may often be recognized by this fact. Lettering made with lampblack will appear light on a background painted with ivory black or drop black.

Its particles are very fine and uniform. It is very permanent and seems to preserve the oil with which it is mixed, thereby producing very permanent paints. It outlasts lead and zinc paints for wood. It has a specific gravity of 1.82 and grinds in 75 per cent of oil to a stiff paste.

It retards drying. This property may be due to the effect of the hydrocarbon oil it contains. Toch says that less than 1 per cent of unburned oil will retard the drying to such an extent as to render the pigment unfit for use.

Carbon Black (*Gasblack*).—This pigment also contains about 98 to 99 per cent pure carbon and is obtained by burning hydrocarbon gases, as natural gas or acetylene gas, in a limited supply of air. It very closely resembles lampblack in most of its properties.

Drop Black (*Vine Black, Ivory Black, Frankfort Black*).—This pigment is made by heating a variety of materials, such as waste cuttings from ivory, vine shoots, cork cuttings, coconut shell, etc., in retorts or crucibles; the residue contains the greater part of the carbon of the original material. The name "drop black" is applied to this substance because the product after grinding is mixed with a little glue water and made into pear-shaped drops for sale. Drop black always contains mineral matter resulting from the ash of the burned material, particularly potassium salts, which are somewhat hygroscopic; consequently, it should be washed and dried carefully. It is very black; lampblack appears gray in comparison.

Graphite is an allotropic form of carbon formerly obtained only native as a mineral, but more recently it has been prepared artificially, notably by the Acheson process (page 79). The native variety occurs both in the crystalline and amorphous form. Both the natural and artificial varieties contain impurities, such as silica, iron oxide, and alumina. The natural form contains the greater amount of such substances and, therefore, the less carbon. The natural variety contains about 80 per cent of carbon, while the artificial variety contains about 90 per cent.

Graphite causes very slow drying of the oil with which it is used; the long life of graphite paints may be due to this fact. Not only will the formation of the linoxyn be delayed but the continued oxidation of the linoxyn after it has formed will also be slow. It is this continued or progressive oxidation of the linoxyn of many paint coatings, notably those containing pigments possessed of marked drying properties, that causes the linoxyn soon to become very inelastic and subject to early failure. Since the oxidation is delayed in the graphite paints, the film remains elastic for a longer time and, therefore, is much less readily disintegrated.

The Lake Pigments[1]

The lake pigments are made by precipitating some organic coloring matter, usually a coal-tar dye, upon some suitable mineral base, as barytes. The base here is similar in its action to the cloth in ordinary dyeing; it is merely a carrier of the color. In addition to barytes, many other white pigments are used as bases. The colors used should be insoluble in water, oil, and the ordinary solvents used in paints and varnishes. It often happens, however, that they are not thus insoluble and then the coloring matter of the pigment dissolves in the vehicle; in repainting, it may even diffuse through the superimposed layer of paint. If the top coat is of a different color, the diffusion is very objectionable. This diffusion of color is known among painters as "bleeding." It may be overcome by taking advantage of the well-known property of carbon in absorbing coloring matters. Charcoal, lampblack, boneblack, and similar substance possess this property to such a degree that they are used to clarify colored solutions. In repainting over a paint containing a lake pigment, any tendency toward "bleeding" may be overcome by applying first a coat of black paint containing pigments of this sort.

Lake pigments are made up in all colors and are much used in painting. They are usually fairly permanent in respect to light and atmosphere and very beautiful effects can be obtained by their use.

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[1] The term "lake" has its origin in the Italian word "lacca," which was the term used to designate the scum that gathered on the top of the vats when dyeing with lac dye, which was much used by the old Italian dyers. Tin and aluminum oxides were used to fix the color on the cloth; the scum consisted of these oxides colored. Since the present lake pigments consist of minerals colored by means of dyes, the English modification of the Italian name has been applied to them.

Paint and Varnish Oils

The oils used as the vehicle or medium with which the pigment in paints or the resinous material in varnishes is mixed are those that are known as drying oils. They are so named because they have the property of being converted into a more or less hardened film when exposed to the air. These oils make up a rather limited group or subdivision included under the general head of fatty oils; consequently, before proceeding to a discussion of the properties of the drying oils, it will be advantageous to consider the fatty oils in general.

The Fatty Oils.—Under this head are included both the liquid and the solid fats; there is no sharp line of demarcation between the two. All of the liquid fats become solid at low temperatures, although some of them remain fluid at temperatures considerably below the freezing point of water. On the other hand, even the hardest fats become fluid at about 50°C. Still those that are fluid below 20°C. are usually called oils, and those that are solid above this temperature are known as fats.

The specific gravity of the oils and fats ranges between the limits of 0.910 and 0.975 at 60°F.

The fatty oils when pure are *odorless*, *tasteless*, and *colorless;* that which is considered characteristic in these respects is due to the presence of certain foreign substances.

Solubility.—The fatty oils are almost completely insoluble in acetone and cold alcohol, but the solubility increases in boiling alcohol. They dissolve very readily in ether, chloroform, carbon tetrachloride, carbon bisulfide, benzole, paraffin oils, and petroleum naphtha. Castor oil is, in respect to its solubility, a distinct exception to the other fatty oils. It is quite soluble in cold alcohol, while it is only slightly soluble in paraffin oils and petroleum naphtha.

Non-volatility.—Fatty oils do not evaporate upon exposure and they cannot be distilled even under reduced atmospheric pressure. They cannot be vaporized by heat without destruction; *i.e.*, in the true sense they cannot be boiled. If the products driven off by heat are collected and condensed, the original oil is not obtained, but in its stead there will be true gases, and waxy, resinous, or tar-like substances. Because of this characteristic the fatty oils are often called *fixed oils.* The decomposition begins at about 250°C., but they can be heated to just below this point with practically no change.

Composition.—The fatty oils do not consist of single compounds; they are made up of mixtures of substances known as triglycerides. These glycerides are products resulting from a union of the trivalent glyceryl radical C_3H_5 of the alcohol glycerine $C_3H_5(OH)_3$ with three monovalent fatty-acid radicals of such acids as stearic, oleic, palmitic, and others. Although it is not likely that reactions of this sort occur in the living organism producing the oil, the following equation between glycerine and *palmitic acid* will serve to illustrate their composition:

$$C_3H_5(OH)_3 + 3H(C_{16}H_{31}O_2) \rightarrow C_3H_5(C_{16}H_{31}O_2)_3 + 3HOH$$

The products are triglyceryl palmitate, known also as palmitin, and water. Other acids, whose triglycerides occur commonly in these oils, are:

Stearic acid, $H(C_{18}H_{35}O_2)$ or $C_{18}H_{36}O_2$, belonging to the $C_nH_{2n}O_2$ series.

Oleic acid, $H(C_{18}H_{33}O_2)$ or $C_{18}H_{34}O_2$, belonging to the $C_nH_{2n-2}O_2$ series.

Linoleic acid, $H(C_{18}H_{31}O_2)$ or $C_{18}H_{32}O_2$, belonging to the $C_nH_{2n-4}O_2$ series.

Linolenic and *isolinolenic acids,* both of which have the same formula, $H(C_{18}H_{29}O_2)$ or $C_{18}H_{30}O_2$, belonging to the $C_nH_{2n-6}O_2$ series.

The corresponding triglycerides of these acids are stearin, olein, linolein, linolenin, and isolinolenin. Palmitin and stearin are white crystalline or semi-crystalline solids, melting at 61 and 72°C. respectively. These two compounds occur in the greatest proportion in the solid fats; the others mentioned are fluid at atmospheric temperatures. Olein is the principal constituent of the liquid fats, especially of olive oil. Olein, linolein, linolenin, and isolinolenin are unsaturated compounds; *i.e.*, they have certain "double bonds,"[1] and are able to absorb more or less oxygen. Olein has one, linolein two, and linolenin and isolinolenin have three such "double bonds."

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[1] The "double bonding" spoken of here is similar to that of the unsaturated hydrocarbons (see p. 49).

Drying and Non-drying Oils.—It is to the presence of the oxygen-absorbing triglycerides that paint oils owe their drying ability. When exposed to the air in thin layers they oxidize to form dry, hard, and generally transparent films, which are insoluble in water, alcohol, and to a very great extent in ether. If the oil is in a rather finely divided state, as in the meshes of oily cotton waste or rags, so that a large surface is exposed for atmospheric action, the heat developed by the resultant vigorous oxidation is sufficient to raise the temperature of the substance to its kindling point and spontaneous combustion will occur.

The non-drying oils, when exposed to the air, do not harden but become disagreeable in smell and acid in taste; they are then said to be rancid. When long exposed they may oxidize and decompose sufficiently to become viscid, but they never harden to a solid mass even though they be exposed to the atmosphere for years. Examples of this sort are whale blubber oil, lard oil, tallow oil, olive oil, and others. Certain oils have properties midway between the drying and non-drying oils and are therefore known as semi-drying oils, but the lines of division between the classes are not distinct.

Cause of Rancidity.—It is not known just what the change is that causes rancidity, but Lewkowitsch says it is something more than mere acidity, although a certain amount of free acid is no doubt always produced first. Fresh vegetable oils, however, usually contain considerable free acid and are not rancid.

Absolutely dry air, if light is excluded, has no action on any of the fatty oils. It is practically impossible, however, completely to exclude moisture in storing the commercial oils, so in any case small amounts of free acid will be produced. The formation of free acid is due to the fact that the oil becomes to a slight extent *hydrolyzed*; *i.e.*, the direct reversal of the action shown by the equation in the preceding discussion of composition takes place. This hydrolysis reaction is probably brought about, according to Lewkowitsch, by the presence in the oil of certain soluble ferments derived from the oil-producing seeds. It is also helped along by albuminous and gelatinous substances present in unrefined oils. The fatty acid and perhaps the glycerine also, which are produced, then further decompose, and the oil becomes rancid.

The fatty oils are quite readily hydrolyzed by heating with water to 200°C. or more. The reaction occurs at much lower temperatures in the presence of acids—even as low as 100°C. in the presence of hydrochloric acid.

Saponification.—When the fatty oils are treated with alkalies, glycerine is liberated and soaps are formed, as is shown by the action of caustic soda on stearin:

$$3NaOH + C_3H_5(O{\cdot}OC_{18}H_{35})_3 = 3Na(O{\cdot}OC_{18}H_{35}) + C_3H_5(OH)_3$$

The soap produced in this case is a sodium stearate.

Examination of Oils and Fats.[1]—When oils and fats are under examination to decide upon their suitability for special purposes, certain physical and chemical properties are determined. These properties vary in amount in the different oils, and so, aside from showing the use for which the oil is suitable, their determination serves to identify the oil. The numbers which show the measure or degree of these properties are referred to as "values" or "numbers" or often as "constants." This last term must not be construed to mean that the numbers are in reality constant for any oil, because the numbers will vary for different pure specimens of the same kind of oil, although the variation will be within well-defined limits.

The values or numbers usually determined are specific gravity, the saponification number, acid number, iodine number, and for paint oils especially, the elaidin test may be applied. In a complete examination of the oil many other determinations and tests are made.

Specific Gravity may be determined by means of the hydrometer, the hydrostatic balance, the specific-gravity bottle or pycnometer, or in other ways. The specific-gravity bottle furnishes the most accurate results. By it, the relation between the weights of equal volumes of oil and water at 60°F. is obtained by direct weighing. The weight of the bottle when accurately filled with pure water is first determined, and then its weight when filled with the oil. The hydrometer allows greater speed in making the determination but furnishes less accurate results. (For the method of using hydrometers see page 662.)

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[1] LEWKOWITSCH, "Chemical Technology and Analysis of Oils, Fats, and Waxes."

The saponification value shows the number of milligrams of potassium hydroxide required for the complete saponification of 1 g. of the oil sample, *i.e.*, for complete neutralization of the *total* fatty acid, whether free or in combination with the glyceryl or other radicles. From this value may be calculated the mean molecular weight of the fatty acids present. Since the hydrocarbon oils, mineral, and rosin oils, are unsaponifiable. this test serves to show their presence when they are admixed with the fatty oils.

The saponification value is determined by boiling the sample with potassium hydroxide dissolved in alcohol, and then determining the excess of potassium hydroxide by titration with standard hydrochloric acid, using phenolphthalein as an indicator.

As a qualitative test, the following is fairly accurate: Dissolve about ½ g. of potassium hydroxide in about 5 cc. of 95 per cent ethyl alcohol, add a few drops of the oil to be tested, and keep at the boiling point for about 5 min. Then add 3 or 4 cc. of distilled water. If the solution remains clear, fatty oil only is present; if it becomes turbid, then mineral oil, or other hydrocarbon oil, is indicated. The fatty oil is converted into soap, which is soluble in water; hydrocarbon oils are not saponifiable. If the sample is not sufficiently boiled, turbidity may be due to unsaponified fatty oil also. The amount of turbidity will vary according to the mixture, but the test cannot be relied upon to show less than 2 or 3 per cent of hydrocarbon oil.

The acid value shows the number of milligrams of potassium hydroxide needed to neutralize completely the *free* fatty acid in 1 g. of sample. The difference between the saponification number and the acid number is known as the "ester number." Esters are compounds produced by the reaction of an alcohol with an oxyacid (page 516). In the fatty oils, of course, the esters are the glycerides.

The determination is made by titrating the sample with standard potassium hydroxide.

The iodine value represents the percentage of iodine absorbed by the sample, *i.e.*, the number of centigrams taken up by 1 g. of the oil. The absorption is due mainly to direct addition but may in part consist of substitution of iodine for hydrogen atoms. This value serves to show the proportion of unsaturated fatty acids present, both free and combined. The direct addition of iodine depends upon the fact that in the unsaturated radicals, which are those of oleic, linoleic, and linolenic acids, there exists a number of "double bonds." For each "double bonding" 2 iodine atoms are absorbed. Then, on this basis, the oleic acid should absorb 2, the linoleic 4, and the linolenic 6 iodine atoms. Since these unsaturated compounds also react quite readily with oxygen, the iodine value is taken as a measure of the ability of an oil to oxidize with the formation of a dry film.

The Elaidin Test.[1]—This is not a quantitative test but still it aids in distinguishing between the non-drying oils and those that are drying or semi-drying. It depends upon the fact that nitric oxide (NO) is able to convert the liquid olein into its solid isomer elaidin, *i.e.*, into a substance having the same empirical formula as olein, but a different structural arrangement of the atoms within the molecule. The glycerides of linoleic and linolenic acids are unaffected, hence the drying oils, which contain a greater proportion of such compounds, remain liquid or at most become only pasty. Since lard oil and olive oil consist largely of olein, this test is especially applicable to them.

Of oil 5 g. are mixed with 7 g. of somewhat diluted nitric acid, specific gravity 1.34, and to the mixture is added about 1 g. of copper. The container is placed in cold water, about 15°C., and the mass is well stirred for about 1 min. After standing for 2 or 3 hr. the solidity of the sample is examined.

The Drying Oils

Linseed Oil.—For the manufacture of paints and varnishes linseed oil is most important. It is obtained from the seed of the common flax, which is grown quite generally over the central, western, and northern portions of the United States, although the bulk of the seed comes from Minnesota and the Dakotas.

The flax is cultivated extensively also in Canada, Argentine, India, and southern and western Russia. The seed is usually the sole object of the cultivation; the fiber of the plant is generally wasted.

Separation of Oil from Seed.—Linseed oil may be obtained from the seed by any one of three different methods: the hydrau-

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[1] Gill, "Oil Analysis," p. 51.

lic-press method, the continuous-expeller method, and the extraction method.

The *hydraulic-press method* is the oldest of the three, and much of the oil is still obtained in this way. The seed is crushed to a very fine meal between chilled-iron rolls, and the meal is then heated to about 80°C. with constant stirring. When sufficiently hot, it is molded into cakes weighing about 20 lb. The cakes are wrapped in cloth and pressed with hydraulic pressure, which amounts at a maximum to about 2 tons per square inch. The seed is but once pressed and the resultant cake, which still contains from 4 to 8 per cent of oil, is used as cattle food. Oil obtained in this way is known as *hot-pressed oil.*

FIG. 81.—Presses for the production of linseed oil.

In order to remove suspended particles of meal, the oil is filtered, but this purification is not sufficient since there are always present in a dissolved state certain amounts of albuminous or mucilaginous substances and water. To precipitate dissolved matter as far as possible, the oil is conducted into storage tanks and allowed to stand from 4 to 6 months. The resultant sediment is known as "foots." The longer it is stored the better, since it seems to be characteristic of linseed oil to deposit foots almost idefinitely. The supernatant clear oil is the raw oil of commerce.

Cold-pressed oil is of superior quality but the quantity produced is relatively small. The oil is lighter in color, and more fluid than the hot pressed; it contains less sedimentary matter, probably because it contains less solid fats and foreign substances. About 15 per cent of oil is left in the cake; in consequence, this method is less in favor among the oil producers. In the *continuous-expeller method* the crushed seed is forced by a screw through a cone-shaped grating. The oil trickles through the grating and the pressed meal comes out at the end. This process requires less hand labor than the older method, but allows somewhat more of the oil to remain in the meal.

In the *extraction process* the oil is dissolved from the meal by leaching with petroleum naphtha. The naphtha is distilled from the extract and used over again. It is very difficult to remove the last traces of naphtha, and the oil obtained by this method generally has the odor of the solvent.

Properties of Linseed Oil.—The properties of the oil depend somewhat upon the origin of the seed; for example, oil obtained from seed grown in the neighborhood of the Baltic Sea has a considerably higher iodine value than that from Argentine.

The following values have reference to oil obtained from the North American seed:

At 60°F. the *specific gravity* varies from 0.932 to 0.936. A falling below 0.932 would suggest the presence of fish oil or mineral oil.

Its *saponification value* ranges from 189 to 195. It should contain no more than 1.5 per cent of unsaponifiable matter. All hydrocarbons, as mineral oils and rosin oil, are unsaponifiable and hence would be shown by this test.

The *acid value* is quite variable, but is usually less than 7. The presence of rosin oil would greatly increase this figure since it is highly acid. On the other hand, the acid figure for mineral oil may be zero.

The *iodine figure ranges from* 170 to 187, which is the highest value of all the known fatty oils. Linseed oil does not yield a solid mass in the *elaidin test.*

It *freezes* at $-28°$C., which is extremely low. Walnut oil is the only oil having a lower freezing point. Menhaden oil freezes at about 0°C., rosin oil at −6, cottonseed at −15, and the heavy mineral oils at about −18°C.

The *adulterants* to be looked for in linseed oil are mineral, rosin, corn, cottonseed, menhaden, hemp, and rapeseed oils. The cheapest and perhaps the most frequently used are mineral and rosin oils.

If the saponification value of linseed oil is low, it may be adulterated with a hydrocarbon oil, as mineral or rosin oil, but a normal saponification value is no proof that the oil is not adulterated. An oil rich in olein, such as cottonseed, might be present; the mixture would still be completely saponifiable. If the iodine value is low, the adulterant might be either a hydrocarbon oil or an oil rich in olein. If both the saponification and iodine values are low, then a hydrocarbon oil is indicated.

Drying of Linseed Oil.—All of the important uses of linseed oil depend upon its great power to absorb oxygen, whereby it changes from the fluid into the solid state. It possesses this power to a greater degree than any other oil. Of the total glycerides in linseed oil, 15 per cent. are solid fats and 85 per cent are fluid; the latter are endowed with distinct drying properties. Oxidized linseed oil is called *linoxyn;* it is a solid, tough, and somewhat rubber-like substance.

The formation of linoxyn does not depend upon the direct addition of oxygen merely; as is usually the case during the oxidation of organic substances, water and carbon dioxide are given off. An experiment on the drying of linseed oil[1] conducted for 74 days showed that the total amount of oxygen absorbed was 37.80 per cent of the weight of the sample; the amounts of water and carbon dioxide given off at the same time were 14.15 and 5.21 per cent, respectively. Through the elimination of these compounds, the oil lost 1.87 per cent of its carbon, and 14.73 per cent of its hydrogen; but because of the oxygen combined in the linoxyn, the residue was still 18.05 per cent heavier than the oil before drying.

The drying of linseed oil in the absence of any drier is at first slow, but after a certain stage is reached, it dries rapidly. This is probably due to the formation of peroxides during drying which

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[1] Olsen and Ratner, "The Decomposition of Linseed Oil during Drying," *Trans. Amer. Inst. Chem. Eng.*, **5**, 100.

act as catalytic agents and hasten the process. The oil dries more rapidly in the light than in the dark. This is undoubtedly due to the action of the actinic or ultraviolet rays. Because of the bleaching effect of these rays, white paints that dry in the light are freer from any yellowish tinge than those that dry in the dark.

Linoxyn is practically insoluble in most of the solvents of linseed oil, hence dried paint and varnish films cannot be readily removed by these solvents. Certain solvents for linoxyn are shown later under "Paint and Varnish Removers." Linoxyn is attacked by the alkalis; hence paints and varnishes are injured by contact with them and may be removed by their use if desired.

"Boiled" Oil.[1]—The drying of linseed oil may be hastened by the so-called "boiling" of the raw oil. This boiling consists of heating the oil with driers,[2] sometimes in an open kettle with direct fire, or more usually, in a steam-jacketed kettle or with steam coils, to about 150°C. During the heating, the driers dissolve to some extent and a certain amount of polymerization[3] of the oil is believed to take place. The driers used consist usually of the linoleates, resinates or borates of lead, manganese, and other metals. Boiled oils prepared with lead driers contract upon oxidizing while those with manganese expand. Usually the two compounds are used together in quantities sufficient to introduce about 0.5 per cent of metallic lead and 0.02 per cent of metallic manganese. Raw oil dries in 3 or 4 days when exposed in a thin layer, while the boiled oil dries to a hard film in less than 24 hr., even in as little as 8 hr. indoors, if conditions of temperature and humidity are favorable. This increased rate seems to be due to the fact that the metallic compounds act as catalytic agents. Boiled oil is usually a dark-red color; the color depends upon the amount and kind of drier used, and the length of time and the degree to which the oil has been

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[1] It must be understood that the term "boiled" as applied to any of these prepared oils is incorrect, since as was explained on p. 489, none of the fatty oils can, in the true sense, be boiled.

[2] For a discussion of Driers, see p. 503.

[3] A substance is said to polymerize when it changes into another form having the same elements in the same proportion but a higher molecular weight such as would result from a combination of 2 or more molecules.

heated. Boiled oil costs usually about 1 ct. per gallon more than the raw oil.

A "cold-boiled" or "bung-hole" boiled oil is prepared by mixing with the cold or only slightly heated raw oil comparatively small quantities of concentrated solutions of the metallic compounds or driers. These concentrated solutions consist of metallic resinates dissolved in hot linseed oil and turpentine. Such "boiled" oils are quite inferior products.

Bleached Oil.—As has been stated previously, the glycerides which compose the fatty oils are colorless, but the oils themselves are usually colored to some degree by the presence of impurities. The yellow color of linseed oil is objectionable for the making of white paints and pale varnishes. The color can be removed in a large measure by the oxidation, or some other chemical transformation, of the colored substance. The process generally employed consists of the addition of sulfuric acid and the blowing of air into the oil at the same time. A cloudiness develops after which the oil is allowed to stand until settling takes place, or it is filtered. Various other bleaching agents such as oxides and peroxides are employed. Chemically bleached oil is said to wear not so well as the raw oil.

Chinese-wood or Tung Oil.—This oil is obtained by pressure from the nut of the tung tree, native to China and Japan. The color of the oil varies from pale yellow to dark brown and it has a strong characteristic odor, which may be used as a ready means of identification.

The following values for tung oil are given by Toch: specific gravity, 0.935 to 0.941; saponification value, 155 to 190; and iodine value, 156 to 165. Lewkowitsch says that the Chinese variety of tung oil has a specific gravity of 0.941 and that this is the highest of any known oil except castor oil. Tung oil consists chiefly of the glycerides of oleic and elaeomargaric acids; the latter acid is $C_{17}H_{31}\cdot COOH$.

Tung oil differs from all the other oils in respect to two rather noteworthy characteristics. In bulk, when exposed to light, a flocculent white precipitate is produced, which gradually increases in amount until after some months the oil becomes a solid whitish mass. This change is known as the *light break*.

When heated to about 250°C. the oil *coagulates* with the formation of a jelly-like mass. After cooling it is not again made fluid by heating nor by the addition of the ordinary solvents. This gelatinization is believed to be due to polymerization. It is not due to oxygen absorption.

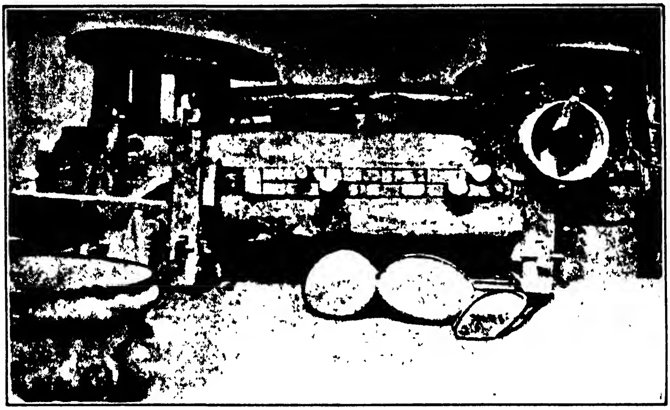

FIG. 82.—Wedge press used for extracting Chinese wood oil. Basket of nuts and oil cake in foreground.

When raw tung oil is brushed out in a thin film, it dries with extreme rapidity, in 30 to 50 min. But raw tung oil is not suitable for paints and varnishes, since its dried film is whitish, opaque, and wax-like, without elasticity. Also, it has a tendency to wrinkle and does not adhere to the surface on which it forms. With proper treatment the oil acquires an ability to dry to a hard, dense, tough, and elastic film, said to be more durable than the linseed-oil film and more impervious to water. The necessary treatment, according to Toch, consists of heating the oil to about 180°C. and adding from 12 to 15 per cent of organic salts of lead and manganese. These organic salts prevent the coagulation. Tung oil is much used in conjunction with linseed oil. In this case the linseed oil is added just subsequent to the organic salt. After sufficient cooling, the prepared oil is thinned with turpentine or benzine or a mixture of both. The treated oil dries much more slowly than the raw oil.

A tung-oil film is less spongy and porous than a linseed-oil film, with consequently less tendency to absorb and allow the passage of moisture. On this account it has proven very useful for the manufacture of enamels, waterproof paints, and varnishes. It is excellent for out-of-door work. Toch says that by the use of tung oil, paints can be prepared that dry well in damp atmospheres.

The film from the prepared oil is hard and not readily scratched. When it is used in large amount with a small amount of resin, floor varnishes can be produced that do not show heel marks.

According to Ware and Schumann[1] excellent varnishes can be made by the use of tung oil and common rosin or colophony. This is rather remarkable, since rosin lacks hardness and is very brittle. Equally good results are not secured when rosin is used in this way with other oils. The value of the oil has been said to lie in its ability to form actual combinations with the abietic acid of the rosin.

Soya-bean Oil.—The soya bean is native to Manchuria, but has been rather extensively introduced into the United States, especially in the southern portion. There are as many as 280 known varieties, and more may exist. All varieties do not yield oil suitable for paints; much of it is used for making food products and soaps.

From 10 to 15 per cent of oil is obtained from the soya bean by the method of hot pressure. Excepting that it has perhaps a slightly darker color, it is very similar in all its physical characteristics to linseed oil, so that it is somewhat difficult to distinguish between the two. Soya oil contains about 15 per cent of saturated fats, largely palmitic. The unsaturated fats are chiefly the glycerides of oleic and linoleic acids, about 56 per cent of the former and 20 per cent of the latter. The values are about as follows: specific gravity, 0.925; saponification value, 192; iodine value, 130.

The raw oil produces an elastic film but dries rather slowly, although it can be converted into a very suitable drying oil by the use of the proper driers, which according to Toch, are mixtures of the tungates and resinates of lead and manganese. The tungates are the soaps produced by the reaction of lead and manganese compounds with tung oil. The resinates are the

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[1] *Drugs, Oils Paints,* **30,** 52–54.

products of the reaction of the metallic compounds with common rosin. The soya oil is said to dry to a hard resistant film in 24 hr. when used with 5 to 7 per cent of this drier. It is very susceptible to the drying action of the tungate of trivalent cobalt, but the cobaltous compound is not active.

The film of soya-bean oil is said to wear not so well as that of linseed oil for exterior use, but is reported to be equally good for interior work. The oil is not used alone but in conjunction with linseed oil.

Fish Oil.—The fish oil generally used in paints is that obtained from the menhaden. From May to November, this fish appears along the Atlantic coast, especially off the coast of New Jersey, in enormous quantities; hundreds of thousands of tons are taken annually. A first quality of oil is obtained by boiling the fish with steam and allowing the oil to rise. A second quality is obtained by pressure. The fish residue is used as fertilizer. The chief objection to the oil is its odor, but this is largely removable by special processes.

Its specific gravity is about 0.931; saponification value, 190; and iodine value, 150 to 165. It is not suitable for paints in the raw state, but when treated with the tungate and resinate driers becomes a fair drying oil. It is a very good oil to withstand combined heat and exposure to the weather. It does not blister and peel under these conditions as readily as other paint oils, and is, therefore, especially suitable for smokestacks and boiler fronts.[1] Mixed with linseed oil it is used for waterproof paints. It has been suggested that its content of stearin may account for its waterproofing qualities.

Rosin Oil.—Although this oil is not a fatty oil and does not possess to any extent the properties that a good paint oil should have, it is nevertheless frequently introduced into paint oils as an adulterant, and on this account mention is made of it here.

When rosin is subjected to destructive distillation, various decomposition products are obtained. Chief among these products is rosin oil; there is about 85 per cent of it in the distillate. The crude oil is dark and viscous, with a marked characteristic odor, and because rosin is carried over mechanically to a small extent during distillation, it is acid in character.

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[1] TOCH, "Chemistry and Technology of Mixed Paints," p. 95.

The oil is refined and various grades are produced with colors varying from dark red to pale yellow. The refined oil consists almost entirely of hydrocarbons and is unsaponifiable. It has a bluish bloom or fluorescence, which is less pronounced in the more highly refined oils. It dissolves readily in ether, chloroform, turpentine, and petroleum spirit. It has some drying properties due to oxygen absorption. It is among the cheapest of all the oils and is consequently much used to adulterate other oils.

DRIERS

Action of Driers.—The drying of the paint and varnish oils is dependent upon their absorption of and combination with oxygen; most of the paint oils when exposed in a thin film will eventually dry thus with the formation of a hard elastic film. The time required for this natural drying, however, is generally so long that dust and dirt from the atmosphere collect and are held by the undried film, which makes it very unsightly. To lessen the time of drying, certain metallic compounds are introduced into the oil. The method whereby these substances hasten the drying processes is not definitely established. There is but little doubt, however, that their effect is largely catalytic; *i.e.*, they act as a medium whereby oxygen from the air is caused to be united with those glycerides in the oil that have the unsaturated bonds, without themselves permanently entering into the product of the reaction. Being catalytic, they are able to work continuously; on this account only a small quantity of drier is necessary, generally less than 1 per cent is sufficient.

Although these driers shorten the period of drying, undesirable results may develop from their use. Their action does not cease with the conversion of the oil into a dry film, but goes on indefinitely, so that if enough has been used, the film is finally oxidized to destruction. If a paint or varnish could be allowed to dry without the use of a drier its life would likely be longer.

Materials Used.—The driers consist of various compounds of such metals as lead, manganese, cobalt, and vanadium. The efficiency of the drier seems to depend more upon the amount of *metallic element* present than upon the compound in which it is. If the different compounds of each metal are used in such quantities that the same amount of the metallic element is introduced into the oil, the drying effects will be about equal.

Classes.—The driers may be divided into two general classes: oil driers and japan driers; the former are used in the dry and the latter in the liquid state.

Oil driers are chiefly the *inorganic compounds* of lead and manganese, and are so named because they are added directly to the oil. They may be mixed with the cold oil, but are not readily assimilated unless the oil is heated as in "boiling." The following metallic compounds are used as oil driers:

Lead Compounds.—*Litharge* is the monoxide of lead. It is yellowish orange in color and may occur either in the powdered or crystalline form. The crystalline form is obtained by fusing lead in an oxidizing flame.

Red lead or *minium* (Pb_3O_4) is made by heating litharge to just below its melting point in a current of air. Red lead causes a brittleness in paint films, while litharge makes them elastic.

Lead borate (PbB_4O_7) and *lead acetate* [$Pb(C_2H_3O_2)_2 \cdot 3H_2O$] are both white. They are more easily introduced into the oil and darken it to a less extent than the oxides.

Manganese Compounds.—*Manganese dioxide* or *peroxide* (MnO_2), sometimes called manganese black, has a very vigorous drying action but being black it darkens the oil and this is objectionable. Other manganese salts used are the sulfate, acetate, and borate, all of which have a white or pinkish color and therefore, produce less darkening effect than the black oxide.

Japan driers are liquid driers, consisting of the *organic compounds*, chiefly the resinates and linoleates of lead, manganese, vanadium, and cobalt dissolved in benzine or turpentine. Their chief advantage is that they dissolve readily in these solvents, and the solution in turn readily mixes with the oils at ordinary temperatures. Their drying action is rapid.

Two general methods may be employed for the preparation of both the resinates and linoleates. The metallic oxides may be dissolved in fused or melted rosin, which produces the resinates. In a similar manner the oxides may be caused to combine with very hot linseed oil, which produces the corresponding linoleates. Or the soluble sodium resinate or linoleate may be first formed by saponifying rosin or linseed oil with caustic soda in the ordinary way. Then, if to a water solution of the resinate or linoleate, solutions of the salts of the metals are added, the corresponding resinate or linoleate will precipitate out. This is collected, washed, and dried.

By dissolving these resinates or linoleates, made by either method, in turpentine or benzine the japan driers are produced.

Comparison of Driers.—Manganese compounds quickly start the drying action and cause rapid surface drying. Lead compounds cause the drying to proceed more generally through the film and should ordinarily be used in larger quantities than the manganese compounds. The percentages[1] found to be most efficient are 0.5 per cent of lead and 0.05 per cent of manganese (*i.e.*, sufficient of the drier to furnish this quantity of metallic content), when used alone in linseed oil. Or still better results are obtained by a combination of the two, in which case 0.5 per cent of lead and 0.02 per cent of manganese are employed. Vanadium compounds form more active driers than the compounds of either lead or manganese. Vanadium resinate hardens linseed oil 2½ times as fast as manganese and 5 times as fast as lead, but it cannot be used for white paints because it forms brownish films.[2] The cobaltic compounds are the most energetic of all; they are slightly more effective than the vanadium compounds.

SOLVENTS AND DILUENTS

Under this head are included a group of organic liquids employed to dissolve oils, resins, and other materials, and thereby to facilitate the application of the paints, varnishes, and lacquers in which the dissolved materials are used. Due to the fact that after the material has been applied, these liquids are not wanted in the film, a suitable volatility is of scarcely less importance than a suitable solvent power. For convenience of study, this group of solvents and thinners may be classified as follows:

- Turpentines
- Petroleum hydrocarbons
- Coal-tar hydrocarbons
- Alcohols
- Esters
- Ketones

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[1] "Theory of Driers and Their Application," *Bull.* 23, Sci. Sec., Paint Manufacturers Association of the United States, 1910.

[2] "Rare Metals" in "Mineral Resources of the United States," p. 451, 1927.

All of the liquids discussed under these headings are inflammable, and their vapors are explosive when mixed in proper proportions with air. Consequently, when using them, suitable precautions must be taken.

American Turpentine.—Under the general head of turpentines a great variety of compounds is included. The name a variety bears on the market is usually derived from its source, such as American, Russian, French, Indian, and others. In the present study only the American variety, which constitutes considerably over half of the world's total output, will be considered.

FIG. 83.—Turpentine forest. Showing method of scoring trunks to secure yield of turpentine.

American turpentine is obtained from a balsam exuded from certain varieties of pine found chiefly in the Carolinas, Georgia, and Florida. The chief producer is the long-leaf pine (*Pinus Palustris*) known also as the southern yellow or hard pine. The balsam or oleoresin is an aromatic fluid consisting of a mixture of a resin with a volatile liquid; it is generally called "crude turpentine." In preparing the commercial product the usual practice is to distill the balsam in copper stills with open steam. Sometimes it is distilled with direct fire, but much care is needed then, since overheating injures the residue. Recently distillation has been carried out in electrically heated retorts in which the heat can be readily controlled. The distillate is the *spirit* or *oil of turpentine.* In steam distillation it will be mixed with water, which separates on standing. The residue left behind in the retort is *rosin* (page 533). The balsam yields from 10 to 25 per cent of turpentine, which seems to be a product resulting from reactions occurring during distillation, because if the rosin is dissolved in it, the original balsam is not obtained.

Turpentine is a water-white, volatile liquid consisting chiefly of pinene ($C_{10}H_{16}$). It is used in paints and varnishes to dilute them and to increase their flowing qualities. It is exceptionally suitable for this purpose, because, although it is volatile, it does not evaporate rapidly; hence, it keeps the freshly applied film fluid for a sufficient length of time that the marks of the brush, which are unavoidable, will flow out and disappear. Many of the turpentine substitutes, for example some of the light petroleum products, *i.e.*, gasolines and naphthas, are too highly volatile; they allow the film to lose its fluidity before the irregularities have been eliminated. Petroleum products can be prepared, however, that very closely resemble turpentine in this important property.

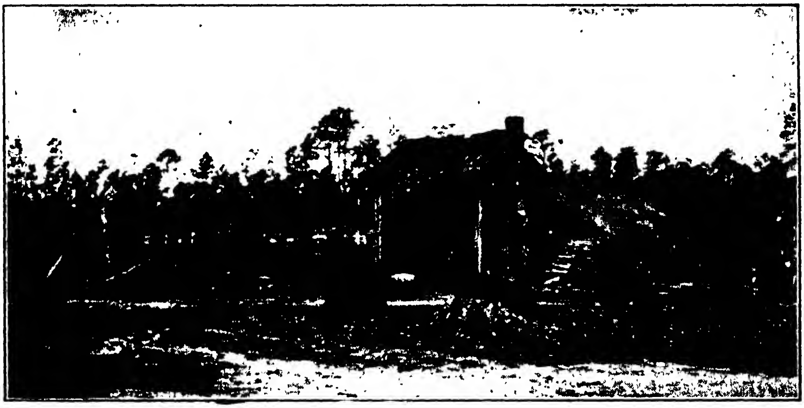

FIG. 84.—Turpentine still.

Turpentine has a characteristic aromatic odor, which, in small quantity is not unpleasant; but if breathed for an extended period, it may become objectionable. Upon some persons it has a marked physiological action, causing headache and nausea; upon others it produces no ill effects.

With continued exposure to the air turpentine undergoes oxidation with the formation of an aldehyde $C_{10}H_{16}O_3$. The sharp odor of old turpentine is due to this. By continued oxidation it turns yellow, thickens, and forms a semi-solid, sticky, resinous mass. By this reaction with oxygen, small amounts of ozone and hydrogen peroxide are produced.[1] Turpentine that has thus thickened is no longer desirable as a paint and varnish solvent or diluent. All turpentines are not equally susceptible to oxidation; some remain clear and thinly fluid for a long time, while others thicken within a few weeks. The change is more likely to occur when the turpentine is kept in containers that are only partly filled, or when they are loosely stoppered or opened frequently.

The fact that turpentine reacts with oxygen in the manner described producing by-products possessed of a distinct oxidizing character, is claimed by some to be a matter of importance in connection with the drying of paint and varnish oils. To whatever degree the turpentine functions in this manner, it is an ideal drier. Not only is the drying of the oil promoted during the critical period when it is most desired, but by the time the film has dried, the drier will have ceased to act. With the usual driers, the oxidizing effect continues even after the film has acquired solidity, with the result that the elasticity of the film is destroyed and its failure is hastened.

Because it is an excellent solvent for all triglyceride oils (page 490) and evaporates at the desired rate, turpentine is eminently suitable as a diluent or thinner for paints and the oil varnishes, but it is not a solvent for linoxyn and other dried oil films, nor is it a solvent for pyroxylin, *i.e.*, the cellulose nitrate or acetate lacquers. Turpentine dissolves also the mineral oils. The mineral waxes, such as paraffin wax and ozocerite, dissolve in turpentine to a moderate degree, but beeswax is readily soluble. A solution of the latter in turpentine is extensively used as a furniture polish. Turpentine dissolves the soft resins such as rosin, dammar, and Manila copal, but it does not dissolve the hard copals (page 535) until after they have been fused and incorporated in oil. Shellac resin is insoluble in turpentine.

Although water dissolves in turpentine to a slight degree, turpentine is practically insoluble in water. Turpentine is

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[1] Note the bleaching of the cork stopper of a bottle in which the turpentine has stood for some time.

miscible in all proportions with gasoline and kerosene, with benzol, with propyl, butyl, and amyl alcohols, amyl acetate, and acetone, but with absolute ethyl alcohol its miscibility is only partial, and with absolute methyl alcohol it is practically immiscible.

Iron vessels are unsuitable containers for turpentine. It causes the metal to corrode, particularly at the surface of the liquid. Zinc-coated ware is also affected by it. In contact with iron, the turpentine acquires a reddish, and in contact with zinc, a whitish turbidity, produced by its reaction products with the metals. Turpentine is generally stored in tinned iron or wooden containers.

Turpentine is expensive. It is consequently liable to adulteration with mineral-oil products, usually benzine and kerosene, which cost considerably less than half as much. Adulteration may be detected by a determination of the following properties:

Specific Gravity.—The specific gravity of pure turpentine lies between 0.860 and 0.870 at 60°F.

Boiling Point.—Pure turpentine begins to boil at 150°C., and 85 per cent should distill between 155 and 163°C., while the remainder should distill below 183°C.

Polymerization.[1]—Turpentine is converted into a thick brownish-colored liquid by the action of sulfuric acid. The mineral-oil products, since they are practically unaffected by sulfuric acid, will float as a separate layer on top of the polymerized liquid.

Spot Test.—When turpentine is dropped upon a piece of absorbent paper, for example filter paper, it should evaporate completely without leaving a stain and without affecting the water-absorbing property of the paper.

Flash Point.[2]—This should not be under 40°C.

Wood Turpentine.—In contradistinction to wood turpentine, that which is obtained by distillation of the balsam is often called "gum spirits." Wood turpentine is obtained by distillation of the wood, such as stumps, knots, and old trunks of turpentine-producing trees. Its composition differs somewhat from the "gum spirits," containing a noteworthy amount of dipentene in addition to the pinene, but as far as its physical effects in

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[1] See footnote, p. 498.

[2] See p. 570.

paints and varnishes are concerned it is as suitable as the turpentine obtained from the balsam. It contains 2 or 3 per cent of impurities, however, such as pyroligneous and formic acids, creosote, and pyridine bases; and unless the turpentine has been carefully refined, it has a disagreeable odor that makes it somewhat undesirable for interior use. The wood turpentine now on the market is generally quite free from these impurities.

Petroleum Hydrocarbons. (*Petroleum Spirit, Turpentine Substitute*).—In the refining of petroleum oils, the light distillate first obtained is refractionated into several grades according to the volatility required by the use for which the fractions are intended. The methods of refining and the grades commonly produced are described on pages 52 to 59.

Petroleum spirit designed for use as a paint and varnish thinner must have a carefully regulated volatility. Although it must be completely volatile at ordinary atmospheric temperatures, it must not be too volatile, or the paint film will set before it has acquired a smooth surface. In the distillation test, the initial boiling point should not be lower than 150°C., and the end point (page 61) should not be higher than 210°C. Ninety per cent should distill below 200°C. If too great a quantity of hydrocarbons that are difficultly volatile, such as those of the kerosene type, are present, the paint or varnish in which the thinner is used will remain indefinitely soft and sticky. Although a sample of the solvent may pass the spot test described for turpentine on page 509, it may not be able to vaporize completely when it has been merged with a varnish or paint. The escape of even a readily volatile fluid is difficult under these conditions. With turpentine, the presence of a small residue of low volatility is less objectionable, because polymerization and oxidation will convert any unevaporated portion of that solvent into a solid mass that will be compatible with the remainder of the film. The petroleum hydrocarbons do not respond in this manner.

Another comparison that may be drawn between turpentine and the petroleum solvent is, that because of its chemical inertness the latter does not serve as an oxygen carrier, to promote in the manner of turpentine the oxidation of the drying oils. On the other hand, the petroleum spirit is greatly preferable to turpentine with respect to its odor.

Petroleum spirit is immiscible with water, but, with the exception of methyl and ethyl alcohols, it mixes in all proportions with most of the other organic solvents. Even the methyl and ethyl alcohols become soluble in petroleum spirit in the presence of a higher alcohol, such as butyl or amyl.[1]

With the exception of castor oil, all fatty, mineral, and rosin oils are soluble in petroleum spirit, but it is not a solvent for the oxidized oils such as linoxyn. It easily dissolves freshly prepared rosin, but old rosin is only partially soluble. Other soft resins are partially soluble in the petroleum spirit, but the hard resins are practically insoluble.[2] The petroleum hydrocarbons are not solvents for cellulose nitrate.

Coal-tar Distillates.—One of the products resulting from the destructive distillation of coal consists of light tar oils. Among the many compounds that appear in the condensate when these oils are fractionated are benzene (C_6H_6), toluene ($C_6H_5{\cdot}CH_3$), and xylene [$C_6H_4{\cdot}(CH_3)_2$]. They are all water-white, limpid liquids, with not unpleasant, aromatic odors. Benzene boils at 80.5, toluene at 111, and xylene at 139°C. The more or less impure forms of these liquids, known respectively as benzol, toluol, and xylol, are widely used as solvents.

The ordinary commercial form of benzol consists of about 70 per cent of benzene and 25 per cent of toluene, with small amounts of other compounds. Benzol is a good solvent for oils, fats, and soft resins, but it is not a solvent for cellulose nitrate. It is miscible in all proportions with the other organic solvents, but it does not mix with water.

Alcohols.—The alcohols included in the group of solvents now to be described are monohydroxyl alcohols of the $C_nH_{2n+1}OH$ series. They are, in effect, the hydroxyl derivatives of the paraffin series of hydrocarbons. The first five members of the group are as follows: methyl (CH_3OH), ethyl (C_2H_5OH), propyl (C_3H_7OH), butyl (C_4H_9OH), and amyl ($C_5H_{11}OH$). Of these, all but propyl are extensively used commercially as solvents.

Methyl Alcohol (Wood Alcohol, Wood Spirit) (CH_3OH).—Methyl alcohol is the simplest of the alcohols. It is a by-product of the destructive distillation of wood; it forms about 1 per cent

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[1] HEATON, "Outlines of Paint Technology," p. 241.

[2] HEATON, *loc. cit.*

of the watery distillate obtained. It is produced also by the dry distillation of certain residues derived from the beet-sugar industry.

Wood alcohol is a clear, colorless liquid which boils at 66°C. (151°F.). When 99 per cent pure, its specific gravity at 60°F. is 0.804 (44°Bé.). It mixes with ethyl alcohol, water, and ethyl ether in all proportions. It is not ordinarily found on the market in the pure state, but contains water, acetone, fusel oil, etc., to which impurities its characteristic odor is due. Pure wood alcohol has scarcely any odor. Administered internally it is poisonous, and this property is greatly increased by its content of fusel oil. Because of the presence of acetone and methyl acetate, crude wood alcohol exerts a greater solvent action on pyroxylin than the rectified spirit, but both the pure and impure varieties are good solvents for resins such as rosin, dammar, and shellac. Insulating varnishes and cheap lacquers for hardware consist of shellac dissolved in wood alcohol.

With the single exception of castor oil, methyl alcohol is not a solvent for the fatty oils. It is not, therefore, a solvent for linseed oil, Chinese-wood oil, and other similar drying oils employed in paints and varnishes.

Methanol.—Synthetic methyl alcohol, known as methanol, is now manufactured extensively in both Germany and France (page 39). Vast quantities have been imported into the United States from Germany at a price so low that the virtual extinction of the domestic wood-alcohol industry is threatened. In France, methanol is employed as a motor fuel. In that future time, when the world's supplies of petroleum and coal, from which we now obtain gasoline and benzol, have been exhausted, it may be that synthetic methanol will become the motor fuel universally employed. The methanol of the present time is made from carbon monoxide and hydrogen obtained from water gas (page 67). Knowing that the vapor of wood alcohol in the presence of zinc dust at a red heat yielded carbon monoxide and hydrogen in substantially the same proportions as they are present in water gas, Patart who took out the French patent, reasoned that the reaction should be reversible under high pressure.[1] Accordingly, he subjected water gas to a pressure of 200 atmospheres at a

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[1] Heaton, "Volatile Solvents and Thinners," p. 86.

temperature of 400°C. in the presence of pure zinc oxide, and found that his hypothesis was correct. Methanol was produced in accordance with the following equation:

$$CO + 2H_2 \rightarrow CH_3OH$$

Synthetic methanol is free from acetone and is practically water free. As a solvent for some purposes, its freedom from water is a factor of great importance.

Ethyl Alcohol (Grain Alcohol, Spirits of Wine, Ethanol) (C_2H_5OH).—Ethyl alcohol is produced by the yeast fermentation of the sugar known as glucose or grape sugar. This sugar may be present as such in fruit juices, or it may be formed by a preceding fermentation of other sugars or starch. About 90 per cent of all ethanol is now made from molasses. The alcohol is obtained from the fermented liquid by distillation.

Ethyl alcohol is the alcohol found in intoxicating beverages; when pure it is a colorless, almost odorless, mobile liquid, which boils at 78.4°C. (173.1°F.). It freezes at −130.5°C. It has a great affinity for water, and absorbs water when exposed to the air. By ordinary distillation all but about 4 per cent of the water can be removed; the distilled product is known as 96 per cent alcohol. By reflux distillation over quicklime, the water can be removed entirely; the distillate is then known as *absolute alcohol.* A more efficient method than the quicklime process consists of distilling the alcohol through a tower filled with anhydrous glycerine and potassium carbonate. By this method absolute alcohol is produced on an industrial scale at a price but little higher than that of the commercial variety containing 4 per cent of water.[1]

Ethyl alcohol dissolves shellac, rosin, dammar, and other soft resins, but not the hard, fossil resins. It is a solvent also for the softer varieties of the phenolic resins, such as bakelite *A* (page 538). Although it is not a solvent for the ordinary form of pyroxylin, it is employed in the lacquers of this type that are prepared to be applied with a brush because it allows them to be spread with greater smoothness. This is probably partly due to the fact that alcohol is a solvent for the resins that are employed in such lacquers. Like methyl alcohol, it is not a solvent for any

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[1] Wilson, "Proxylin Enamels and Lacquers," p. 28.

of the fatty oils except castor oil. Its miscibility with other solvents is practically the same as that of methyl alcohol.

For the purposes of taxation, the alcohol content in alcoholic liquids is designated in proof degrees. In the United States, the standard for comparison is an alcohol-water mixture containing 50 per cent of alcohol *by volume*, which is equal to only 42.7 per cent of alcohol *by weight.* This mixture is termed *proof spirit* (100 U. S. proof degrees). An alcohol containing, for example, 90 per cent of alcohol by volume is called 180-proof spirit. For medicinal and other lawful uses, the excise tax on alcohol is $1.10 per proof gallon (1 gal. of proof spirit), but this makes the alcohol too expensive for many industrial purposes to which it would otherwise be put. Ethyl alcohol has many industrial applications for which equally good substitutes have not been found. In order to provide alcohol for such purposes, in 1906 Congress removed the tax on alcohol that had been treated to render it unfit for use as a beverage. Alcohol so treated is known as *denatured alcohol.*

According to the regulations issued by the Commissioner of Industrial Alcohol, the following are some of substances allowed as denaturants:-wood alcohol, benzine, pyridin bases, camphor, castor oil, caustic soda, nicotin, ethyl ether, acetone, aldehol, which is an oxidized kerosene product, and alcotate, a specially-treated distillate obtained from California petroleum. The indiscriminate use of all of these materials is not allowed. Indeed, most of them are to be used in manufacturing specially denatured alcohol, the sale and use of which is permitted only under special restrictions. The variety used for ordinary industrial purposes, which is known as completely denatured alcohol and may be bought freely by the public, contains 1 part of aldehol and 1¼ parts of alcotate in each 100 parts of ethyl alcohol of at least 160° proof. By the addition of these fluids, which impart a disagreeable odor and taste, the alcohol is rendered unfit for use in liquors, but its usefulness in the industrial arts is unimpaired.

Butyl Alcohol (Butanol) (C_4H_9OH).—Four alcohols derived from butane are known. They are the normal, iso-, secondary, and tertiary forms; but that which is employed industrially as a solvent is practically the pure normal alcohol. In preparing the butyl alcohol of commerce, a mash of corn flour is inoculated with a special type of bacterium and allowed to ferment. In addition to a little water and ethyl alcohol, the distillate obtained from the fermented mash contains about 30 per cent of acetone and about 60 per cent of butanol, which is then parted from the acetone by fractional distillation.

Normal butyl alcohol is a water-white fluid having a specific gravity of 0.810 and a boiling point of 117°C. Its odor is not unpleasant, but if inhaled in quantity, its vapors have an astringent or dessicating effect on the throat. Like other alcohols, it is toxic.

The commercial butanol is approximately 98 per cent pure. It contains small quantities of ethyl alcohol and acetone, but it is practically anhydrous. Unlike methyl and ethyl alcohols it is not freely miscible with water. At 20°C., 12 parts of water are required to dissolve 1 part of butanol, but the solubility varies with the temperature. It is miscible in all proportions with the other alcohols of this series, ethyl and methyl acetate, acetone, ethyl ether, and benzol.

Butanol is an excellent solvent for both the drying and non-drying fatty oils, including castor oil. This is a distinction from the methyl and ethyl alcohols, because, unless heated, they are not solvents for any members of the triglyceride group except castor oil. Because butanol is a solvent for drying oils, it allows their use as plasticizers (page 544) to increase the elasticity of the resinous films of spirit varnishes, where formerly only the alcohol-soluble, but non-drying, castor oil was indicated. Another point worthy of note is that butanol dissolves linoxyn and other oxidized oils very freely, a property not possessed by turpentine and some other good solvents of the unoxidized oils. On this account butanol is employed in paint removers (page 552), for which purpose its comparatively low volatility is an added advantage.

Butyl alcohol is also a very good solvent for resins, not only for the softer varieties, such as shellac, dammar, and Manila, but also for some of the harder copals. Although it is not a solvent for cellulose nitrate, it is employed in cellulose-nitrate lacquers because it retards the evaporation of the more volatile solvents and thus allows the film to spread more freely and smoothly. Another advantage arising from its retardation of the evaporation of the more volatile solvents of a lacquer is that butanol tends to prevent the "blushing" (page 546) of the lacquer.

Amyl Alcohol (Pentyl Alcohol, Pentasol) ($C_5H_{11}OH$).—The word amyl means starch. Amyl alcohol may be derived from the fermentation of grains, or it may be prepared synthetically. It is a liquid almost insoluble in water, is moderately volatile, has a disagreeable odor, and is quite poisonous. It has an oily appearance and boils at 130°C. Its vapor, like that of butyl alcohol, is a throat irritant. At 15°C., its specific gravity is 0.819 (41°Bé.). *Fusel oil* is almost entirely amyl alcohol. Because it is found in grain alcohol, it is known also as grain oil. The word *fusel* is taken from the German and means "spirits of inferior quality." Fusel oil is also found in wood alcohol in considerable amount, and it is to the fusel-oil content that wood alcohol owes, in part, its poisonous property.

Amyl alcohol mixes with practically all of the other organic solvents, and is an excellent solvent for oils and soft resins. It does not dissolve cellulose nitrate, but like butanol, it is employed in pyroxylin lacquers to promote the formation of a smoother film.

Esters.—When an oxygenated acid reacts with an alcohol, a product known as an ester is formed. Only a few of the more active acids will form esters without aid, and because water is evolved as a by-product, sulfuric acid is usually employed as a dehydrating agent. The reaction may be illustrated by the formation of methyl acetate, as follows:

$$CH_3OH + H(C_2H_3O_2) \rightarrow CH_3(C_2H_3O_2) + H_2O$$

Although the esters form a large group, and many of them are employed in varnishes and lacquers, only four of the more widely used will be considered here. These are the acetic esters of ethyl, butyl, and amyl alcohols, and the lactic ester of the ethyl alcohol.

Ethyl Acetate (Acetic Ether) [$C_2H_5(C_2H_3O_2)$].—This ester is a limpid, water-white fluid, with a pleasant ethereal odor. The commercial variety, which contains about 14 per cent of alcohol has a boiling range of 70 to 85°C.[1] The ester is markedly hygroscopic and is hydrolyzed by the absorbed water to form

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[1] HEATON, "Volatile Solvents and Thinners," p. 119.

alcohol and acetic acid. This fact militates against the use of ethyl acetate in lacquers for metal, because the metal is attacked by the acid, and the reaction product discolors the film. Ethyl acetate is one of the best pyroxylin solvents, but because it evaporates rapidly it appears to have a tendency to cause blushing in lacquers.

Butyl Acetate [$C_4H_9(C_2H_3O_2)$].—Butyl acetate is a clear liquid with a pleasant odor, boiling at 125°C. when pure. Although it is somewhat inferior to ethyl acetate in this respect, it is a very good solvent for pyroxylin, and is widely used in pyroxylin lacquers. It evaporates at a slower rate than the ethyl acetate, and allows the formation of a clear, smooth, lacquer film without much tendency to cause blushing. Unlike the ethyl acetate, it is not hygroscopic and develops no acidity.

Amyl Acetate [$C_5H_{11}(OH)$].—This product, when pure, boils at 150°C., and has an odor resembling that of bananas. On this account it is not infrequently called "banana oil." The amyl acetate is a somewhat less effective solvent for pyroxylin than the corresponding butyl form, but being less volatile than the latter, and also non-hygroscopic, it has even a less tendency than butyl acetate to induce blushing in lacquers. The commercial amyl ester, having been produced from fusel oil, which is composite in character, contains only about 85 per cent of amyl acetate. It mixes freely with all other organic solvents, but like butyl acetate, it is almost insoluble in water.

Ethyl Lactate [$C_2H_5(C_3H_5O_3)$].—This solvent is prepared by the ethyl-alcohol esterification of lactic acid produced by fermenting cane and other sugars with lactic bacilli obtained from putrid cheese. Lactic acid is a colorless viscid liquid. Its ethyl ester has greater solvent power for cellulose nitrate than any other common solvent, and the addition of as much as 25 per cent of water seems to affect its solvent action but little.[1] It is also an exceptionally good solvent for resins, and thus is able to act as a blending agent for resins and cellulose nitrate, a property of great value in pyroxylin lacquers. It has a relatively low vapor pressure, a characteristic that is also desirable in a lacquer solvent.

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[1] KEYES, "Solvents and Automobile Lacquers," *Ind. Eng. Chem.*, **17**, 564, June, 1925.

When used in lacquers, it produces a good gloss, and its odor is not unpleasant.

Ketones.—This group of compounds may be described as consisting of two alcohol radicals joined together by the carbonyl group CO. When produced synthetically, they are formed by replacing the hydroxyl radical in the carboxyl group COOH of an acid with an alcohol radical. Thus, by substituting the methyl group CH_3 for the hydroxyl group in acetic acid ($CH_3\cdot CO\cdot OH$), the simplest ketone called acetone ($CH_3\cdot CO\cdot CH_3$), may be formed. Commercially, this ketone is at present obtained chiefly as a by-product in the manufacture of butanol (page 514), and wood charcoal.

In the manufacture of hardwood charcoal, the volatile substances that distill off are condensed. The condensate consists of two layers, one tarry and one aqueous. From the tar, wood creosote and other medicinal preparations are obtained. The aqueous portion, which is known as crude pyroligneous acid, is neutralized with lime and is redistilled. The condensate is known as *methyl acetone.* Although the proportions vary with different producers, the main components are methyl alcohol, methyl acetate, and methyl acetone. The solid matter remaining in the still, which consists chiefly of calcium acetate, with a little tar and other salts, is called "gray acetate of lime." When stirred and heated, the gray acetate yields methyl acetone and *acetone oils.* Among other components, the oils contain *methyl-ethyl ketone* ($CH_3\cdot C_2H_5\cdot CO$), higher ketones, and aldehydes. By fractional distillation, it is separated into light and heavy oils.

Methyl Acetone.—As indicated in the preceding paragraph, crude methyl acetone is a mixture of liquids. Being composite, it is a good general solvent for oils, soft resins, and cellulose nitrate. In fact, it will dissolve some forms of cellulose nitrate that are not soluble in any one of its components alone. A mixture of methyl acetone with benzol or petroleum spirit, thickened with paraffin wax or soap to prevent evaporation, is employed extensively as a paint and varnish remover (page 552).

Pure methyl acetone, or dimethyl ketone [$(CH_3)_2CO$], is a water-white, volatile liquid boiling at 56°C. It mixes in every proportion with water; methyl, ethyl, propyl, butyl, and amyl alcohols; petroleum spirit and other solvents. It dissolves oils and soft resins, and it is a very good solvent for cellulose nitrate. Because it evaporates at a rapid rate, it causes blushing of lacquers, and on this account cannot be used alone as a vehicle in applying them.

Methyl-ethyl Ketone ($CH_3 \cdot C_2H_5 \cdot CO$).—This ketone is the principal constituent of light acetone oil. Both the light and heavy oils are employed as solvents and as paint and varnish removers, but they are unacceptable for some purposes because of their objectionable odors. Methyl-ethyl ketone is, when pure, a water-white liquid boiling within the range of 70 and 82°C. Like acetone, it is soluble in water, but it is superior to acetone, both because it has greater solvent power and lower volatility.

Other Solvents.—It must be understood that the solvents that have been mentioned do not constitute the complete list of liquids that are available. Research workers are constantly trying out new substances, and compounds that were laboratory curiosities only recently are now being manufactured on a large scale for use in the lacquer industry.

PAINTS

As was pointed out in the beginning of this chapter, the characteristics of the pigments and oils determine the properties of the paints made from them. Now, since the properties of the pigments, oils and other components have been to some extent explained, it will be possible to discuss the properties of paints, both with reference to the liquid paint used and the film after it has dried. Before proceeding with the discussion, however, it may be advisable to review briefly the characteristics that a good paint is required to possess.

General Requirements of a Good Paint.—The paint should possess the proper *spreading quality*. This varies in direct proportion to the fineness of the pigment used. If 1 gal. covers 300 to 400 sq. ft. on a fair surface, it is a good average. The paint should oppose a certain amount of resistance to spreading and not flow excessively so that "slicking" results. At the same time it must not be difficult to spread and it must flow sufficiently so that brush marks are not retained. Fine pigments such as zinc oxide and lithopone have a tendency toward excessive flow, while the coarser pigments as white lead, barytes, and asbestine tend to resist spreading. The paint should have sufficient *opacity* so that an excessive amount is not required to hide the underlying surface. Basic-carbonate white lead has the greatest hiding power, volume for volume, while zinc oxide excels weight for weight. The paint should have sufficient *penetrative power* that it can enter into the pores of the wood to aid it in sticking; otherwise it may peel. This happens frequently on very hard woods. Penetration may be increased by the use of thinners. When the paint is stirred up it must *not settle* rapidly, so that a surface may receive a uniform application of the pigment in all parts. While standing in the warehouse or on the dealer's shelves the pigment should not settle to a hard compact mass in the botton of the package. White lead has a pronounced tendency to settle. When exposed in the paint film, the pigments should be as *chemically inert* or *stable* as possible. They should have no tendency to bring about the destruction of the linoxyn film or to react with the atmospheric gases. There should be the least possible tendency to *check*, *crack*, or *peel* because of a lack of elasticity of the film.

Exclusion of Voids in a Paint Film.—A coating of pure linoxyn is very soft and does not possess moisture-excluding properties. On this account mineral substances, *i.e.*, pigments, are used to fill up the pores, to harden the surface and to strengthen the film. If a pigment consisting of large particles only were used, the particles would be sufficiently hard and strong in themselves but they would not be well joined together; the interlying areas of linoxyn, known as voids, would still be soft and easily destroyed. Now, if the spaces between the large particles are filled with a pigment consisting of extremely fine particles only, the surface of linoxyn exposed would, of course, be reduced, but owing to the numerous small joints the strength would not be great and the moisture could still find its way through the joints. But if there had, secondly, been used particles of a medium size, strong in themselves, to fill in between the largest particles, and then, thirdly, the very fine particles to fill the remaining spaces, maximum strength with maximum excluding power and minimum surface of exposed linoxyn would be secured.

Then, by the use of at least three pigments: (1) with large particles, like basic-carbonate white lead, or barytes; (2) a pigment with medium-sized particles, like calcium carbonate or blanc fixe, including here the paint-coat strengtheners such as asbestine and China clay; (3) a pigment with very fine particles like zinc oxide, or sublimed white lead, less linoxyn and more pigment, which is the indestructible part of the paint, will be exposed, and the most compact paint film will be secured, just as by the use of crushed rock, gravel, and sand the best concrete is produced. The fact that two pigments are better than one, and three better than two for the purpose of excluding moisture and gas has been shown by test. The decrease of porosity is in direct proportion to the decrease in voids.

FIG. 85.—Showing the condensing effect of milling a paint pigment with oil. The filled barrel of pigment on the right with oil forms one-third barrel of paste as shown on the left. (*Heath.*)

On three test fences, one at Atlantic City, one at Pittsburgh, and one in North Dakota, the above statements were borne out.[1]

Frequently, certain percentages of varnishes are added to paints. According to tests it appears that this is not good practice when painting on wood; the coat is thus made non-porous to too great a degree. There is always moisture in wood,

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[1] These tests were conducted by the Scientific Section of the Paint Manufacturers Association of the United States, and from their reports the above discussion has been derived.

even in kiln-dried lumber; this moisture, as well as gases that arise from decomposition of the wood, must find a way out. If the paint coat is too impervious, blistering results. For painting on iron, however, the addition of a good varnish is beneficial.

Single-pigment and Composite-pigment Paints.[1]—Each of the pigments used in paints has, as a rule, good properties for which it is noted. But, with practically no exception, each has defects as well that must not be overlooked. Single-pigment paints have been much used, especially that containing the basic-carbonate white lead. Although this pigment confers upon the paint many qualities that a good paint should have, it gives to it certain serious defects also. In a like manner the other pigments are desirable or not desirable, depending upon the standpoint from which they are considered. By a proper selection of pigments, a paint can be made in which each pigment will tend to offset the defects of the other. This is illustrated in the following discussion in which the basic-carbonate white lead and zinc oxide are considered.

If a paint were made up using the basic-carbonate white lead alone, it would be very opaque, would be quite compact and free from voids and when it failed, as all paints do in time, it would possess a uniformly, finely roughened surface, characteristic of chalking, that would be easily repainted. On the other hand, this chalking begins at a rather early period and because of the peculiarly roughened surface that results, the paint coating holds very tenaciously any dust that settles on it so that it soon is caused to appear unsightly. Moreover, white lead is blackened in the presence of the rather prevalent atmospheric hydrogen sulfide, because of the formation of the black lead sulfide. Furthermore, a basic-carbonate white lead paint lacks spreading power, affects delicate colors with which it may be tinted, and settles badly.

A paint containing zinc oxide only as a pigment would be very white and glossy, would not retain dust particles and darken on this account, nor would it darken because of the action of hydrogen sulfide, and it would have great opacity and spreading qualities. But it dries to a very hard, inelastic film and cracks and peels badly. On this account it would be impossible to

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[1] From *Bulletins* of Science Section of Paint Manufacturers Assoc.

produce a uniformly smooth surface in repainting unless the old paint were removed.

Now, in a good composite white paint a certain amount of basic-carbonate white lead must be used to contribute opacity, elasticity, and to counterbalance the spreading quality of zinc oxide and to offset its tendency to peel. A considerable amount of zinc oxide is necessary to contribute spreading power which the white lead lacks, to increase the ease of application, to increase the resistance to the darkening influence of hydrogen sulfide, and above all to offset the chalking tendency of the white lead. The fine particles of the zinc oxide help to fill up the voids between the larger pigment particles of the white lead and thus decrease the spaces that would be otherwise filled only with oil. On this account, the surface of the paint will have greater wearing qualities. In addition, a small percentage of asbestine or China clay may be advantageously used to prevent settling and to strengthen the coat.

The two pigment formulas following gave very good results on a 2-year test in Pittsburgh:

	Per Cent		Per Cent
Basic-carbonate white lead	22	Basic-sulfate white lead	60
Zinc oxide	50	Zinc oxide	27
Whiting	2	Asbestine	10
China clay and asbestine	26	Whiting	3

In inspecting these paints, there was taken into consideration chalking, checking, color, and general condition, partly in respect to repainting.

Paints for Metals.—Concerning paint coatings for metals, practically all that has been said previously holds true. But because no moisture can possibly be in the metal afterward to escape and cause blistering as with wood, the paint is improved by the addition of some fossil-resin varnish of good quality to aid in filling up the pores.

Any metal surface that is to be painted must be *well cleaned.* It should not even be oily, although it is to be painted with a linseed-oil paint. The paint does not mix with the oil layer and so does not adhere well. Galvanized iron is usually oily when new, and in addition is likely to have zinc salts on its surface. Zinc chloride is produced by the action of the ammonium chloride used as a flux in hot galvanizing. And small amounts of zinc salts may be carried by coatings of zinc deposited by the electrolytic method. Zinc chloride especially is very hygroscopic; by absorbing water underneath the paint it causes peeling. Galvanized iron may be cleaned by washing it well with soapy water, rinsing it thoroughly, and allowing it to dry. Mill scale and rust may be removed from iron by the sand blast, scratch brush, file, or by pickling (acid treatment).

Corrosive and Anti-corrosive Pigments.—As was explained on page 469, the pigments are divisible into groups in accordance with the manner in which they affect the corrosion rate of iron. Those which retard corrosion are called inhibitors; those which hasten corrosion are called stimulators, or accelerators; and those which apparently do neither are called indeterminates. Zinc chromate is a very good inhibitive pigment. No doubt it is active in causing the iron to assume the passive state as explained under Iron Corrosion. Where indeterminates or other inhibitive pigments are used with it, only a very few per cent of zinc chromate are required to make a good inhibitive paint. The vehicle itself may also be made inhibitive by introducing into the oil from 5 to 10 per cent of chromium resinate or linoleate (see metallic resinates under Driers). Such a paint would be very good on tinned iron roofs and elsewhere. All of the chrome pigments are inhibitive, as are also the basic-carbonate white lead (corroded lead) and the basic-sulfate white lead.

The red leads are inhibitive and are much used for first coats on iron and steel where they serve well because they dry quickly to a hard layer that forms a good bond with subsequent layers of paint.

Stimulative pigments should never be used in paints for metals. Venetian red, because of its calcium-sulfate content, which dissociates in water and furnishes sulfate ions, is not good for iron. The values of the various pigments for painting on iron are stated in the discussions of the properties of the pigment (which see).

ALUMINUM PAINT

Probably because copper alloys in powdered form had previously been used as paint pigments under the name of "bronze powder," when powdered aluminum came into use for the same purpose it was named "aluminum bronze." It is unfortunate that this term was chosen, because the same name has long been used in metallurgy to denote a copper alloy containing from 7 to 11 per cent of aluminum. The fact that this alloy is sometimes used to produce a paint powder, which is sold under the name of "gold bronze," makes the nomenclature still more confusing. Because it is misleading, the use of the term "aluminum bronze," when referring to flake aluminum for paints, will be avoided here.

Paints consisting of oils, varnishes, or lacquers in which fine flake aluminum has been incorporated have been known for many years, but only recently have they acquired industrial importance. They are now used on wood, metal, concrete, and other surfaces, both as priming and finishing coats. Due to the continuity produced by the overlapping flakes, and to the opacity of the flakes themselves, paints of this type produce films having high moisture-excluding and hiding qualities.

Preparation of the Metal.—To prepare aluminum flake for use in paints, cast aluminum, 99 per cent or higher in purity, is rolled into sheets, and the sheets are then transformed into a fine powder by a series of power-driven stamping machines. To prevent the flakes from welding together, lubricants such as stearic acid (page 490) or tallow are employed. The continued deformation by stamping embrittles the metal, and on this account it breaks up more readily. When as fine as desired, the powder is graded by sieving and air floating. Most grades of aluminum powder are polished or burnished by placing them, with a little stearic acid as a lubricant, in a drum fitted with revolving brushes that lightly sweep the sides of the drum. By rubbing the flakes together in this way, their luster is increased. It is claimed also[1] that polished powder possesses the property of "leafing" or flocculating at the surface of the vehicle, which will be described later (page 526).

Vehicles for Aluminum Powder.—The vehicles employed in aluminum paint may be "heat-bodied" oils, "blown" oils (page 563), varnishes, pyroxylin lacquers (page 542), bituminous paints,

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[1] Edwards and Wray, "Aluminum Paint Manual," p. 4, publ. by the Aluminum Company of America.

or "bronzing" fluids. The "heat-bodied" oil is prepared by holding the temperature of the oil at about 300°C. until sufficient polymerization occurs to produce the degree of syrupy consistency desired. The varnishes employed are oil varnishes made with drying oils and copal or other natural resins (page 535), or rosin ester (page 534). The bituminous paints consist of an asphaltum or similar material dissolved in a suitable solvent, such as benzol. Due to the "leafing" effect, bright, metallic films, of an aluminum-like character, may be produced even with a bituminous paint. Bronzing fluids are of variable composition, but a typical preparation of this type consists of rosin ester dissolved in petroleum spirit. Sometimes a small quantity of linseed or other drying oil is added, but vehicles of this kind are probably the least durable of those employed for aluminum paint.

Aluminum paints are generally mixed just prior to application. On standing in most vehicles, the flake aluminum has a tendency to lose its leafing power. In some vehicles, the metal powder darkens. With others it may react chemically with the liberation of hydrogen gas, the pressure of which may rupture the container. To mix the flake powder with the vehicle, grinding is unnecessary; in fact, it is undesirable, because it abrades the surface of the flakes and lessens their sheen. For thorough mixing, stirring the powder and vehicle together is all that is required.

Properties of Aluminum Paint.—It has been noted in an earlier paragraph that aluminum paint has superior moisture-excluding and hiding qualities. These properties seem to be enhanced by the leafing of the aluminum powder. The term leafing is employed to designate a movement of the metal flakes to the surface of the vehicle, where they spread out in a layer of overlapping leaflets that form a continuous bright metallic film. This movement is probably caused by the forces of surface tension. It does not take place in all vehicles. It occurs in oils, and oil varnishes, but not in pyroxylin lacquers. When aluminum paint is applied, the leafing helps to obliterate brush marks. More important is the fact that the continuous layer of metal flakes, being opaque, protects the vehicle from the action of light. Destructive oxidation of the vehicle, which is one of the chief causes of failure in paint films, is hastened by the actinic rays of the sun. With the opaque layer of aluminum on the surface, the oxidation of the vehicle is lessened. The overlapping arrangement of flakes accounts also for the well-known water-excluding character of aluminum paints.

Aluminum is not affected by atmospheric hydrogen sulfide, and discoloration of the paint is not due to this gas, but aluminum paint darkens rather rapidly in industrial atmospheres. The darkening is probably due to a corrosion of the aluminum to aluminum oxide, which roughens the surface so that soot from the atmosphere adheres.

COLD WATER PAINTS

For each essential ingredient of an oil paint a water paint contains a component with a similar function. An oil paint consists of finely ground mineral matter suspended in an oily medium containing an insolubilizer, called a drier, and an organic solvent, or thinner, to lessen the viscosity. Water paints contain finely ground mineral pigments with a binder and an insolubilizer, while water is the solvent and thinner. In oil paints, the dried oil becomes the binder. The binders employed in water paints are generally casein, glue (page 578), dextrine, and silicate of soda, the first two of which are the most important. For casein, which makes the best water paint, the insolubilizer is calcium hydroxide. Glue may be rendered at least partially insoluble by alum, or by a dichromate in the presence of light.

Casein Paints.—If a suitable mixture of finely ground casein[1] and powdered slaked lime is worked into a paste with water. the calcium hydroxide coagulates the casein and causes it to become insoluble when dried (page 593). Use is made of this fact in preparing washable cold-water paints in which casein acts as a binder to hold the pigment particles together. Casein paints are comparatively cheap, are easy to apply, and may be used on practically any type of surface. Because they are not injured by free lime, they may be used on stucco, where oil paints cannot be used advantageously (page 450).

Distempers and Calcimines.—Preparations of this kind are usually mixtures of pigments with glue dissolved in water. In distempers a small amount of alum may be used to act as an insolubilizer for the glue, but the product is only damp resisting

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[1] For the method of preparing casein, see p. 590.

and is not weatherproof. If the surface to which distemper is applied is exposed to bright sunlight, the addition of sodium bichromate in an amount equal to about 3 per cent of the weight of the glue will render the glue practically insoluble, but even this preparation is not weatherproof.

Calcimines are similar to distempers, but no insolubilizer is used, and they are suitable only for interior walls where dampness does not prevail.

THE VARNISHES

Varnishes are resinous solutions applied to surfaces to produce hard, lustrous, and generally transparent, protective coatings. The specific solvents or vehicles used, as well as the resins dissolved in them, are quite numerous and varied, but broadly speaking, varnishes are classified under two heads according to the general character of the solvent employed, as spirit and oil varnishes. In the spirit varnishes, the solvent serves merely to facilitate the spreading, since it practically all evaporates and leaves a thin layer of resin only on the varnished surface. In the oil varnishes, a drying oil, which contributes to the elasticity and durability of the dried varnish film, is used as the vehicle. In all cases the quality of the varnish depends in a large measure upon the properties of the resin employed; hence, before proceeding further with the discussion of varnishes, the characteristics of at least the more common resins will be considered.

THE VARNISH RESINS

Source.—The resins are peculiar products of vegetable origin that are secreted in special reservoirs or cells of trees and come to the surface either spontaneously or because of incisions. Although their chemical and physical properties vary a great deal, probably all of them are products resulting from the oxidation of the hydrocarbons of the essential, *i.e.*, volatile oils.

Gums.—Because of loose usage of the term, the word "gum" has grown to have the same meaning in popular language as the word resin. But strictly, a gum is a substance soluble in water but not in alcohol or similar solvents. It belongs to the class of carbohydrates; its typical formula is $(C_6H_{10}O_5)_n$. Examples of true gums are gum arabic and gum tragacanth.

Resins.—True resins are never soluble in water, but are soluble in alcohol or other volatile liquids such as are enumerated under Solvents. Some of them, however, dissolve only with difficulty in these liquids and some may not be soluble at all unless fused. Resins are not definite chemical compounds with a fixed composition; different specimens of the same resin may vary considerably in chemical and physical properties. Some resins are neutral substances but many have weak acid characteristics, and form soaps when treated with alkalies or alkaline salts. Some are not susceptible to the action of atmospheric oxygen, while others are considerably affected. They are divisible into two groups: (1) soft or recent resins; and (2) hard or fossil resins.

The *recent resins* are products of trees now living. Examples are dammar, shellac, and rosin, as well as some of the copals. The *fossil resins* are products of trees growing in other ages and now extinct. The resin, being practically non-perishable, is now dug from the earth. In these resins the essential oil has been eliminated and partial oxidation has taken place. They are very hard and many of them are not soluble in the organic solvents unless they are first roasted or fused. During this process, certain molecular changes take place, which in part amount to decomposition with the formation of a by-product of oil. Examples of fossil resins are amber, a great number of the copals, and kauri resin. Resins having properties midway between the two preceding groups are known as *semi-fossil resins.*

Balsams.—Belonging to the general class of resinous secretions is a variety of substances known as oleoresins or balsams. They contain a greater amount of volatile oil than the recent resins, and have usually a syrup-like consistency, although a few are solid or become so on keeping. Examples are Venice turpentine and Canada balsam.

Artificial Resins.—These are laboratory products, which in some respects resemble the true resins.

RECENT RESINS

The recent resins are quite numerous, but the properties of only the most important ones will be discussed here.

Lac.[1]—This resin, from which *shellac* is prepared, unlike all the other resins we shall consider, is not a direct secretion produced by a tree or plant, but is a resinous excretion of a parasitic insect that infests various trees, notably certain varieties of fig trees[2] native to northeastern India. Lac is then the digested sap of this tree.

The lac insect is *Tachardia Lacca*, of the family *Coccidae*, and is somewhat similar to the cochineal insect, which belongs to the same family. The word *lac* is the East Indian term for "a hundred thousand;" it is without doubt applied to this resin to indicate that such countless numbers of insects are connected with its production.

The young insects appear at two seasons, in June and December, which are known as the swarming periods. When hatched they are about 1/40 in. long and are of an orange-red color. They migrate from the parent cells in which the eggs are laid, and take up a position on the tender twigs of most recent growth in such numbers that the twigs are practically covered. The young insect inserts its proboscis, sucks up the sap, and excretes a substance that dries about it in the form of an incrustation which serves as a protective covering. The life of the female insect continues for about 6 months. The life of the male insect is shorter; it is completed in about 2½ months. Since the insects are so thickly clustered on the twigs, the incrustations they produce grow together and form a layer that eventually covers the twig entirely.

Preparation of Shellac.—The twigs containing the resinous incrustation are cut or broken off and constitute the *stick lac* of commerce. The lac is usually not marketed in this condition, however, but is further refined. Generally the resinous incrustation is separated from the twigs by rolling or crushing in some manner. The resin is then agitated with warm water and the aqueous extract thus obtained is evaporated to dryness. The residue constitutes the *lac dye*. This dye formerly was of much importance but is now scarcely more than a commercial curiosity, since it has been replaced by synthetic dyes of coal-tar ori-

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[1] For a more complete discussion see Livache and McIntosh, "Manufacture of Varnishes," vol. III, p. 285; also *Wood Craft*, June, 1911.

[2] HEMMING, "Moulded Electrical Insulation and Plastics."

gin. It is necessary to remove the dye as much as possible in order that the resin may be pale. After extraction, the resin is taken up from the bottom of the vat and dried by exposure to the atmosphere. In this condition it is known as *seed lac*, because it is in the form of granules about like grains of wheat.

At this time orpiment and rosin are admixed. Orpiment is arsenious sulfide (As_2S_3), a substance which possesses a fine yellow color. The reason given to justify the addition of orpiment is that it confers elasticity by acting in a manner similar to the metallic sulfides in the vulcanization of rubber. It serves also to impart to the shellac a fine pale straw color. The original object in the addition of rosin was that the melting point might be lowered so that the lac could be melted without decomposition. An addition of about 3 per cent is required for this purpose, and although such an addition is justifiable and probably even necessary, so that little lac is exported that is entirely free from it, advantage has been taken of this fact and shellac is not infrequently found on the market containing as much as 10 to 20 per cent of rosin or even more. Such quantities, of course, must be classed as adulterations.

When the seed lac is dry, it is melted and strained through fine-mesh cloth. The drippings are caught in warm water or on heated flags. While still warm, the mass is taken up and stretched into thin sheets, which when broken into small pieces furnish the *shellac* in its familiar form. The name applied is without doubt intended to indicate the shell-like or scaly appearance of the lac. It is prepared in this form to increase the surface in proportion to the mass and thus to render it more readily soluble. The lac as it is strained may also be poured into a mold, producing that which is known as *button lac*. Further, the residue left after straining may be extracted with some solvent, which produces *garnet lac*, so called because of its dark-red color.

Properties of Shellac.—The melting point of shellac is somewhat indefinite. It begins to soften at about 40°C., emitting a characteristic odor, but it cannot be melted to a thin fluid without decomposition. It is soluble in both ethyl and methyl alcohol, although ethyl or denatured alcohol does not dissolve shellac properly if it contains less than 95 per cent alcohol by volume. Even when dissolved in the 95 per cent alcohol the solution is rather turbid because the resin contains about 6 per cent of wax that is insoluble in alcohol. On the other hand, the wax is soluble in petroleum naphtha, and the resin proper is insoluble in this solvent. Shellac is only partly soluble in ether and chloroform and is almost insoluble in turpentine.

It is completely soluble in solutions of the alkalies and those salts that ionize to produce alkaline solutions, as borax and sodium and potassium carbonate. Advantage of this fact may be taken to free the resin from the wax. To do this the shellac is boiled in about a 2.5 per cent solution of sodium carbonate. Upon cooling, the wax rises to the surface and may be skimmed off. The solution is then filtered and acidified, whereupon the resin is precipitated. This wax-free resin when washed and dried may be dissolved in alcohol with the formation of a clear solution.

The ordinary orange-colored shellac is very stable and does not depreciate in value even during long storage.

Bleached Shellac.—Shellac may be whitened by bleaching. This is generally accomplished by treating the shellac dissolved in alkali with a solution of sodium hypochlorite ($NaClO$) from which, by the action of the carbon dioxide of the air, hypochlorous acid ($HClO$) is liberated. The bleaching results from the action of oxygen derived from the hypochlorous acid. By the use of sulfuric acid, which neutralizes the alkali, the shellac is thrown out of solution. The precipitated lac is then repeatedly washed in water. Or it may be melted under water and kneaded and pulled, under water, further to increase its whiteness.

Bleached shellac has a marked tendency to polymerize or undergo other molecular transformation on standing so that it becomes less soluble in the ordinary solvents, *i.e.*, the alcohols. The longer it is kept, the less soluble it becomes. The change is hastened by high temperatures but it cannot be prevented even under the best of conditions. Consequently, bleached shellac should be used promptly. It is possible, however, to dissolve bleached shellac that has been thus transformed by standing. If it is allowed to stand about 24 hr. in ether, it absorbs ether and then is much more readily soluble in alcohol.

Uses.—Shellac is much used in the making of spirit varnishes. It is the best resin for this purpose, since it has a higher degree of combined hardness and elasticity than any other spirit-soluble resin. It is also used as an electrical insulator, as a binder in abrasive wheels, and in many forms of composition goods.

Dammar.—The word dammar is the generic Malayan term for all resins that exude from the tree and solidify upon exposure to the air. There are many varieties, but the Singapore variety is perhaps the most commonly used.

Dammar resin is used for both spirit and oil varnishes, but it is not of exceptionally high quality for varnish making, especially for oil varnishes, since it is too soft and brittle. Nevertheless, it is used in these varnishes because of its color, which is almost white. It is somewhat harder than common rosin but it can be scratched with the finger nail and the heat of the hand renders it sticky. It is soluble in benzol, petroleum spirit, turpentine, and in ethyl alcohol with the aid of heat, but it is only partially soluble in cold alcohol. It is used to a considerable extent for making spirit varnishes, but the varnish coat is rather friable so that if it is rubbed with the fingers it becomes powdery.

Rosin is the residue left in the still after the turpentine has been distilled from the balsam. The term *rosin* must not be confused with the generic term *resin*. Rosin is only a particular resin. Colophony is another name for it.

After the turpentine removal,[1] the rosin is freed from any moisture left by the steam distillation of the turpentine by a steady application of heat while yet in the still; then it is filtered under pressure through heavy cloth. When filtered, it is run into molds or barrels and allowed to solidify. Rosin varies in color from extremely pale, through various shades of yellow and brown, to black. Its value increases as its depth of color diminishes. There are various factors that affect its color. If the temperature during its preparation is too high, it will be darkened due to decomposition products. The balsam yielded the first season the tree produces, furnishes the paler grades of rosin, and the product darkens with each succeeding year. The grades of rosin are indicated by the letters A, B, C, etc., to N. Following N are WG and WW, indicating "window glass" and "water white." Grade A is poorest and blackest, while WW is palest

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[1] See p. 506.

and best. The grade is determined by inspection of the barrels usually as they stand on the docks of the port of shipment, generally Savannah, Ga.

Properties.—Rosin is slightly heavier than water. The melting point ranges from 100 to 140°C. It is insoluble in water, but is soluble in about eight times its weight of ethyl or methyl alcohol; it is much more easily soluble in amyl alcohol, acetone, ether, chloroform, turpentine, benzol, and the fatty oils. It is very soluble in petroleum naphtha. Rosin consists largely of abietic acid ($C_{19}H_{29}\cdot COOH$), and its anhydride. By boiling with alkalies, rosin is changed into rosin soap, a constituent of many laundry soaps. The rosin soap is known also as a resinate. The so-called "hardened rosin" is the product resulting from the treatment of rosin with lime or zinc oxide. Because rosin is soft and brittle, and is affected by water, as a component of varnishes it has little of value to contribute, although in the cheaper varieties of varnish it is sometimes used. Varnishes containing a noteworthy quantity of rosin turn white when in contact with water.

Rosin Ester (*Ester Gum*).—It has long been known that linseed oil varnishes containing rosin are of decidedly inferior quality, because of the lack of resistance of rosin to water. After Chinese-wood or tung oil (page 499) came into more general use, it was soon discovered that the rosin-tung-oil varnish (page 501) possessed exceptional resistance to water. While working on the varnishes made of tung oil and rosin, it was discovered that if the acidic rosin was caused to react with an alcohol of high boiling point, the resulting ester (page 516) was a very desirable resin for varnishes.

In producing the rosin ester, glycerol [$C_3H_5(OH)_3$] is the alcohol that is generally used. After the rosin has been melted, it is heated with the glycerol in an aluminum kettle equipped with a reflux condenser. The temperature of the condenser is so controlled that the water produced by the reaction is allowed to escape, while the distillation of the glycerol is prevented. The rosin ester prepared in this manner is essentially a triglyceride (page 490) containing as much as 40 per cent of the glyceryl radical.[1] The neutralization of the rosin is sometimes completed

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[1] HEATON, "Outlines of Paint Technology," p. 286.

by adding a little lime at the end of the process, but this practice yields a product of inferior quality.

Unlike the rosin from which it is made, rosin ester is resistant to both hot and cold water. It is even unaffected by alkaline liquids, such as a 10 per cent solution of sodium carbonate.[1] It is completely soluble in benzol and turpentine. Weather-resistant spar varnishes are now made of rosin ester and tung oil at relatively low cost, but equal in quality to those formerly made of the expensive, hard fossil resins. For the purpose of imparting gloss to pyroxylin lacquers (page 545), no resin is as extensively used as rosin ester.

FOSSIL RESINS

In the manufacture of the oil varnishes, the fossil resins are extensively used. Some of the varieties enumerated in the following pages occur in both the recent and the fossil form; the fossil form is the more valuable.

Amber.—This is the hardest of all the known resins, and varnishes made from it are the hardest of the varnishes. It is chiefly the chippings and turnings left after the manufacture of amber ornaments that are used for making varnishes, since the resin is too costly to use to any great extent.

The Copals.—The term "copal" does not indicate a specific resin, but is used as a generic term, covering a wide range. In the varnish-making industry it is applied to all fossil resins other than amber or kauri.

All of the copals are by no means equal or approximately equal in quality. According to their degree of hardness, they are named: (1) hard, (2) medium-hard, (3) soft copals. Copals of the first class are the true copals, but those of the second and third classes are known commercially as copals. Other things being equal, the quality of the varnish varies directly in proportion to the hardness of the resin used.

The *hard copals* comprise the excellent East African resins, which are known as the *animé resins.* These include the Zanzibar, Madagascar, and Mozambique sorts. The most noted and valuable comes from the coast of Zanzibar, where the fossil is dug from the earth at a depth of about 4 ft. The resin occurs in

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[1] WILSON, "Pyroxylin Enamels and Lacquers," p. 88.

flat tabular pieces, which may vary from the size of a pea to that of a man's hand. The surface is peculiarly roughened by small papillae, which gives rise to the trade name of "goose skin." Like the other fossil resins, the animis are not soluble without fusion. They are so hard that they cannot be scratched with the thumb nail. They are not affected by boiling with caustic-soda solutions or mineral acids, which is a somewhat exceptional property for resins. The animis are probably the standard for excellence among resins.

The *medium-hard copals* comprise the West African sorts of which the Sierra Leone copal is probably the best. It is very hard, especially the smaller pieces known as the pebble form. They are almost equal in hardness to the Zanzibar animé.

A medium-hard copal obtained from the Congo River region, called Congo copal, has been extensively used in varnishes. Some varieties are fairly hard; the hardest comes from the Belgian Congo.

Of the *soft copals*, the Manila and South American resins are the most important.

Under the name Manila copal are included all of the known Asiatic resins except dammar. They are not found in the Philippine Islands but are called "Manila" because that is the port of final shipment. Generally they are not extremely valuable, although they vary greatly in quality. Some of them, notably those from Borneo, are almost identical with the excellent kauri fossil resin, from which they grade to the soft resin from Singapore, which is almost identical with the dammar from that region. Usually these resins as a class are employed in making only ordinary grades of varnishes.

Kauri.—This resin is obtained from New Zealand and Australia. It was of considerable importance in the varnish industry a few years ago, but the consumption has declined somewhat since the use of Congo copal and rosin ester have increased. Kauri occurs in both the recent and the fossil form; the fossil variety is, of course, the more highly prized. The fossil resin is dug from the earth at depths varying from a few inches to several feet and in pieces ranging in size from that of a small pebble to others weighing 50 lb. or more. The recent resin obtained from the living trees is known as "young" kauri; it is very pale, almost water white. The fossil varies from amber to dark brown in color, and resembles the true copals in many of its properties.

In the manufacture of varnish, kauri resin assimilates the linseed oil at lower temperatures and more quickly than other similar resins. Because lower temperatures are required, carbonization is less likely to occur, and so a paler varnish may be produced. Kauri yields a hard and glossy varnish that is very durable for interior use, but it does not stand exposure to the weather so well. In general, the varnish is considered not so good as that made from the animé and Sierra Leone copals.

FIG. 86.—Digging kauri resin.

BALSAMS

The balsams are relatively unimportant in varnish manufacture; *Venice turpentine* is the only one that is much used. Even its use is largely limited to those cases where it is desired to lessen the brittleness of other resins used in conjunction with it. Venice turpentine is obtained from the branches of the European larch. It comes on the market and is used in the form in which it is obtained from the tree. It has a clear yellow color and is thick and viscous at ordinary temperatures, but increases greatly in fluidity on warming. It contains 15 to 20 per cent of an essential oil.

ARTIFICIAL RESINS

A great many artificial resins, produced from a variety of non-resinous materials by condensation and polymerization reactions, are now being manufactured in commercial quantities. In the preparation of the condensation resins, the earlier steps involve the interaction of at least two substances, generally with the elimination of water. The phenol-formaldehyde resins, of which bakelite is a well-known example, are of this type. In the polymerization process, the resin is formed probably by the combination of two or more molecules of the initial material. Although the product contains the same elements in the same proportions as the original material, its molecular weight is greater, and its properties are different. The cumarone resins belong to this class.

Phenol-formaldehyde Resins.—As has been stated, *bakelite* is a phenol-formaldehyde-condensation resin. Resins of similar characteristics are known by the trade names of *redmanol*, *condensite*, *novolak*, and many others. Dr. L. H. Bakeland, who presented the first general account of his work on such resins in 1909, prepared bakelite by boiling about molecular-weight proportions of phenol (carbolic acid, C_6H_5OH) and formaldehyde (CHOH) in the presence of a small amount of ammonia or sodium hydroxide as a catalyst. Acid catalysts, such as a dilute solution of sulfuric acid, may also be used. A condensation product of the phenol and formaldehyde is formed and water is eliminated. Bakelite exists in three stages, known as *A*, *B*, and *C*.

A is the initial product and may exist in either the liquid, pasty, or solid form. The solid form melts and sets again on cooling. It is soluble in caustic soda and in general resembles a true resin. Also it is soluble in alcohol, acetone, and similar solvents, and its solutions may be used as a varnish or lacquer. By the proper application of heat, *A* may be converted into either *B* or *C*.

Bakelite *B* is somewhat similar to solid *A*, except that it is insoluble. It is softened by heat so that it may be molded or welded.

Bakelite *C* is the final form and is made by the application of heat to either *A* or *B*. It is infusible and insoluble in the ordinary solvents. It withstands boiling water, oil, strong acids, and other reagents except caustic soda which most varieties of *C* do not withstand. It is usually transparent or yellow, but it may be prepared in other colors.

A great point in favor of bakelite is that it may be used to impregnate or coat various substances in the form of *A*, or may be molded in the form of *B* and then be converted afterward into the hard, infusible, insoluble substance *C* by the application of heat.[1]

Albertol (*Amberol*).—In their normal form the phenol-formaldehyde resins are not soluble in the fatty oils. They may be rendered soluble in these oils, however, by fluxing them with natural resins, such as the soft copals and rosin, or with other artificial products, such as rosin ester or the cumarone resins. Oil-soluble preparations of this type have received the trade name, *albertol.* An improved form, known as *amberol* resembles rosin or rosin ester in appearance, but it is harder, less fusible, and possesses greater luster and durability than either of the latter.[2] Amberol dissolves in benzol and other coal-tar hydrocarbons, and may be used in pyroxylin lacquers.

Glyptal Resins.—These resins are yellowish or reddish transparent condensation products resulting from the reaction of glycerol [$C_3H_5(OH)_3$] on phthalic anhydride [$C_6H_4{\cdot}(CO)_2{\cdot}O$] and oleic acid (page 490). Succinic acid [$(CH_2{\cdot}COOH)_2$] and citric acid ($C_6H_8O_7$) may also be used with glycerol. The physical properties of the resins may be varied according to the proportions of the materials employed and the conditions of manufacture. It is stated[3] that the product formed of glycerol and phthalic anhydride, which is soluble in acetone, becomes insoluble in this solvent and in alkalies when heated, and that another variety, soluble in benzene and turpentine, made by substituting oleic acid for part of the phthalic anhydride employed in the reaction, is transformed by heat into a product, which, although still flexible, is both insoluble and infusible.

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[1] For additional information on bakelite, see *Jour. Ind. Eng. Chem.*, March, 1909, August, 1909, and December, 1911. Also various pamphlets issued by the General Bakelite Co.

[2] Wilson, "Pyroxylin Enamels and Lacquers," p. 90.

[3] Barry, Drummond, and Morrel, "Natural and Synthetic Resins," p. 165.

Cumarone Resins.—Cumarone, a water-white, oily liquid boiling at 172°C., occurs in small amounts in heavy benzol or solvent naphtha, boiling between 160 and 180°C., which is obtained by the distillation of coal tar. The resins are formed by polymerizing the cumarone and other unsaturated compounds, by treating the impure naphtha with a polymerizing agent, such as sulfuric acid or aluminum chloride. The cumarone resins, which are among the most important of the artificial group, are light colored, hard, and similar to rosin in appearance. They are unaffected by alkalies and most acids. They are soluble in animal and vegetable oils, but the best solvents are benzol, toluol, solvent naphtha, and turpentine. Like natural resins, the cumarones are used in varnishes, lacquers, and in other composites, such as rubber goods, linoleum, etc.

SPIRIT VARNISHES

Composition and Properties.—Spirit varnishes are made of the recent resins—shellac, dammar, sandarac, and mastic—but shellac is most important. The varnishes are merely solutions of these resins in alcohol or some other volatile solvent.

The solvent only facilitates the spreading; none of it is left in the dried varnish layer. Hence, the dried varnish consists merely of a thin coating of the original resin; it is, therefore, very brittle and liable to crack and flake off. The coating is hard and usually very brilliant, but it must not be applied to any article that will receive rough handling. Since the resins used are dissolved and converted into soaps by the action of alkaline substances such as washing soda, borax, etc., articles coated with spirit varnishes must not be washed with soaps or other cleansing preparations of similar nature.

Because the drying is rapid, spirit varnishes are somewhat difficult to apply, but because they dry rapidly, they are suitable for application to wood patterns. In addition they are good excluders; they prevent alteration in the size of the pattern due to moisture absorption, and they furnish a hard, smooth coat. Shellac varnish is especially suitable for this purpose.

The brittleness of the spirit-varnish coat may be reduced by mixing with the varnish 1 to 1.5 per cent of castor oil, or some balsam, as Venice turpentine, or better still, a small quantity of an oil varnish. Oil varnish, however, lengthens the period of drying. Resins by themselves are very unyielding substances, so that any expansion or contraction of the article to which they are applied causes cracks to appear in a spirit-varnish coat.

A very clear, almost water-white varnish may be prepared by dissolving dammar in alcohol. *Colored varnishes* may be prepared by dissolving with the resin an aniline dye soluble in alcohol, or by the use of dragon's blood, gamboge, or cochineal.

Spirit varnishes may be prepared on a small scale by putting the materials into a well-stoppered receptacle and shaking periodically until solution is complete. The necessary shaking may be secured by attaching the receptacle to a slowly revolving shaft. Free flame for heat must not be used on account of the great inflammability of the materials. The proportions are about 5 lb. of resin to 1 gal. of 95 per cent alcohol.

Resin Lacquers.—It is very difficult to draw any line of distinction between varnishes and lacquers. Resin lacquers are spirit varnishes generally, and so prepared that they may be applied to metals. They are usually pale, but may also be colored to heighten the natural color of the lacquered article. "Gold" lacquers contain saffron, gamboge, etc., and all the various colors may be prepared by the use of aniline dyes. The article to be lacquered is usually warmed before the application of the lacquer, in order that it may spread out to a thin, even coat.

Resin lacquers are made of the recent resins, including recent kauri, dissolved in one of the solvents. If a spirit lacquer must be thinned, it should be done only with absolute alcohol, or other water-free solvent, since any water present prevents transparency.[1]

Japans.—When lacquers are applied to metals, or sometimes even to wood and other materials, and the article baked in an oven to render the coating harder and more durable, the process is known as japanning. The name is derived from the fact that the process originated long ago in Japan, where the natives employ a certain rather thinly-fluid balsam that possesses naturally the requisite properties for a most excellent varnish or

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[1] Directions for making up lacquers may be obtained from Hurst and Heaton's "Painter's Colors, Oils, and Varnishes," Griffin and Company, London.

lacquer. As it exudes from the tree, it has a creamy tint, but it blackens upon exposure to the air.

The baking of a lacquer, *i.e.*, japanning, causes the surface to be more lustrous and far more adhesive than when allowed to dry in the ordinary way. The baking is carried out on metals at a temperature of about 130°C. During the baking a certain amount of decomposition takes place and also some oxygen is absorbed.

PYROXYLIN LACQUERS AND ENAMELS

Pyroxylin.—This widely used material is a mixture of cellulose esters.[1] Cellulose, which is found in the fibers of all plants, and in its purest natural form in cotton wool, is a complex substance to which the formula $(C_6H_{10}O_5)_x$ has been assigned. The value of x is not definitely known, but cellulose is an alcohol with three hydroxyl (OH) groups in each unit. No organic solvent for cellulose has been found, but it can be rendered soluble in organic solvents by treating it with acids to form esters. At the present time, these esters are produced in large quantities for the manufacture of lacquers, which have become very familiar, particularly in the automobile industry, under the trade names of "Duco," "Zapon," and others. The esters usually employed are cellulose nitrate and cellulose acetate, the former especially. The cellulose acetates are, in fact, employed to only a limited extent in the lacquer industry. They are more difficult to prepare, their solvents are less plentiful, and their solutions are less stable than those of the nitrates.

Cellulose Nitrate.—The raw material used for the manufacture of cellulose nitrate is usually cotton linters, but a fine quality of tissue made of wood cellulose is sometimes employed. Cotton linters are the short fibers next to the seed. To secure pure cellulose, the linters are boiled in a solution of caustic soda, are bleached, washed, and dried. The purified cellulose is then nitrated by treating it with a mixture of nitric and sulfuric acids at a carefully controlled temperature. After nitration, the acid that is mechanically held is removed by centrifuging, and the combined sulfuric acid is eliminated by boiling with water.

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[1] For the formation of esters see p. 516.

When finished, the appearance of the nitrated cotton still resembles that of the fiber from which it was made.

Pure, dry cellulose nitrate is unstable and unsafe to transport, but the water must be eliminated because its presence is objectionable to the lacquer manufacturer. Before leaving the nitrating plant, therefore, the water is removed from the product by forcing alcohol under pressure through the mass until all of the water has been replaced by the alcohol. About 30 per cent of alcohol is left in the finished material when shipped.

Nitrated cotton is not a single substance, but is a mixture of the hexa-, hepta-, and octonitrates. Assuming that in the formula $(C_6H_{10}O_5)_x$, the value of x is 4, these compounds may be represented as follows:

$$C_{24}H_{34}O_{14}(NO_3)_6,\ C_{24}H_{33}O_{13}(NO_3)_7,\ \text{and}\ C_{24}H_{32}O_{12}(NO_3)_8.$$

When cotton is nitrated to the degree represented by these formulas, although readily inflammable, it is not explosive. The explosive variety is more highly nitrated.[1]

Pyroxylin Lacquers.—When cellulose nitrate is subjected to the action of a solvent, and in some cases to the action of a nonsolvent, the liquid is absorbed and the solid swells greatly, much after the manner of glue and gelatin when they are allowed to stand in cold water. When complete solution has been effected and the liquid is then spread out in a thin layer and the solvent allowed to evaporate, the reverse process occurs and a contraction takes place. Although the cellulose nitrate yields a hard, durable, transparent film, because of the contraction, the film tends to spring away from its support. Besides, it is brittle

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[1] In this connection it may not be out of place to mention guncotton, a compound which, on the basis of the formulas given, contains 12 nitrate radicals in each unit. It is very unstable, and on explosion decomposes as represented by the following equation, given in Thorpe's "Outlines of Industrial Chemistry," p. 440:

$$C_{24}H_{28}O_8(NO_3)_{12} \rightarrow 14CO_2 + 10CO + 6N_2 + 8H_2 + 6H_2O$$

Reducing the gases to standard conditions (0°C. and 760 mm.), and calculating the water as vapor, 1 g. of guncotton, exploding, yields 859 cc. of gaseous product, a greater volume than is produced by any other explosive. Because of the heat liberated by the reaction, the volume of the gases at the time of the explosion is increased much beyond that shown by the figures here given.

and likely to crack. This is true particularly when pigments have been added to the mixture as in the preparation of enamels, because the pigments increase the brittleness of the film. To lessen contraction and to increase the elasticity of the lacquer, a material called a plasticizer is added.

Plasticizers.—In addition to improving the toughness and elasticity of the lacquer, the plasticizer should aid in preventing blushing. It should improve the flow of the lacquer just before it sets, and thus help to make the film smooth and glossy. The plasticizer must be chemically inert, must be soluble in the pyroxylin solvent, and must be entirely non-volatile. Because the hardness of the dried cellulose nitrate is one of its most desirable properties, it is important in selecting a plasticizer, also to choose a material that will lessen the hardness as little as possible. When cellulose nitrates were first employed in lacquers, the raw material used was celluloid, which contains *camphor.* Although it was unintentional, the camphor acted as a plasticizer. Camphor, however, sublimes slowly and films containing it soon disintegrated.

Later *castor oil* (page 560) was used, and although it has disadvantages, it is still employed to a considerable extent. It is practically non-volatile, but it is not entirely chemically inert. Castor oil becomes rancid (page 491) upon exposure and oxidizes slightly. If it should happen that it is used in very slight excess, it renders the lacquer too soft.

A great many plasticizers have recently come into use, and the research laboratories are constantly trying new materials. As yet, the ideal plasticizer has not been found. Among the many substances that are used, *triphenyl phosphate* $[(C_6H_5)_3PO_4]$ and *tricresyl phosphate* $[(C_6H_4{\cdot}CH_3)_3PO_4]$ may be noted. The former is a white solid, which when melted, resolidifies at 49.9°C. The latter is a viscous liquid, which, although it does not solidify, becomes thick and glassy at $-30°C$. Both are non-volatile, are stable in contact with water and air, and do not discolor upon exposure to light. The amount of either substance employed in the lacquer is about 10 per cent of the weight of the cellulose nitrate used. Although it would be impractical to list here all of the materials now employed as plasticizers, *dibutyl phthalate* $[(C_4H_9)_2{\cdot}(COO)_2{\cdot}C_6H_4]$ and *diamyl phthalate* $[(C_5H_{11})_2{\cdot}(COO)_2{\cdot}$-

C_6H_4], should not be omitted. They are in some respects better than the phosphates previously mentioned.

Resins.—When a solution of pyroxylin dries, it has a matte surface. To impart a gloss and also to increase the adhesion of the film to its support, resins are introduced into the lacquer. In lacquers of good quality, the quantity of resin employed is equal to about two-thirds of the weight of the cellulose nitrate, but the proportions vary considerably, and the cheaper lacquers contain resins in excessive amounts. The quality of the resin also is important. The softer varieties are easier to incorporate with the other ingredients, but the harder ones yield more durable films. As the resinous ingredient, *rosin ester* (page 534) is extensively employed.

Pigments.—In order to establish a color, pigments are used, and the lacquer is then called an *enamel.* In addition to imparting a color, pigments serve another useful purpose. Cellulose nitrate is slowly decomposed by the action of sunlight, and the pigments prolong the life of the enamel by contributing opacity. The less transparent pigments are, therefore, more desirable. For the same reason, the application of a clear pyroxylin lacquer over a pigmented ground coat is not the best practice.

Solvents and Thinners.—In preparing the lacquer for application, a mixture of several solvents, rather than one only, is generally employed. Some solvents, when used alone, cause only a swelling of the nitrated cotton, and a second liquid must be employed to produce complete dispersion. To reduce the viscosity, other liquids, called thinners, are added. Although they are not solvents, they act as diluents, and being cheaper than the solvents, they lessen the cost of the lacquer. Typical solvents are ethyl acetate, butyl acetate, amyl acetate, and methyl ketone or acetone (see pages 516 and 518). Typical thinners are benzol and petroleum spirit (pages 510 and 511). Butanol or butyl alcohol and amyl alcohol (pages 514 and 516) are used to retard the evaporation of the solvents and thinners and thereby to produce a smoother coat.

Application.—Cellulose-nitrate lacquers may be applied either by means of a brush, by dipping, or by some sort of spraying device. The latter is the method usually employed. For lacquers to be applied with a brush, solvents having a lower volatility are required. Many of the best solvents possess high volatility and out of this fact grows one of the greatest difficulties encountered by the lacquerer. This is the phenomenon called *blushing*. Some solvents evaporate so rapidly that the temperature of the air in the vicinity of the film is lowered to such a degree that on days when the relative humidity is high, moisture condenses on the lacquer and produces a whitish emulsion. Occasionally, when the lacquer solvents contain traces of water, the chilling produced by the evaporation may prevent the water in the solvent from evaporating as it otherwise would, and the milky emulsion may result from this cause also. Because blushing is very troublesome, any solvent that tends to prevent it becomes at once of importance to the lacquerer.

Priming Coat and Fillers.—In lacquering rough surfaces, such as automobile bodies, which are file marked and hammer dented by the finisher of the metal, a priming coat is first applied and then, generally, three coats of metal filler. With regard to the type and number of its components, the filler is similar to the enamel, but it has a much higher ratio of pigment to pyroxylin than the latter. Depending upon the pigments employed, fillers may be white, gray, black, or colored. Like the priming coat, they are applied with a spraying device. They must possess high adhesion, and have as much flexibility as possible, but they are always more brittle and less durable than the enamel itself, the durability of which they tend to lessen. If the surface is not too rough and if time will permit, or if price will allow it, successive coats of enamel rubbed down will produce a more durable foundation. When the ground coats of filler or enamel are thoroughly dry, they are rubbed to a smooth surface with sand. Upon the base prepared in this manner, three or four coats of enamel are sprayed. When all of the volatile ingredients have evaporated from the final coating, the enamel is polished to the semi-gloss characteristic of these finishes.

OIL VARNISHES

Manufacture.—The process of manufacturing oil varnishes consists of six stages. (1) The resin is melted. Care is necessary, since overheating darkens the varnish and underheating lessens its durability. (2) The oil is boiled. Lead, manganese, or other compounds are added to the raw linseed or other oil being used, and the whole is kept at about 260°C. for 1 to 2 hr. The metallic compounds dissolve in the oil. (3) The materials are mixed. The necessary quantity of boiling oil is poured into the melted resin and stirred well. (4) The mixture is boiled. When the mixture is first made, it is cloudy, so that it must be boiled again to make it transparent and to increase its tenacity or to make it "string." (5) The mixture is thinned. It is first allowed to cool to about 120°C. and then the necessary amount of turpentine or other thinner is introduced so that the viscosity is lessened to the desired degree. (6) The varnish is now allowed to clear and age. It is allowed to stand until the more insoluble matter settles out and the top layer becomes clear.

FIG. 87.—Varnish chimney. Showing method of heating resin with oil.

Properties.—Oil varnishes are used wherever durability is required. The durability of a varnish is dependent upon the proportion of oil used in it and the elasticity of its film when dried. It depends also upon the hardness of the resin used. Oil varnishes should combine the hardness and brilliance of the resins with the elasticity of the dried oil films.

The brilliancy and luster also depend upon the proportions of oil and resin; the greater the amount of resin, the greater the brilliancy and luster. But beyond a certain point, the greater the amount of resin the less the durability also, consequently the proportions must be determined with both these properties in view. Where great brilliance is desired, the resin must be no less than one-third or one-fourth of the dried coat.[1] If great elasticity is required, the resin must be no more than one-sixth of the dried coat. Also, the harder the resin, the greater the brilliancy. Other things being equal, a varnish made from Manila copal will be less lustrous than one made from Zanzibar animé.[1]

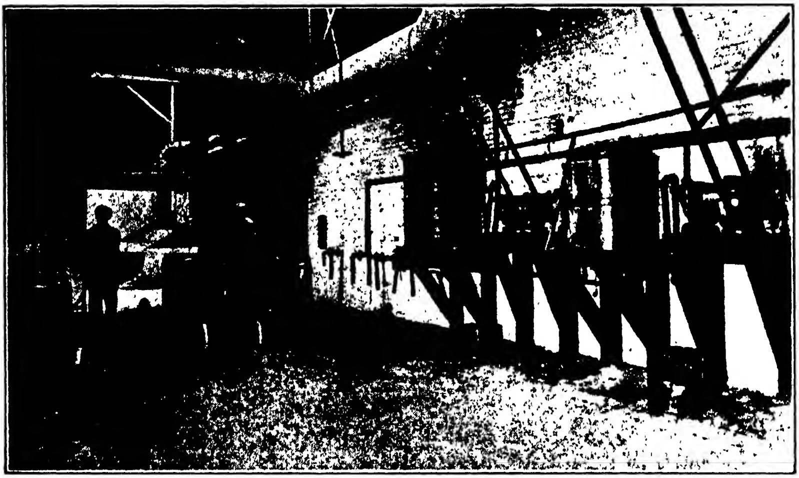

FIG. 88.—Thinning varnish by the addition of turpentine.

Varnishes should be used only for the purpose for which they are made, since different properties reside in varnishes designed for different uses, as exterior, interior, coach, cabinet, floor, polishing, rubbing varnishes, etc. An outside varnish contains a large percentage of oil to give it toughness and elasticity; hence it dries slowly. Interior varnishes contain less oil in order that they may dry quickly, and be hard and suitable for rubbing and polishing. Floor varnishes must be hard and durable as well as elastic; they require the use of the hardest of resins in a carefully determined proportion of oil.

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[1] LIVACHE and McINTOSH, "Varnish Materials and Oil Varnish Making," vol. II, p. 120.

Other things being equal, pale varnishes are more expensive than dark ones, because they require the use of special, hand-selected, pale resins. The use of cold-pressed and bleached oil lightens the product; even the use of oil that has been tanked or aged for a long time is of value in this respect. Overheating during any stage of manufacture darkens the varnish. On the other hand, varnishes may be rendered lighter in color by underboiling, but this produces an inferior product. Dammar resin is of great aid in lightening the color, but the use of this resin detracts from the hardness and toughness of the varnish.

Fig. 89.—Storage tanks.

The drying qualities of the varnish depend upon the resin used as well as upon the kind and amount of drier, and the degree of boiling. Some inferior varnishes contain balsamic or pitchy, resinous materials that prohibit drying.

WOOD STAINS

Practically all the wood used in cabinet making or in finishing the interior of buildings, etc., is stained in some manner, either to augment its natural beauty or to cause a less valuable wood to assume the appearance of a more valuable one.

The staining materials include a great variety of substances. Organic dyes, both of vegetable and coal-tar origin, acids, alkalies, metallic salts, and mineral pigments are used. The stains are usually classified according to the solvent or vehicle with which they are applied, as water, spirit, acid, and oil stains.

Water stains are the most used. The advantages of water as a solvent are its low cost and the ease with which it may be applied, but water causes the fibers of the wood to rise. This produces a roughened surface and necessitates refinishing. It is said that the raising of the fiber may be minimized by the addition of a small quantity of glycerine to the water. The water stains may consist of solutions of the aniline dyes or of water extractions of logwood, Brazil wood, madder, gall nuts, etc. The colors of these materials may be modified or changed entirely by the action of alkalis or acids. The aniline dyes are quite susceptible to the action of the substances contained in the wood, especially the tannic acid. The action will be most noticeable, of course, on those woods rich in tannic acid, such as oaks.

Spirit stains are preparations made by dissolving the coloring materials such as the aniline dyes and other materials in alcohol or in a good spirit varnish. Spirit stains dry very rapidly—so rapidly that it is difficult to apply them properly. The spirit stain may "bleed" also, *i.e.*, it may come through the varnish coat because of the dissolving action of the oil or solvent contained in the varnish. This difficulty may be overcome by selecting a dye that is soluble in some solvent as nitrobenzol, petroleum spirit, amyl acetate, acetone, or other liquid not contained in the varnish that is being applied. Many dyes of the various colors are obtainable, the solubilities of which are entirely different, so that they may be chosen with this point in view. All solutions of spirit stains must be clear without sediment or excess crystals. This is important because colors are frequently produced by the dye manufacturer by mixing two or more distinct dyestuffs. It may be that one of these dyestuffs will be soluble in the solvent chosen and the other not, so that if it be not all dissolved the true value of the dye will not be secured. To fix stains after the manner of a mordant in dyeing cloth, there may be applied after the stain has dried about a 5 per cent solution of alum or ferrous sulfate.

Acid stains comprise a great variety of substances. In this connection, the term "acid" is often employed to designate many materials that are not acids in any sense. It includes the true acids such as sulfuric, nitric, and picric; salts such as alum, ferrous sulfate or copperas, potassium chromate and dichromate, potassium permanganate, sodium, and potassium carbonate; and even the alkalies, sodium and potassium hydroxide themselves.

Wood may be "aged" by the direct application of ammonium hydroxide or by allowing the wood to stand in chambers containing vessels of ammonium hydroxide from which the ammonia gas may arise and act upon the wood. Oak is especially susceptible to this action; the product is known as *fumed oak*. This treatment with ammonia is useful only with those woods containing considerable gallic or tannic acids, since the color is dependent upon the formation of the ammonium compound of these substances.

Oil stains do not penetrate deeply and are most suitable for woods that are not to be filled. The oil used in the stain, when dried, partly fills the pores of the wood so that proper filling with a suitable filler cannot be accomplished. The oil stains are prepared by adding mineral pigments, such as burnt sienna, umber, chrome yellow, etc., to the oils, together with turpentine and some japan drier. Colors produced by oil stains are less clear and transparent than those produced by acid stains.[1]

Bleaching of Woods.—Dark woods may be bleached by the action of chlorine. A thin paste made of bleaching powder [$Ca(OCl)_2$], is applied and allowed to dry. Then a solution of some acid, such as a 5 per cent solution of hydrochloric or acetic, must be applied. The acid reacts with the hypochlorite and liberates hypochlorous acid the oxygen of which causes the organic coloring matter of the wood to be destroyed. If the action is insufficient, the operation may be repeated.

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[1] For further information on wood stains and methods of use, see *Wood Craft*, September, 1906; July and August, 1907; March, 1908; August, 1909; February and August, 1911; and March and April, 1912. Also Schmit, "Problems of the Finishing Room."

WOOD FILLERS

Fillers are used to close the pores in open-grained woods. If not filled, capillary action would occur in the pores and produce "sinking of the varnish." There are two kinds: paste and liquid fillers.

Paste Fillers.—The best grade of paste fillers consist of silica or barytes, boiled oil, and japan drier. Both silica and barytes become practically transparent in oil (page 476) and so produce a transparent filling. Fillers of poorer quality consist of corn starch, whiting, boiled oil, turpentine, and drier. Such fillers have a tendency to shrink after drying, especially if made of the starch, thereby defeating the object for which the filler was applied. If intended to produce some color effect, the filler may also contain a coloring matter. The paste fillers are used in conjunction with the liquid fillers which are applied subsequently. The oaks, the walnuts, mahogany, ash, chestnut, and red gum are open-grained woods, and are filled with either paste or liquid fillers.

Liquid fillers consist of practically the same materials as the paste fillers, but in liquid fillers the liquid constituents preponderate. Liquid fillers are used only on close-grained woods, as cherry and birch. When using fillers in conjunction with stains, the filler must be applied after the stain. If the filler contains whiting or marble dust, and the stain is an acid stain, then a thin coating of shellac should be applied over the stain before filling to prevent the acid from acting on the calcium carbonate of which these substances consist.

Putty usually consists of whiting and raw linseed oil kneaded together. It may also consist occasionally of whiting, lead carbonate, white clay, or other similar materials with linseed oil.[1]

PAINT AND VARNISH REMOVERS

There are a number of liquids that exert a solvent action on dried paint and varnish films, but being highly volatile also, they do not remain in place long enough to become effective. Consequently, if the liquids are entangled in some medium that will serve to prevent their evaporation and the whole is applied in a paste form they may be advantageously used.

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[1] For a description of various putties see *Furniture Manufacturer and Artisan*, p. 93, February, 1914.

A solvent paste of this sort may be prepared as follows: Dissolve with the aid of heat 8 parts of finely divided paraffin wax in 8 parts of benzol. (*Care! Benzol is inflammable.*) To this solution while still warm, add 7 parts of methyl alcohol. The alcohol is miscible with the benzol, but is not itself a solvent for the wax, consequently the wax is precipitated out in the form of a gelatinous mass that holds the liquids entangled. The solvent power of the paste may be increased by stirring into it about 1 part of acetone or about one-half of 1 part of amyl acetate.

A number of the solvents employed in the lacquer industry, which have been described under Solvents and Diluents, are also finding application as paint and varnish removers. Among those that are used for this purpose are methyl ketone, methyl ethyl ketone, and butyl alcohol.

An active preparation of an entirely different sort is the following, used also in paste form: caustic soda, 1 part; fresh powdered quicklime, 3 parts; and whiting 4 parts, with sufficient water to form a paste. This is applied and allowed to remain for a short time. This preparation is active because it converts the linoxyn into soap. Or a 10 to 12 per cent solution of sodium carbonate may be used, as may also a moderately concentrated solution of ammonium hydroxide. These liquids are used with an abrasive as steel wool, or a stiff-bristled brush. After the removal of paint or varnish by any one of these alkaline substances, the residual alkali on the surface of the wood must be corrected with some weak acid, as for example, about a 5 per cent solution of oxalic acid, which both neutralizes the alkali and acts as a bleaching agent.

CHAPTER XIV

LUBRICANTS

Object.—When two metals are caused to slide in contact with one another there is more or less resistance to motion, which results in an absorption of energy that is manifested as heat. The resistance to motion is probably due in largest part to molecular cohesion, but it may be partly due to interlocking of minute projections on the surfaces of the metals. When it is desired to lessen friction, as in machinery bearings, a lubricant, generally an oil, is employed to keep the surfaces apart.

General Characteristics of the Lubricating Oils.—The lubricating oils belong to two major classes: (1) the fatty oils, which are of both animal and vegetable origin; and (2) the mineral oils.

The fatty oils are in general more or less affected by exposure to the atmosphere. Some of them are quite susceptible to *oxidation* and are converted into a dry hardened mass. These are the paint oils, and this property, which makes them suitable for paints, manifestly renders them useless for lubrication. Others of these oils that do not oxidize sufficiently to form a hardened mass become thickened to such an extent that friction would be much increased by their use. To some extent the fatty oils react with moisture in the air; the reaction which they undergo is known as *hydrolysis*. The structure of the fatty oils[1] bears a close analogy to the structure of metallic salts. They consist of mixtures of compounds made up of a trivalent basic radical (C_3H_5) called glyceryl, united with various fatty acid radicals, which may be typified by the radical of oleic acid $HOOC \cdot C_{17}H_{33}$. Thus glyceryl oleate, called olein, is $C_3H_5(OOC \cdot C_{17}H_{33})_3$. The hydrolysis that occurs upon exposure to the air is small in amount compared to that which occurs in steam cylinders where fatty oils are often used. Hydrolysis is represented by the following equation which shows the reaction between water and stearin; the products are glycerine and stearic acid.

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[1] For a more complete discussion see p. 490.

$$C_3H_5(O_2C_{18}H_{35})_3 + 3HOH = C_3H_5(OH)_3 + 3HOOC{\cdot}C_{17}H_{35}$$

The mineral oils, on the other hand, are relatively indifferent to the action of the atmosphere. One of the most important series of hydrocarbons of which mineral oils consist is known as the paraffin series. It is because of its chemical inertness that it is so called—from the Latin *parum*, too little, and *affinis*, allied, which indicates that it has a lack of affinity for other substances.

The Theory of Lubrication.—Gill[1] says: "the cardinal principle underlying all lubrication is to *use the thinnest (or least viscous) oil that will stay in place and do the work.*" In all lubrication, the lubricant should adhere to the moving solid parts so that there is a shearing of the lubricating layer. A good lubricant is, then, one that adheres well to the surface and offers but little resistance to shearing, or, in other words, that has but little friction between its own moving particles. The term viscosity is used in designating the amount of this internal friction. An oil that flows sluggishly is said to be high in viscosity. A lubricating oil should have sufficient adhesion and viscosity to enable it to stay in place, but if it possesses greater viscosity than this, power is wasted in shearing the oil. In brief, as long as it can resist the force that tends to squeeze it out, the value of a lubricant increases with its mobility.[2]

Lubrication may be divided into two major classes according to the conditions of speed and pressure:

1. With a shaft or journal running at moderately high speed and under fairly light pressure there may be perfect fluid-film lubrication. If such is the case, the journal does not come into

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[1] Gill, A. H., Rogers and Aubert's "Industrial Chemistry," 2d ed., p. 602.

[2] In experimental work, air has been used as a lubricant, furnishing almost perfect lubrication. A steel cylinder 6 in. in diameter and 6¼ in. long, weighing 50½ lb. was fitted into a cast-iron journal with a fit of 1/2000 in., and supplied with a detachable crank-rotating mechanism. After a speed of 500 r.p.m. had been obtained, the harsh grating noise ceased, and the cylinder ran smoothly of its own accord for 4 or 5 min. Attempts to establish electrical connection between the journal and shaft failed until after the cylinder had slowed down, thereby showing insulation due to the supporting film of air. No grease or oil was used in this experiment. Archbutt and Deeley, "Lubrication and Lubricants," p. 90, 1912.

contact with the bearing at all; a film of oil keeps the metallic surfaces apart. Then the friction is due only to the viscosity of the lubricant.

2. With very slow speeds or high pressures or both, or when starting after a period of rest, there may be actual solid or "contact" friction between the journal and bearing. Under such conditions, that property of a lubricant which most enables it to be effective in lessening friction has, for want of a better term, been designated as "oiliness."

Just what constitutes oiliness is only very imperfectly known. It has been defined[1] as that property of a lubricant by virtue of which one lubricant gives lower coefficients of friction (generally at slow speeds or high loads) than another fluid of the same viscosity. Under conditions of perfect fluid film lubrication, the oiliness of the lubricant is of no consequence.

It has long been known, learned through experience, that under excessive pressure, fatty oils are much superior to mineral oils as lubricants. Moreover, the addition of a fatty oil to a mineral oil increases the oiliness of the latter. Recent work has shown that it is the chemically reactive constituent of a lubricant that promotes its oiliness. Free fatty acids, employed in very limited amounts, greatly improve the friction-reducing qualities of mineral oils. Consequently, it is believed that the improvement in lubricating power caused by adding a fatty oil to a mineral oil is due more to the small content of fatty acid contained in the fatty oil than it is to the neutral glyceride.[2] It has been found that under very slow speed and high pressure, which were employed to ensure a certain amount of solid friction between the journal and bearing, 0.5 per cent of fatty acid[3] from rapeseed oil reduced the friction about as much as 60 per cent of neutral glyceride from the same rapeseed oil.[4] Oil-soluble soaps have a similar effect.

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[1] Wilson and Barnard, "The Mechanism of Lubrication," *Jour. Ind. Eng. Chem.*, **14**, 683, August, 1922.

[2] See p. 491.

[3] Although a small amount of free fatty acid is beneficial, the amount should not be excessive because soaps that will cause the oil to "gum" may be formed by reacting with the metal.

[4] Wells and Southcombe, "The Role of Fatty Acids in Lubrication," *Jour. Soc. Chem. Ind.*, **39**, 47R, February, 1920.

The increased oiliness appears to be due to selective absorption of constituents in the oil by the metal surface. The adsorbed film is of colloidal character and of appreciable thickness rather than of molecular dimensions.[1] The new surfaces formed by adsorption lessen friction by opposing less resistance to shear than the unlubricated surfaces. That the constituents of the lubricants which form the adsorbed layers are selectively adsorbed may be shown by shaking the oil repeatedly with a finely divided metal. After such treatment, the ability of the filtered oil to form a lubricating layer is very much less because the layer-forming material has been largely exhausted.

Classification of Lubricants.—As has been shown, lubricants may consist either in whole or in part of either fatty or mineral oils. Mineral oils are the cheapest of all oils and are the most used as lubricants. For some kinds of lubrication, however, they are improved by the addition of a certain amount of fatty oil or fatty acid. Such mixtures are called "compounded oils." Fatty oils are to only a comparatively small extent used alone. For especially heavy burdens, the oils are thickened to form a grease by the addition of soaps or lime; the greases may be further reinforced by the use of mica, graphite, and similar substances. For convenience in discussion, then, the lubricants will be divided into the following classes:

1. Mineral oils.
2. Fatty oils.
3. Greases.

1. The Mineral Lubricating Oils. *Preparation.*—After the naphthas, burning oils, gas and fuel oils have been removed from the paraffin-base crude oil as described on page 53, the wax distillate and cylinder stocks are further refined.

Treatment of the Wax Distillate.—The wax distillate is first redistilled in fire stills with a small amount of open steam. A relatively high temperature is required and some cracking takes place. The distillate obtained is chilled by coils of calcium-chloride brine, with the result that a soft sludge, containing about 10 per cent of wax crystals, is formed. The chilled mass is now filtered through canvas in filter presses under a pressure of

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[1] Wilson and Barnard, *loc. cit.*, p. 683.

about 300 to 400 lb. per square inch. The oil running from the press is known as pressed distillate. The wax remaining in the press is known as "slack wax"; it still contains 30 to 40 per cent of oil. The pressed distillate is next "reduced" with steam, that is, it is distilled in steam stills until the volatile components, produced by the mild cracking in rerunning the wax distillate, are removed and the fire test of the residual oil in the still is raised to the desired point. In the steam reduction, the first and second fractions passing over belong with the kerosenes and fuel oils respectively; they are added to these same fractions obtained from the crude. A third fraction constitutes a low-viscosity lubricating oil. This fraction is again reduced with steam and is clarified by filtering through fuller's earth. It is then known as non-viscous neutral oil, or spindle oil. Sometimes after filtering, the oil is exposed in shallow vats to the action of sunlight and air. In this way the greenish fluorescence or "bloom," so characteristic of mineral oils, is removed; it is then known as "debloomed" oil. The deblooming does not in any way improve the lubricating character of the oil; it is debloomed in order that there will be less probability of detection when it is used to adulterate the fatty oils, such as linseed, neatsfoot, lard oil, etc.

The fourth fraction, also purified by filtering through fuller's earth, constitutes a medium-viscosity lubricating oil.

The fifth fraction, the residue in the still, is a heavy lubricating oil. It is treated with sulfuric acid to remove traces of asphaltic or tarry substances, after which it is washed with water, treated with a solution of sodium hydroxide to neutralize any remaining acid, and then is washed again. The oil thus purified is engine or machinery oil.

The slack wax remaining in the filter press may be freed from its residual oil by precipitating the wax from solution in naphtha. A solution of the wax containing about 60 to 80 per cent of naphtha is chilled to about −15°F., or lower. At the low temperature employed, the wax precipitates from solution, and is removed by a centrifuge or filter press. The wax may be refined by melting and filtering through heated bone-black or fuller's earth, which whitens it. The product is the *paraffin wax* of commerce.

Treatment of the Cylinder Stock.—The oil left in the still by the fire and steam distillation of crude oil, as described on page 54, is now further fractioned by the use of steam into spindle oils, steam-cylinder oils and gas-engine oils. An effort is made to avoid cracking completely, since cracking increases the amount of asphaltic or tarry substances, which are very undesirable, especially in the oils designed for use in the internal-combustion engines, where the high heat causes a deposition of carbon from such compounds. After being fractionated, the oils are brought to the fire test desired by heating them in steam stills in the same manner as the wax distillate after the wax has been separated from it.

The spindle oils and gas-engine oils produced in this way are clarified by filtering through boneblack or fuller's earth to remove the asphaltic matter which is always present in small quantity. The first oil coming through the filter is practically colorless, but the filtering material loses its efficiency gradually and the oil that comes through later is not so clear. The cylinder oils may be sold as *unfiltered cylinder oils* or they also may be filtered. The unfiltered oils are a dark green, while the *filtered cylinder oils* are likely to be a dark red. The filtering process is very slow and much increases the cost of the oil.

In some cases, the original still residue is diluted with naphtha, chilled by brine coils, and allowed to stand. An amorphous wax separates. The oil remaining is redistilled with steam to recover the naphtha. The wax may be sold either as a lubricant for stuffing boxes, etc., or it may be diluted with naphtha, filtered through fuller's earth, reduced with steam to remove the naphtha, and sold under such names as *vaseline, cosmolene, petrolatum,* etc.

Lubricating Oils from Mixed-base and Asphaltic-base Crudes.—Lubricating oils are prepared also from mixed-base and asphaltic-base crude oils. The general scheme of treatment is similar to that described for the paraffin-base oils, except that in many cases the original crude is run to dryness or "coke" in the first distillation.

2. The Fatty Oils.—The fatty oils used for lubrication are selected from among those of this class that are the most stable, but all fatty oils oxidize somewhat when exposed to the air and are, therefore, to some degree susceptible to "gumming" when in use. Although the fatty oils are less inert than the mineral oils, they have an advantage over the latter in that the viscosities of the fatty oils are lowered to a lesser degree by warming. And, as has been stated before, their adhesion to metallic surfaces is greater than that of the mineral oils. The fatty oils that are most commonly used for lubricants are castor, lard oil, tallow oil, rapeseed, neatsfoot, and sperm oil. Sperm oil is the least viscous of this class and castor oil is the most viscous.

Castor oil is obtained from the seeds of *Ricinus Communis*, a plant native to India, but grown quite commonly elsewhere. The oil that is obtained by cold pressure from the ground seeds is practically colorless, and is used medicinally. A second quality of oil, darker in color, is obtained by heating the once-pressed mass and subjecting it to further pressure. This lower grade is used as a lubricant as well as for other purposes, such as for belt dressings and soap making.

Castor oil consists chiefly of the glyceride of ricinoleic acid, a hydroxylated acid ($C_{17}H_{32}\cdot OH\cdot COOH$), but it also contains a little palmitin which separates out in cold weather, although the oil as a whole does not solidify until about $-18°C.$ is reached. It is not entirely free from gumming tendencies, but it is much less susceptible to this action than most of the fatty oils, and it does not turn rancid as readily as the majority of them do.

Unlike other fatty oils, castor oil is easily soluble in absolute alcohol. Because of this fact, its adulterants may be detected by means of absolute alcohol if they are present to as much as 10 per cent, since a turbidity will then show itself in the alcoholic solution. Further, unlike other fatty oils, it cannot be mixed with mineral oils without separating out again on standing, although it will make a permanent homogeneous mixture with other fatty oils. And when mixed or adulterated with a small quantity of some other fatty oil, it will then remain dissolved in mineral oil. It does not dissolve very well in the light petroleum products in which the other fatty oils are readily soluble.

At ordinary temperatures castor oil is the most viscous of all the fatty oils. It is suitable for the lubrication of heavy machinery running at relatively high speeds.

The common adulterants of castor oil are linseed, rapeseed, cottonseed, or rosin oil that have been thickened by blowing air through them while warm.

Rapeseed or colza oil is obtained from the seeds of several varieties of *Brassica Campestris*, a plant belonging to the mustard family. It is cultivated extensively in Europe but not in America. The expressed oil is refined by the sulfuric-acid and alkali treatment. The refined oil has a pale-yellow color, characteristic odor, and rather unpleasant taste. It thickens noticeably when exposed to the air.

It has a moderately high viscosity and is often employed as a standard for comparison in testing the viscosity of other oils. It is extensively used as a lubricant in European countries, but not so much in America, because of the high price of the imported oil. The more common adulterants are cottonseed, hemp, and refined fish oils.

Lard oil consists chiefly of olein; it is separated from the solid fats of lard by pressure. Melted lard is allowed to cool slowly to about 30°C. and then is kept at this temperature for about 24 hr. Under these conditions the stearin and palmitin largely solidify in granular form. The mass is then subjected to a pressure of about 4 tons per square inch in a filter press, and the more fluid olein is filtered out. About 40 to 60 per cent of oil is obtained from the lard. It is chiefly olein but contains some other glycerides, especially palmitin. The solidifying point or cold test can to a degree be regulated by the temperature at which the mass is filtered. The oil used as a lubricant will usually bear a temperature of 0°C. without solidifying.

The market price of lard oil varies largely according to color, which ranges from a pale or greenish yellow to a reddish brown. The odor varies from practically none to a very pronounced odor in the brown or poorer grades. The best grades contain only a little free fatty acid, usually less than 1 per cent, but the poorer grades contain a considerable quantity.

Lard oil is used as a lubricant when mixed with mineral oils, and also as a cooling agent for cutting tools. Its more common adulterants are corn, cottonseed and neutral petroleum oils.

Tallow oil is obtained from tallow in a manner similar to that by which lard oil is obtained from lard. Its odor is characteristic of tallow. As a lubricant it is used chiefly with mineral oils in steam-cylinder lubrication.

Neatsfoot Oil.—As the name indicates, this oil is obtained from the feet of cattle. After the hide and hoofs have been removed the feet are boiled in water with the result that an emulsion forms from which the oil ultimately separates. The oil is pale yellow, and consists chiefly of olein, but contains also a small quantity of stearin which separates out on standing.

It is a very good lubricant having but little tendency to gum; it may be used alone or with mineral oils. It is also much employed as a leather dressing. It is subject to adulteration because it is relatively high in price. Cottonseed, corn, rapeseed, and refined fish or mineral oils are used for this purpose.

Sperm Oil.—This is not a fatty oil but a liquid wax. Its composition has not been definitely ascertained, although it is known to contain a considerable amount of cetyl palmitate [$C_{16}H_{33}(OOC{\cdot}C_{15}H_{31})$]. It contains practically no glycerides.

The true sperm oil is obtained from the head cavity or "case" of the sperm whale (*Physeter macrocephalus*). A great many barrels of free oil[1] are not infrequently obtained from the head of a single specimen. The name *sperm oil* is also applied to the body or blubber oil; very often the head and body oils are mixed prior to refining. Aside from these oils, the oil obtained from the blubber or body fat of the Arctic sperm or bottle-nose whale is also called sperm oil.

When first obtained from the animal the true sperm oils contain much solid wax. The wax is separated by chilling and filtering with pressure. Different grades of oil are thus obtained depending upon the temperature at which the oil is pressed. The solid wax which is retained by the filter yields, when refined, that which is commonly known as *spermaceti wax*. It is white, lustrous, and very brittle; it is used chiefly for the making of candles.

Sperm oil has a lower viscosity than any fatty oil, and its viscosity is much less decreased by increase of temperature than is that of the true fatty oils. It does not gum or become rancid.

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[1] Hurst, in his "Lubricating Oils, Fats and Greases," says the head cavity will hold as much as 200 bbl. of oil.

It is therefore an excellent lubricant especially for light machinery running at high speeds.

Sperm oil is much subject to adulteration; it may contain mineral oils, other whale oils, and fish oils.

"Blown" or Thickened Oils.—Lard oil, fish oils, cottonseed oil, rapeseed oil, corn oil, peanut oil, some varieties of soya-bean oil, and other animal and vegetable oils, when heated to above 100°C. may be given increased viscosity by oxidation with a current of air. Even petroleum products, especially olefins, naphthenes, and asphalt-base oils (pages 48 and 49) may be thickened in this manner. To meet special requirements, mixtures of fatty and mineral oils are "blown" in the same way. Such mixtures, or blown fatty oils alone, may be used as substitutes for castor oil. Like castor oil, blown fatty oils retain a high viscosity at high temperatures. Castor oil may be distinguished from substitutes of this sort by the fact that it is soluble in cold ethyl alcohol, while its substitutes are not.

3. Greases.—For heavy pressures and slow speeds, greases may be employed as lubricants, but it is not under these conditions only that greases are used. They may be employed for other reasons, for example, to prevent oil from being thrown from the bearings, as in textile mills, and when it is desirable to lessen the attention that the bearings require. In general, however, because of the greater amount of work that must be done in shearing the lubricating film, greases show higher coefficients of friction than oils, and an oil, instead of a grease, should be used whenever possible.

Much of the following information concerning the preparation and properties of greases has been derived from Klemgard's "Lubricating Greases" and Lockhart's "American Lubricants," to which treatises the student is referred.

Cup Greases.—Of all types of lubricating greases, those known as cup greases are now the most widely used. They are emulsions of mineral lubricating oils with water, stabilized with calcium soap. The calcium soaps of oleic and stearic acids will dissolve in mineral oil when heated, and on cooling, a gel (page 579) will be formed, but if the mixture is anhydrous, it is unstable; globules of oil tend to separate. The gel is particularly unstable if an excess of lime is present; when stirred, the soap is precipitated and the gel character of the mass is destroyed. If water is added to the mixture at a temperature of 190°F., a stable product may be formed.[1] The amount of emulsified water in the grease is usually less than 0.4 per cent.[2]

When a cup grease is subjected to violent stirring such as it may receive between a rapidly rotating journal and its bearing, it may lose much of its gel nature and break down into an oil and a soap.[3] Inasmuch as the lime soap is not in itself considered to be a good lubricant, it is important, in preparing the grease, to select an oil that may be depended upon for satisfactory lubrication under the conditions of service. The chief difference between ordinary cup greases and those known as pressure lubricants employed in the grease "guns" for servicing automobiles is the viscosity of the oil employed in preparing the grease. Whereas the ordinary cup grease contains an oil having a Saybolt viscosity (page 569) of 100 to 180 sec., the oil in the pressure lubricant may have a viscosity of 300 sec. or more. The advantage of the pressure lubricant is that it offers greater resistance to being forced from the bearing.

Soda-base Greases.[4]—If an aqueous solution of sodium hydroxide is boiled with a fatty substance, the usual hard soap is formed, but if the saponification is carried out in the presence of a mineral lubricating oil, a heavy sponge of fibrous texture is produced. Because of their fibrous appearance, greases formed in this way are frequently called *fiber greases*. The term is usually applied to soda-base greases of medium consistency. They are stable, but because the soap content is soluble in water, and will be dissolved away if water is present, such greases should be employed where water will not come into contact with them. Because of the solubility of the sodium soap, soda-base greases may be recognized by rubbing a small portion in the palm of the hand with water. By this test, the presence of the water-soluble soap may be readily noted.[5]

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[1] Klemgard, "Lubricating Greases," p. 7.

[2] Lockhart, "American Lubricants," p. 163.

[3] Klemgard, *loc. cit.*, p. 15.

[4] Klemgard, *loc. cit.*, p. 73.

[5] Caplan, "Processes in Soda-soap Grease Manufacture," *Petroleum Eng.*, 1, 10, p. 54, June, 1930.

Soda-soap greases vary from thick liquids to an extremely hard material, and in color from light-golden shades to pitch black.[1] According to Klemgard, the texture, melting point, and appearance of the grease is influenced by the relative amounts of saturated and unsaturated glycerides (page 490) in the fatty substance saponified. Practically any lubricating oil may be incorporated satisfactorily with sodium soap, but it is more difficult to produce a grease of smooth texture with a highly refined, acid-washed, and filtered cylinder stock from a Pennsylvania crude than it is with the heavy California and Texas stocks.

In cup greases, the internal or disperse phase is water, but in the fiber greases the disperse phase is oil. Klemgard classes the cup greases as water-in-oil emulsions, but states that soda-base greases cannot be so considered because they are practically anhydrous.

Non-fibrous Greases.—Non-fibrous, soda-base greases constitute the most important and widely used greases for automobile transmission and differential gears. Formulas given by Klemgard show that as much as 96 per cent of heavy black asphalt-base petroleum residues are employed in the preparation of non-fibrous soda-base greases of this type. He says that when tested under service conditions, the commercial greases show a marked variation in stability. Some break down to thin oils with continued agitation and tend to cause excessive leakage from the differential to the axle housing and thence past the felt washers to the wheels and brake bands. Some greases are sensitive to temperature increases, and tend to break down to thin oils at 150°F.

Lead-soap Greases.—For automobile transmissions, lead-soap greases also are employed to a considerable extent. The lead soap may be made in two ways: first, by making a soda soap and then replacing the sodium with lead, generally derived from litharge; or second, by a direct combination between the fatty substance, fish oil for example, and a lead compound. Afterward, mineral oil of suitable quality is added. The addition of sulfur above that carried by the oil is reported as increasing the "oiliness."[2]

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[1] CAPLAN, *loc. cit.*, p. 54.

[2] MATTHEWS, "Progress in the Use of Grease," *Petroleum Eng.*, **1**, p. 98, midyear, 1930.

Aluminum-soap Greases.—Aluminum-stearate grease has an attractive appearance and is growing in favor. It is usually transparent and is frequently called "solidified oil." It does not oxidize or harden.[1] The content of aluminum soap is usually only about 10 per cent as compared to the 18 to 20 per cent of calcium soap in lime greases.[2]

Rosin-oil Greases (*Set Grease, Axle Grease*).—Greases of this type consist generally of slaked lime and rosin oil, with or without the addition of mineral oil. The lime may be incorporated with the rosin oil either by sifting into it dry slaked lime with constant stirring, or by first preparing a cream-like fluid of the lime which is then introduced into the oil. The lime cream may be formed of lime and water or of lime and light mineral oil. In the latter case a little rosin oil is first added to the mineral oil in order that a small amount of rosin soap may be formed, which will act as a protective suspensoid and aid in dispersing the lime through the mineral oil. Whether dry or in suspension in a vehicle, the lime is introduced into the bulk of the rosin oil at room temperature, or at least only moderately warmed. While the rosin oil and lime are being assembled, the mixture is stirred thoroughly and then is allowed to stand quietly. The mass sets to a stiff grease very quickly, frequently in less than 5 min. If any water is present, as when an aqueous suspension of lime is employed, it is expelled by the grease when setting. The rejected water is then run off, and the grease may be thinned if desired by stirring into it a mineral lubricating oil.

The setting of the grease is caused by the saponification of the rosin in the rosin oil. Rosin oil is formed by the destructive distillation of rosin (page 502), and during the process a portion of the rosin, which is an acid substance, is carried over mechanically with the distillate. Thus, rosin oil, which is essentially a hydrocarbon, has an acid reaction.

Set greases are employed as axle greases. For this purpose, mica, talc, and similar mineral substances are not infrequently added to increase the resistance of the grease to being squeezed out under heavy loads. Rosin greases may be used on any heavy slow-moving bearing, and sometimes they are employed as gear

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[1] MATTHEWS, *loc. cit.*

[2] *Petroleum Eng.*, **1**, no. 1, p. 29.

greases. They serve for the lubrication of street-railway-track curves and in similar locations where a cheap grease is required.

GRAPHITE

Benson[1] states that graphite serves as a lubricant for cast-iron bearings where it acts as a surface evener of the porous metal, but that on finer surfaces it does not work so well because it has a tendency to collect in such quantities as seriously to score or abrade the journal and bearing. To serve as a lubricant under these conditions Acheson has prepared graphite in an extremely fine condition, which is known as deflocculated graphite.

Deflocculated graphite is so extremely fine that it will remain suspended indefinitely in water; it is in colloidal solution. It is prepared[2] by first heating carbon in the electric furnace to 7500°F. All material other than the carbon is volatilized; the carbon may thus attain a purity as high as 99.9 per cent (page 79). This purified carbon is then masticated with a solution of tannin, whereby it is deflocculated. After allowing the material treated in this way to stand until any suspended matter settles out, it is filtered under pressure through canvas impregnated with thin films of rubber, by which process a large part of the water is separated and a carbon paste is formed. To this preparation has been given the commercial name colloidal-graphited water. By working the aqueous paste with oil in a mixing or pugging machine, the water is separated and a paste with oil is left, which bears the commercial name colloidal-graphited oil.

Deflocculated graphite seems to have a very remarkable value as a lubricant. It is said to surpass ordinary graphite in unctuous quality, and the ease with which it remains suspended in water and purified oils renders it very convenient to use. It is very important that any medium into which it is introduced be free from any substance capable of ionizing, or, in other words, that will act as an electrolyte, since carbon in colloidal solution is precipitated by such substances. Hence, it cannot be used with an oil that contains any acid either mineral or fatty.

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[1] "Industrial Chemistry," 2d ed., p. 185.

[2] *Chemical Eng.*, p. 127, March, 1915.

Oildag has been found specially suitable for automobile lubrication.[1] Dr. Acheson himself found that with a four-cylinder car, 0.35 per cent of deflocculated graphite, which is the amount usually specified for use in oils, added to the cylinder oil reduced the consumption of oil from 1 gal. per 200 miles to 1 gal. per 750 miles. The graphite film which is formed on the piston rings and inside surfaces of the cylinder is said to produce such a perfect fit that the compression is increased.

Aquadag is said to be useful in place of the oil-and-soap mixture for lathe and die threading, for boring, reaming, planing, and general machine-shop work. It is also said to be useful for air-compressor lubrication, since it eliminates the risk of explosion from the inflammable vapors generated from lubricating oil when the cylinder becomes heated.

Examination of Lubricants

Mineral oils may be distinguished, as a rule, from fatty oils by means of the greenish fluorescence which mineral oils show. Distinction on this basis cannot always be relied upon, since mineral oils may be debloomed, and because in rare cases fatty oils also show a certain sort of fluorescence. The saponification test (page 493) is a far more certain test for the detection of such admixtures, but it must be remembered that rosin oil also is largely unsaponifiable.

The color of an oil is not a reliable aid in determining the kind of oil since oils may be colored as desired by means of the oleates and butyrates of iron and copper. An oil may be identified by a careful determination of its iodine number (page 493), saponification value, specific gravity, and other properties, but the determination of the nature of mixtures of fatty oils is complex and difficult. The odor and taste of oils, particularly when warm, yield much information to one having had some experience with them, since many have a decidedly characteristic odor and taste. It is not the oil proper that possesses this odor and taste but certain characteristic impurities that are always present in the oil.

Aside from tests for identification, lubricating oils are generally examined for specific gravity, viscosity, flash point and fire test, tendency to gum, solidifying point, volatility, acidity, the pres-

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[1] Archbutt and Deeley, *op. cit.*, pp. 150–152.

ence of soap, and if it be a solid lubricant or grease, its melting point.

Specific Gravity.—This is sometimes determined by means of the hydrostatic balance, but more usually by means of the hydrometer. Hydrometers may be divided into two classes, those from which the specific gravity may be read directly and those graduated with arbitrary scales; of the latter type, the Baumé is the most common example in this country. For a description of hydrometers and their methods of use, see Chap. XX.

Viscosity.—A thick or gummy liquid is said to be viscous while at the same time it may be either high or low in specific gravity. Viscosity is then the measure or degree of fluidity of an oil or other liquid.

A very rough idea of the relative viscosities of two oils may be obtained by shaking them in bottles and noting the time required for bubbles of equal size to rise. The more sluggish the movement of the bubbles, the greater the viscosity. It is necessary, of course, to allow the oils to stand side by side for an hour or more in order that they may be at the same temperature.

Viscosity is usually represented by the number of seconds required for a stated amount of oil at a definite temperature to pass through a small orifice. This is in reality also a relative test since the time must be compared to the time required for the flow of an equal quantity of water under the same conditions; sometimes it is compared to the rate of flow of standard oils, as sperm or rape. There are a great many varieties of viscosimeters, differing essentially in the method employed for stirring the sample and keeping it at a uniform temperature. Temperature is a very important factor in the determination of viscosity; even 0.1° produces a noticeable variation. Unfortunately the various viscosimeters do not conform to any fixed standard and the values obtained on each cannot be compared directly with those of another instrument, but tables have been prepared by the U. S. Bureau of Standards by which comparisons can be made. The Engler[1] viscosimeter has been adopted as the standard instrument for accurate scientific work. The Saybolt

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[1] For method of using the Engler viscosimeter see Lewkowitsch, vol. 1, p. 354, 1913; or Sherman, "Organic Analysis," p. 226, 1912.

and Tagliabue instruments are commonly used in the oil trade; the Saybolt Universal is recommended for American practice by the American Society for Testing Materials.

A rough quantitative method that may be of service for commercial use consists of filling a 100-cc. pipette with the oil and then counting the number of seconds required for the oil to flow from a mark on the upper stem to another on the lower stem. The test must be repeated with some standard oil and, of course, to secure good results the oils must be at the same temperature. Oils may be quickly graded by this method.

Viscosity is an important factor in choosing an oil for any special use. It is also of great value in comparing an oil with another that has been found to give good results in practice. Since viscosities of different oils change at different rates with changes of temperature, Gill[1] says that the viscosity should not be taken at any arbitrary temperature, as 70, 100, 212°F., but at the temperature or between the temperatures *at which the oil is used.* It often happens that one oil is less viscous than another at one of these temperatures while at the temperature of use the reverse is the case. Of the mineral oils, paraffin-base oils show the least change in viscosity with temperature change and naphthene-base oils (page 49) the greatest.[2]

Flash Point and Burning Point or Fire Test.—These points are not determined in order to furnish any information concerning the lubricating value, but in order that safety may be insured while the oil is in use. The *flash point* is the lowest temperature at which the oil will give off sufficient vapor to support a momentary flash when a small flame is brought to within about ¼ in. of the surface of the oil. The *burning* or *ignition point* is the lowest temperature at which an oil will give off vapor at a rate sufficiently rapid that it will burn continuously when ignited. The flash point is always lower than the burning point or fire test and both are below the boiling point.

These points are determined[3] usually by either the "open" or "closed" tester. In the closed tester the vapors do not escape

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[1] GILL, "Oil Analysis," p. 26.

[2] *Petroleum Eng.* **1,** no. 1, p. 28, October, 1929.

[3] For methods see Lewkowitsch, vol. 3, 1909 ed., p. 57; or Thorp, "Outlines of Industrial Chemistry," p. 311; or Hurst, "Lubricating Oils, Fats and Greases," p. 245.

so readily by dissemination into the air; consequently, the results obtained on an instrument of this type are always lower, perhaps from 12 to 20°. With the closed tester, the results are also likely to be more uniform and accurate. Then, in stating the flash point or fire test, the type of instrument used should be specified.

Cloud Test[1] (*Cold Test*).—The cloud test indicates the temperature at which waxes, such as paraffin, or solid fats, such as stearin or palmitin, separate from solution in the oil. The point at which the sample becomes opaque under specified conditions is known as the cloud test.

Pour Test[1] (*Cold Test*).—The pour test indicates the temperature at which a sample of oil in a cylindrical container of specified diameter and length will just flow under given conditions. This temperature is determined by placing the sample in a refrigerating mixture and noting the temperature at which the oil ceases to flow.[2]

THE SELECTIONS OF LUBRICANTS

General Requirements.—An oil must be especially adapted to the purpose to which it is put. The amount of pressure is a very important determining factor, the heavier the pressure the more viscous the oil and *vice versa.* At the temperature at which the oil is used it must have sufficient viscosity to resist being forced out by the maximum load that is placed upon the bearing; any viscosity above this means only a waste of power. On general principles the most fluid oil that will stay in place must be used.

Pressure and speed are closely associated. High speeds are usually accompanied by light pressures and heavy pressures by slow speeds. The higher the speed the less is the density and the viscosity of the oil required. If a viscous oil were used for high speeds, as for spindles rotating at 6,000 to 8,000 r.p.m., the cohension of the particles would be too great to be overcome with sufficient rapidity. Thus there would be a tendency to

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[1] *Proc. Amer. Soc. Testing Materials*, **15**, 281.

[2] STILLMAN, "Examination of Lubricating Oils," p. 10.

retard the motion. On the other hand, an oil that would be suitable for a rapidly rotating spindle would be squeezed out at a slow speed.

As has been stated before, it is very important to consider the temperature at which the oil is used. If the oil solidifies at a relatively high temperature, the friction would be unduly increased if used in exposed situations in cold weather. And an oil that would work satisfactorily in a cold location would not be equally satisfactory for the same speed and pressure in a warm room; under these conditions its viscosity would likely be too low.

The oil should not thicken when exposed to the air or while in use, either because of chemical alteration, or because of the evaporation of a volatile portion that would leave a more viscous residue. The oil should not lose more than 4 per cent by weight when exposed for a working day (8 to 10 hr.) at the temperature of the bearing. The flash point should be above 300°F. The fire test is usually from 30 to 50°F. above the flash point. Viscosity usually increases with increase of flash point and fire test.

Although a small amount of free fatty acid appears to be advantageous, there should not be an excess. Free fatty acid to the extent of about 1 per cent increases the oiliness of the lubricant, which is an important factor with slow speeds and high pressures. It apparently is responsible for the formation of a lubricating layer that adheres very tenaciously to the metal. An excess of the acid causes the oil to gum because of the formations of soaps.

Special Requirements.—The characteristics of the oils suitable for the various purposes indicated in the following paragraphs are largely as stated by Gill.[1] In some cases extracts from specifications are given to serve as examples of the requirements demanded for special uses.

Spindle Oils.—The oils known by the name of spindle oils have usually a low specific gravity and may be either thinly fluid or quite viscous. They are used for a variety of light machinery operating both at low and high speeds. The spindles in textile mills, sewing machines, and typewriters may be considered examples.

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[1] ROGERS and AUBERT, "Industrial Chemistry," 2d ed., p. 606.

The density varies from 35 to 27°Bé.; flash point from 320 to 430°F.; viscosity 30 to 400 sec. Saybolt at 70°F. The evaporation test should not be over 4 per cent.

Engine Oils.—These oils are classed as light and heavy oils. Aside from being used on engines they are applicable to shafting and machinery in general.

The density varies from 32 to 23°Bé., flash point from 300 to 430°F., and the viscosity from 50 to 400 sec. Saybolt at 70°F. For heavy pressures or rough bearings they may contain about 20 per cent of animal oil, as lard or whale oil.

Electric-motor and Dynamo Oils.—These oils are subject to very high speed, medium pressure, and low temperature. The following specifications have been issued by the S. T. Chase Machine Co.[1]

The specific gravity should be between 32 and 24°Bé., the specific viscosity[2] taken at 70°F. should be between 3.50 and 7.50 with a preferred viscosity of about 5.25; flash point (closed tester) must not be less than 330°F., and the burning point (open tester) should not be less than 420°F.; acidity must not exceed 0.1 per cent of free mineral acid or more than 1.5 per cent of fatty acid calculated as stearic. The congealing point must be below 28°F.

Crank-case Oils.—For crank cases, an oil having the following characteristics has proved to be very satisfactory: density 27 to 26°Bé., flash point 455°F., viscosity Saybolt 100 sec. at 212°F.

Steam-cylinder oils are usually compounded oils, unless the cylinder is operated with superheated steam in which case it is advisable to use a pure mineral oil. The compounded oils are prepared by mixing with the mineral-oil-cylinder stock, from 5 to 25 per cent of fatty oil, preferably tallow oil. The advantage in using the mixture depends upon the fact that fatty oils adhere to the moist metal to a greater degree than mineral oils, and also that they enable the lubricant to retain a greater viscosity at the higher temperatures. In the high-pressure cylinders, however, the fatty oil is not necessary since the metal in this case is

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[1] Quoted by Stillman, "Examination of Lubricating Oils," p. 82.

[2] Specific viscosity is obtained by dividing the time of efflux of the sample by the time of efflux of pure water. Specific viscosity obtained in this way is not a constant factor; the type of viscosimeter used affects the value.

absolutely dry. Besides with the superheated steam, the fatty oil might be sufficiently hydrolyzed with the production of enough fatty acids to corrode the bearings. In either high- or low-pressure operation, if it is desired to use the condensed steam for feed water, or for ice making or similar purposes, it is advisable to use only pure mineral oil since the fatty oils produce emulsions with water that are more lasting than those produced by mineral oils. Because the working temperature in steam cylinders is not sufficiently high to decompose the asphaltic or similar hydrocarbons in a mineral oil, the use of filtered oils is not so essential as it is for gas-engine lubrication.

The mineral oil stocks which may be used for compounding have the following characteristics: density 28 to 23°Bé., flash point 500 to 630°F.; viscosity 100 to 230 sec. Saybolt at 212°F.

Gas-engine Cylinder Oils.—It is obvious that an oil that is suitable for the lubrication of a steam cylinder would not be equally suitable for a gas-engine cylinder. The temperature within the steam cylinder ranges usually between 300 and 400°F., while the temperature within a gas-engine cylinder when in operation lies in the neighborhood of 1200°F. Aside from having a relatively high viscosity at a high temperature, these oils must be free from any material that will leave a carbonaceous deposit when burned. Practically all of the oil that enters the cylinder is destroyed by combustion.

In order to remove the asphaltic and similar matter which seems to have a pronounced tendency to yield a carbonaceous deposit, these oils are usually carefully filtered through bone-black or China clay in the refining process. The removal of the asphaltic matter lessens the viscosity.

It is said that other unsaturated hydrocarbons, such as the olefins, which are produced in a certain amount by the process of destructive distillation, described on page 54, also tend to yield a carbonaceous deposit. Assuming this to be true, it follows that oils of both paraffin and asphaltic base, if refined by the cracking process are not so suitable for gas-engine cylinders as are the paraffin-base oils refined by steam distillation.

For automobile engines, oils having the following characteristics are indicated: density 33 to 30°Bé., flash point 380 to 450°F., and viscosity 180 to 185 sec. Saybolt at 100°F. For larger-sized gas engines a heavier oil is used: density 28 to 26°Bé., flash point 400 to 475°F.; viscosity 250 sec. at 70°F.

Steam-turbine Oils.—Turbine bearings are lubricated by a force or circulating pump system; hence the oil used should be comparatively low in viscosity. Because the working temperatures are frequently rather high, a thin oil is more desirable since such an oil loses its viscosity to a less degree than a more viscous one. A thin oil is also demanded by the high speed of the turbine. Another important requirement is that it shall separate readily from water; consequently the oil should be purely mineral. Gill says an oil of 30°Bé., 150 sec. Saybolt at 70°F., and 420°F. flash point has given good results.

Cooling Liquids and Lubricants for Cutting Tools

Water as a Cooling Agent.—In the various operations of the machine shop, such as turning, planing, boring, sawing, milling, etc., the tool employed becomes more or less heated. To prevent overheating and injury to the tool, a stream of liquid is directed against it. Because water has a high specific heat and a high latent heat of vaporization and is, therefore, a good cooling agent, it might be supposed that water would serve very well as a cutting fluid. As a matter of fact, however, water is used for this purpose to only a very limited extent, and even then for rather simple operations, such as rough turning and grinding. An objectionable feature is that it rusts the machines and the work also, if it is of iron or steel. This difficulty may be overcome by adding soap or alkaline salts to the water, but with difficult operations, water and simple aqueous solutions do not serve well, because they have a poor lubricating value and do not yield a smooth finish. Moreover, the tool becomes quickly dulled. Lubrication must, therefore, be considered.

Lubrication.—Because the nose of the tool is thrust into the stock being cut, it might appear on first thought that to apply a lubricant at any point where it could be of service would be impossible. The situation, however, is not as it seems. In cutting operations it has been found that the cutting tool has a splitting or wedging effect; the chip is parted from the stock at some distance ahead of the edge of the tool. The edge of the tool then cleans up the rough surface. The heaviest pressure occurs where the chip bears on the surface of the lip, a point located at some distance from the edge of the tool. Here the friction is very great. The fluid applied is drawn in between the chip and the face of the tool; if the fluid has a lubricating effect, the friction is lessened and the production of heat is to a large extent avoided. It has been learned through experience that mineral oils are in most cases very poor cutting lubricants; fatty oils are much superior as a rule. Lard oil is the best of all for general work. Although it has lower viscosity and different chemical composition, being a liquid wax and not a glyceride, sperm oil is comparable with lard oil.

The chief reason for the superiority of fatty oils over the mineral oils was explained in discussing the theory of lubrication on page 556. It is due to their better adhesion. In cutting operations, the chip bears on the face of the tool with very heavy pressure; consequently the general principles stated in the discussion of the theory regarding the greater effectiveness of the lubricants when absorbed films are formed hold true here. High adhesion is necessary in such cases.

Materials Employed in Cutting Fluids.[1]—The materials employed in cutting fluids may be classified under three heads: oils, aqueous solutions, and emulsions.

Oils.—In addition to lard oil and sperm oil, other animal oils, such as tallow oil, neatsfoot oil, fish oil, etc., may be employed. Many vegetable oils, for example olive oil, are also used. Although they are not fatty oils, turpentine, pine oil, and rosin oil may be classed among the vegetable oils. For tapping and threading by hand, white lead in linseed oil is a common lubricant. The white lead enables the oil to stay in place.

Although mineral oils may be used in special cases, they are not very satisfactory for general work. They neither adhere as well as the fatty oils nor cool as well as the aqueous solutions and aqueous emulsions. The so-called compounded oils, which are a mixture of fatty oils and mineral oils, are used to some extent. These mixtures are prepared in an effort to combine the cheapness of mineral oils with the adhesion of the fatty oils.

Aqueous Solutions.—Where cooling is of prime importance and a smooth finish is not necessary, water is used. In order to

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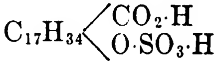
[1] Bingham, "Cutting Fluids," *U. S. Bur. Standards Tech. Paper* 204, 1921

overcome the corroding tendency of water, caustic soda or alkaline salts, such as sodium carbonate and borax, are dissolved in it. Soaps, such as the ordinary sodium soap, potassium or soft soap, and sodium resinate are also employed. There is a disadvantage in using soap because, as the water evaporates, the solution may become sticky and clog the feed pipe.

Emulsions.—When it is necessary to have a pronounced cooling effect coupled with effective lubrication, emulsions serve very well. Emulsions contain both water and oil; they combine the cooling effect of the former with the lubricating value of the latter. According to Bingham[1] two classes of so-called "soluble oils" are used.

One class is made up of mineral oil compounded with a neutralized sulfonated oil. Fixed oils treated with sulfuric acid react to form so-called sulfonic acids. With stearin, for example, the product represented by the formula  $C_{17}H_{34}{<}\begin{matrix}CO_2\cdot H\\ O\cdot SO_3\cdot H\end{matrix}$ is formed. When the sulfonic acid is neutralized with alkali, it is readily soluble in water; with mineral oils it forms emulsions when heated.

A second kind of soluble oil is made from a mineral oil compounded with an alcoholic solution of soap, preferably potassium or "soft" soap. Both soluble oils are marketed as clear solutions. They are prepared for use as emulsions by mixing them with water, usually 1 part of oil to 4 parts of water.

A third type is sold as a paste made of a thick soap solution with a mineral oil; it also is prepared for use by mixing with water.

One of the functions of the soap in these preparations is that it acts as a "protective emulsoid;" it tends to prevent the oil globules from coalescing. If they should coalesce the mineral oil would separate from the aqueous solution. The emulsions are relatively cheap and quite effective, both as to their cooling and lubricating values, especially those made of the so-called "soluble oils."

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[1] *Loc. cit.*, p. 69.

CHAPTER XV

GLUE

Glue is a product obtained by boiling with water suitably prepared animal matter, such as hides, bones, sinews, etc., and then drying the resultant solution. It is generally believed that the boiling brings about a process of hydrolysis, *i.e.*, a definite chemical combination between water and the glue-yielding substance. Certainly the process accomplishes more than the mere extraction of a substance or substances that exist naturally in the tissue, for the material used contains no glue as such.

Composition of Glue.—Glue is a very complex material. It consists of other more definite substances, such as gelatine, chondrin, keratin, etc. The gelatine makes up the larger bulk of the glue and is itself a substance from which a great number of compounds have been isolated.[1] But even then, the chemical constitution of gelatine is very imperfectly known. Still less is known of the more complex glue.

Distinction between Glue and Gelatine.—It is rather difficult to make an exact distinction between glue and gelatine. Commercially they are distinguished by their appearance. Gelatines are usually transparent; they produce very clear solutions and jellies, while glues are darker. Gelatine is obtained like glue by boiling hides, bones, etc., although the stock is much more carefully selected and washed, and the process is carried out under more sanitary conditions. In a broad sense, glue may be considered as an impure gelatine, or gelatine as a refined glue. It should be noted that the boiling process in the production of glue is carried out at higher temperatures, and glue is generally considered to be more hydrolyzed than the gelatine. The higher degree of heat employed in the production of glue makes it more liquid and lessens its gelatinizing power, probably because of the greater hydrolysis. Although glue has a lower gelatinizing power than gelatine, its adhesive power is greater.

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[1] Rogers and Aubert, "Industrial Chemistry," 2d ed., p. 961.

Colloidal State of Glue and Gelatine.—Glue and gelatine are excellent examples of substances that exist naturally in the colloidal state. In fact, from the Greek κόλλα (glue), the term colloid has been derived. Substances that exist in the colloidal state are distinguished primarily from those that exist in the crystalloidal state, but most substances can be caused to assume either state by suitably adjusting conditions.

Colloidal Sols and Gels.—When colloids are added to water they may appear to dissolve and the resulting fluid state is commonly called a "solution," as for example, a "glue solution." In reality, the degree of dispersion or physical subdivision is not so fine as in the case of a true solution such as is produced when crystalloids dissolve; the so-called solution is more properly considered as a state of extremely fine suspension. In colloidal chemistry this state of fine suspension is known as the *disperse phase* or *sol* of the colloid. Thus the fresh white of egg, just as it comes from the shell, is a colloidal sol of albumin. Although the suspended particles in the sol are considerably larger than the dissolved particles in a true solution, they are nevertheless sufficiently fine that they do not readily settle out as do the particles of coarser suspensions, such as muddy water, for example. Neither can they be filtered out by ordinary filters. They are too coarse, however, to pass readily through parchment paper or other dialyzing membranes that are permeable to particles in true solution.

When water is extracted from a sol its viscosity increases and eventually a solid, jelly-like mass is produced. To this form the name *gel* has been applied. In the cases of glue and gelatine, this swelled, jelly-like state is also assumed when the dry substance is allowed to stand in cold water. The swelling is due to the water imbibed and the amount taken up may amount to several times the weight of the dry substance. Glue and gelatine do not form sols in cold water, although they very readily assume this state when the softened gel is gently warmed. When the sol is allowed to cool, the gel forms again and the process may be repeated. Of course, it is possible to prepare sols of these substances so weak that they will not form gels on cooling, but Rideal[1] says that if the concentration of the gelatine sol is not

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[1] "Glue and Glue Testing," p. 6.

under 1 per cent, a gel will be formed when the sol is allowed to cool.

It must be understood that gels are not always soft substances like the water-saturated glue jelly. The degree of softness or hardness depends upon the degree of swelling. Gels may become very hard when they are allowed to dry out, but they are still gels. Thus the familiar, hard-flake or sheet glue is a hard gel produced by drying a voluminous, swelled jelly.

Reversibility.—All dried gels are not able to be transformed into sols again in the manner just described for glue. Upon the basis of whether or not they can be thus transformed, colloidal substances are divided into two classes known as *reversible* and *irreversible colloids.* As has been shown, glue and gelatine are excellent examples of the reversible class. Those colloids that become impermeable to water as they dry cannot be caused to swell or to be directly transformed into the sol state and are known as irreversible colloids. The colloidal carbon of drawing inks and silicic acid are examples of this class.

Coagulation is the term applied to the formation of a precipitate in sols by the application of heat or by the addition of precipitating agents. Thus, the albumin sol of natural egg-white is coagulated by heating to the temperature of boiling water for a short time, the product being known as "hard-boiled white of egg." The same effect may be produced by the addition of nitric acid to the albumin sol. Coagulation is due to a coalescing of the colloidal particles to form larger aggregates, too large to remain in colloidal suspension.

Glue and gelatin sols are coagulated by formaldehyde, tannin, and alum; the coagulated product is "irreversible" in that it is immune to the action of water. The same effect is produced by chromium salts upon exposure to light. This effect is of importance in using glue where it is required to resist being softened by water.

Materials Used for the Manufacture of Glue.—The stock used in the manufacture of glue consists chiefly of the hides, bones, and sinews of cattle; the hides of horses; the skins of the sheep, goat, deer, and pig; together with the bones of some of these. The air bladders and other portions of fish are used also. Aside from these materials, glue is made also from the rabbit skins left after the hair has been removed for the manufacture of hats, from clippings of parchment and gloves, and from any other form of hide waste. The calf, cattle, goat, deer, pig, and horse skins are valued in about the order given. Of these hides and skins, it is only the portions that are unsuitable for leather that are used for glue. Tanned hides are not available for glue stock because the tannin renders the glue-yielding substance insoluble.

Preparation of Stock.—If the stock to be used consists of skins, it is first necessary to treat it with lime water, except in those cases where it has been delivered from the tannery and is already sufficiently limed. The lime treatment is necessary to remove the hair and fleshy portions; it also causes the hide to swell and makes the extraction more easy. The length of time required for the liming process depends upon the stock; it varies generally from 1 to 3 days, but for very heavy pieces several weeks are necessary. Care must be taken to prevent both over- and underliming, since either will produce defects in the stock that cannot be prevented from producing defects in the glue. After liming is finished, the hides may be merely washed, or the remaining lime in the skins may be neutralized with sulfuric acid. Calcium sulfate is formed in this way. Because the calcium sulfate is insoluble it is carried into the finished glue and produces a certain cloudiness. For very clear glues hydrochloric acid is used. The very soluble calcium chloride is formed which may be more readily washed out. Depending upon the treatment at this stage, *i.e.*, whether the lime is removed as much as possible by washing or more completely by treatment with acid, the finished product may be acid or alkaline in reaction. Fernbach says[1] that this is important since the bacteria which bring about the decomposition of a glue multiply rapidly when it is alkaline, but have a much harder struggle for existence in a glue having an acid reaction. Hence the latter keep longer than the former in a state or solution of jelly without the use of preservatives.

If the stock consists of bones, they are generally ground and the grease is removed by steaming or by extraction with benzine. After degreasing, the mineral matter, calcium phosphate, is removed by leaching with dilute hydrochloric or sulfuric acid

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[1] "Glue and Gelatine," p. 7.

and washing with water. A soft cartilaginous mass, equal to about one-third the weight of the original bone, is left. This, when dried, is commercially known as *ossein*. From ossein, glue may be made by boiling. In order to differentiate them from glues made from untreated bones, the term "acid-treated bone glue" is used to indicate glues made in the manner just described. Mixtures are often made of bone and hide stock or of sheep, goat, or ox stock; thereby better glues than the straight glues are produced.

Boiling.—After the stock has been prepared as desired, it is boiled with water to convert the glue-yielding substance into glue. The change produced by the boiling is generally believed to consist essentially of a process of hydrolysis, but it is very probable that other changes occur also; the transition process, as a whole, from glue-yielding substance to glue is not very well understood.

According to the nature of the stock and the preference of the manufacturer, the glue may be obtained from the stock in one operation or in several "runs." If the latter method is used, the extraction is begun by using only a small quantity of water and the lowest temperature by which glue may be formed. After this extraction has been drawn off, more water is added and the boiling is continued for a longer time and at a higher temperature. Four or five extractions may be made in this way; the temperature employed for the last extraction is about 100°C. The higher the temperature and the longer the heat is applied, the lower will be the quality of the glue. Thus, the glue obtained by the first extraction has the greatest gelatinizing power and the greatest strength, while these qualities in the later "runs" grow less. In producing glue from untreated bones, pressure tanks are used and the glue made in this way has usually less strength than that produced by the open-tank method because of the higher temperature employed.

Preservatives.—During the extraction, if it is thought necessary, preservatives are added. There are at least three of these that may be used: formaldehyde, phenol, and boric acid. Rideal says[1] that the minimum concentrations that will prevent putrefaction are as follows:

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[1] "Glue and Glue Testing," p. 40.

Formaldehyde	1 part in 20,000
Phenol	1 part in 1,000
Boric acid	1 part in 200

Formaldehyde is a good preservative but has a tendency to cause the glue sol to coagulate when the glue is prepared for use. Phenol, or carbolic acid, is barred to some extent on account of its odor. Boric acid, although low in antiseptic power, necessitating the use of greater amounts than the other preservatives, is found to be very satisfactory.

Clear Glues.—Calf and acid-treated bone stock generally yield very clear glues. Clear glues may be produced also by bleaching and clarification while the glue is still in the liquid form. Bleaching is generally accomplished by the use of sulfur dioxide, after which the glue solution is treated with milk of lime to neutralize the sulfurous acid formed. Depending upon whether an insufficient amount or an excess of the lime is used, the final reaction may be either acid or alkaline, and this should be remembered in testing. Or the coloring matter may be swept from the solution by producing therein flocculent precipitates which upon settling carry down the coloring matter. Alum, albumin, and other substances are used for this purpose. Fernbach says that alum has a tendency to make the glue solution very stringy and low in penetrative power.

Opaque or Molding Glues.—The appearance of the glue may also be modified by the addition of zinc white (ZnO); chalk ($CaCO_3$); barytes ($BaSO_4$), or talc, a hydrated magnesium silicate. A limited amount of such additions produces that which is known as a "colored" glue, while greater amounts produce a white or "opaque" glue. The latter is also known as *molding glue.* Its price is always somewhat higher than natural glues of the same strength.

The Glue Jelly.—After the glue solution has been treated as desired, it is run into pans and allowed to cool, or is chilled artificially, in order that it may gelatinize. When the jelly has formed it is removed from the pans, placed in frames, and sliced by wires into sections averaging ½ in. in thickness. These slices are then placed on nets of twine or galvanized wire and dried, either artificially or by natural air currents. The glue pieces often retain the impression of these nets; the marks are readily seen in the sheet and flake glues of commerce.

Commercial Forms of Glue.—Since the glue jelly when placed on the drying nets consists largely of water, the drying process greatly diminishes the thickness; as a result, the slices acquire the form of more or less thin sheets. The amount of the decrease is, as a rule, greater in the glues of better quality, since in the formation of their jellies, less glue by weight was required to produce a jelly firm enough to handle. The dried glue may be marketed in the form of sheets, but usually the sheets are broken into small pieces, which constitute the familiar flake glues. The flakes may also be ground to varying degrees of fineness. There are other forms, as strip, ribbon glue, etc.

Grades of Glue.—When the glue is marketed it must be classified or graded in order that its price may be fixed. The grades are determined by comparison with accepted standards. The comparison is based on the determination of certain physical factors, of which the viscosity of the solution and the strength of the jelly are considered most important. Other factors such as odor, keeping qualities, acidity or alkalinity, presence of grease, tendency to foam, etc., may also be ascertained. Only by determining the grade of the glue can the manufacturer properly assign a price. Cost of stock and cost of production cannot govern this entirely, since variations in the conditions of production, perhaps accidental or uncontrollable, may markedly affect the quality. In the same manner the consumer should determine the grade in buying. A more or less fixed price pertains to a definite strength of glue, and by determining the strength it can be determined whether or not its quality is commensurate with the price paid.

There is no absolutely fixed system of standards in use, but the 11 grades originally employed by Peter Cooper, both because they were among the very first manufactured in this country, and because they have maintained a certain reliability, have been more or less commonly chosen as standards by both manufacturer and consumer. Ranging from strongest to weakest they are: A Extra, 1 Extra, No. 1, 1x (one cross), 1¼, 1⅜, 1½, 1⅝, 1¾, 1⅞, and No. 2. Although these standards are chosen for discussion here, it is not meant to indicate that they only are reliable. Grades exceeding the strength of the best of the series are regularly manufactured, as well as grades that may lie between any two.

Glue Testing and Information Derived from Tests.[1]—As has been indicated, the tests applied to glue are concerned chiefly with the determination of certain physical characteristics of the glue solution and the jelly formed from it. In addition, a preliminary examination of the dry glue is of value. Although the tests applied are largely only comparisons, they are of sufficient accuracy to furnish a definite idea of the strength of the glue and the price that should be paid for it.

Preliminary Examination of the Dried Glue. *Cut and Flexibility.*—The cut of a glue may give some indication of its quality. Thin-cut glues are obtained by making a jelly that consists largely of water and cutting in slices varying from ¼ to ½ in. thick. These slices reduce to about ¹⁄₁₆ in. upon drying. If an attempt is made to cut the glue into such thin sections directly from a solid jelly, it curls badly. It is only a very good glue that can stand the large excess of water and still form a jelly solid enough to cut. A thinly cut glue that is flexible enough to be bent into the shape of a horseshoe is a good glue. Moisture tends to increase the flexibility of glues and this fact should be remembered in testing.

Fracture.—When a piece of glue is broken, if the fracture is splintery, a strong glue is indicated. A glassy fracture indicates a brittle glue of less strength. Glues made from bone stock generally break with a clean fracture, as do also those that have been overheated in manufacturing.

Bubbles.—The surface of the piece of glue, examined in a good light, should be free from bubbles. Bubbles are generally considered to be evidence of putrefaction, which began in the glue stock and continued in the jelly while on the drying nets. Further information may be obtained by moistening the glue and

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[1] The discussion given here on methods of testing and information derived from tests is largely as given in Fernbach's "Glues and Gelatines." For detailed directions for carrying out tests, see that volume, p. 50. For Standard Methods for Determining Viscosity and Jelly Strength of Glue, adopted by the National Association of Glue Manufacturers, see *Jour. Ind. Eng. Chem.*, **16**, 311, March, 1924.

noting the odor. Sometimes bubbles may occur in the glue beneath the surface due to the incorporation of air while the glue solution was being poured into the mold to gelatinize. Such bubbles are apt to be found in good glues whose solutions have higher viscosity and hence allow bubbles of air to separate less readily. Air bubbles are generally small and more or less regular in outline, while bubbles resulting from decomposition are larger and more irregular in shape. The marks of the drying net must not be mistaken for surface bubbles.

Mixtures.—Flake, and particularly ground glues, may consist of mixtures. Whether they are mixed or not may be determined by visual examination in a good light. If the glue is ground, it is necessary to compare pieces of the same size, since smaller pieces possess apparently a lighter color. Glues may be mixed either to cause the jelly strength of the mixture to accord with the specifications or perhaps to lower the price to suit the requirement by the introduction of a cheaper glue.

Examination of the Glue Solution. *Odor.*—The odor of the solution will vary according to the stock from which the glue was made, but there should be no trace of putrefaction.

Acidity and Alkalinity.—Strictly neutral glues are very seldom found. Enough acid or alkali will likely be present to show a reaction with litmus paper. Correction of overliming, bleaching, and acid treatment to remove mineral matter in the making of bone glue, may cause the finished product to be acid. Since "colored" and "opaque" glues are generally made from bleached stock, these glues may be acid unless the whitening agent used was some "anti-acid" as chalk or zinc white. Overlimed stock that has been washed only, will be alkaline. If a glue has an earthy smell, it quite likely has been overlimed.

Viscosity.—This term refers to the rate of flow of a glue solution through a specified opening, as compared with a standard, usually water. A solution that flows sluggishly is said to be high in viscosity and *vice versa.* The viscosity determination is of great value but is not alone sufficient for grading glues. Acid-treated bone glues are much lower in viscosity than would be expected according to their true strengths. Opaque and colored glues are slightly higher in viscosity than natural glues of the same strength. The majority of foreign glues, having been clarified, are low in viscosity, unless clarified by alum, when the reverse is the case. Very clear glues that are exceedingly high in viscosity—so that they are "stringy"—are likely to have been alum clarified.

Jelly Strength.—This is the most important and determinative of all the tests. The strength of a glue jelly may be determined by especially designed apparatus, such as plungers weighted with shot and by other devices, but for all practical purposes it can be well enough measured in comparison with standards by its resistance to the pressure of the finger.[1] The real strength of a glue bears a fixed relation to the strength of its jelly.

Foreign Glues.—Fernbach says that the foreign glues are generally made from more carefully selected stock than are the domestic glues, the stock being frequently hand picked, a process that is out of the question for the American glue maker because of the cost of labor. He says further that the glue liquor is generally clarified, which causes the glue to be lower in viscosity than is usual for glues of their jelly strength, just as is the case with domestic acid-treated bone glues. But, on the other hand, the attempt to remove the viscous, non-adhesive elements by clarification is apt to result in the loss of adhesive material as well. Foreign glues appear usually in the form of more or less thick cakes.

Fish glues are prepared from the heads, bones, swimming bladders, and other portions of fish. With the exception of isinglass, they are not marketed in the dry state, but in the form of heavy solutions or pastes, which have the characteristic odor of fish. An effort is generally made to mask this odor by the use of essential oils, such as sassafras and wintergreen. Fish glues in general possess high adhesive properties. Unlike the other fish glues, isinglass occurs in various solid forms, as sheet, lump, etc. It is very hard, transparent and practically colorless. It is prepared from the swimming bladder of the Russian sturgeon and possesses the highest adhesive properties of all the glues.

Selection of Glues for Wood Joints.[2]—Other factors being satisfactory, glues ranging in strength from 1⅜ to A Extra are suitable

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[1] For method of conducting test, see Fernbach, *loc. cit.*, p. 50.

[2] For tests for the selection of glues for wood joints, see Truax, Brown and Brouse, "Wood-joint Tests for the Selection of Woodworking Glues," *Jour. Ind. Eng. Chem.*, **21**, 74, January, 1929.

for wood joints; the exact grade is determined by the character of the work. The viscosity of the solution should be as low as possible, since the adhesive power of the glue is dependent upon the degree to which it enters the pores of the wood. On this account, thin solutions produce stronger joints than thick ones. A well-made, acid-treated bone glue will make a strong joint because its solution will be thin. Hence it is necessary to consider both viscosity and jelly strength. Clarified glues, unless clarified by alum, have lower viscosity and, therefore, greater penetrating power. Foreign glues are generally clarified; therefore, of a foreign and domestic glue of the same jelly strength, the former will likely produce the stronger joint because it will penetrate the wood more readily than the latter. But, if a foreign and a domestic glue of equal price are chosen, the domestic will be by far the stronger. Consequently, more glue solution of a specified quality can be made from a pound of domestic glue than from a pound of foreign glue costing the same amount.[1]

Preparation of Glue Solutions for Use.—To prepare the glue solution for use it is very important first to soak the dry glue in cold water. Then, after it has been entirely softened by soaking, it should be warmed in a water-jacketed container at a temperature not exceeding 80°C.; a thermometer should be used to determine the temperature. Hot or even warm water must never be poured upon dry glue. If this is done, a layer of partially dissolved glue is formed on the surface that is practically impermeable to water; then the glue cannot be dissolved without the application of heat to either a high degree or for a long period. Such excess heating greatly injures the glue. The damage done is generally considered to be due to an increased hydrolysis brought about by the overheating; the change is described as comparable to the softening desired in the cooking of meats to prepare them for food. Glue solutions should never be boiled.

For the preliminary soaking it is advisable to have the glue as finely divided as possible. A heavy mortar with a cardboard cover, having a hole through which the pestle may pass, can be used very advantageously to crush the glue if it is not as fine as desired. The soaking process will require from 4 to 12 hr., or even overnight, depending upon the degree of fineness. Good

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[1] Fernbach, *loc. cit.*, p. 108.

glues will generally absorb from 1½ to 2½ times their weight of cold water. It should be seen to that all pieces of glue are covered during the soaking process. If portions are not sufficiently softened, prolonged heating is necessary to effect their solution; then all of the glue in the vessel will be injured. Thin, voluminous, flake glues may be softened without increasing the amount of water, by adding only portions at a time. Being thin, they absorb water rapidly and recede quickly. During soaking it is advantageous to stir the mass, at least at first, to prevent sticking, since if this occurs a prolonged period of soaking is necessary. If sufficient time is not allowed for soaking, protracted heating is required. If ground glue is used, particles will float and stick to the sides of the container, with the result that they will be only partially soaked and hence insoluble without undue heating. To prevent this, only about half the proposed amount of water is added at first; when partial soaking has occurred so that the particles will no longer float, the remainder of the water is added. In this way, the original surface line where the sticking occurred will be submerged.[1]

When the glue has been softened by proper soaking it may be readily dissolved by warming as has been described. Since glue solutions cannot be used cold, but must be continuously heated to keep them in a condition suitable for use, the strength of the joints will be far greater if successive small portions of glue are dissolved and used, rather than to prepare large amounts that must be kept heated for long periods.

The glue container should be very frequently cleaned. Glue solutions and jellies form excellent breeding media for liquefying bacteria and other microorganisms.

Flexible glues consist of glue, glycerine, and water. The glue is dissolved in the ordinary way and an amount of glycerine about equal to the weight of the glue is added. Flexible glue is used for bookbinding, for preparing writing pads, etc.

Liquid glues may be fish glues as was stated under that head, or may be animal glues that have been kept from gelatinizing by the addition of certain salts or acids. For this purpose weak animal glues, that possess the gelatinizing power in low degree, are generally chosen. Consequently, their strength is far less

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[1] FERNBACH, *loc. cit.*, p. 137.

than the fish glues they may be designed to imitate. Acetic and nitric are the acids most used.

Some so-called "liquid glues" contain no glue whatever, being merely solutions of corn dextrine, preserved generally with formaldehyde. This adhesive is used in manufacturing paper boxes, postage stamps, etc.

CASEIN GLUES

Preparation of Casein.—Casein is a phosphoprotein, which, next to water and fats, is the principal ingredient in milk. Cow's milk, which contains about 3 per cent of this protein, is the chief source of commercial casein. After the fats have been removed from the milk, the casein may be separated by various methods, but it is usually precipitated as a curd by means of an acid. The acid employed may be a mineral acid, such as a dilute solution of hydrochloric or sulfuric, or it may be lactic acid developed in the milk through the fermentation of its lactose or milk sugar content by the lactic-acid bacillus. The precipitated curd is separated from the whey, and then is thoroughly washed with cold water. By means of a filter press or centrifugal separator, as much water as possible is removed from the curd, which when dried is ready for use.

Types of Casein Glues.[1]—Casein is acid in character and reacts readily with alkalies to form compounds, which, for want of a better term, are called *caseinates*. The sodium, potassium, and ammonium caseinates are soluble in water. They yield colloidal sols, which, by the evaporation of water may be converted into gels. These gels are reversible (page 580). Irreversible gels may be formed by converting the soluble alkali caseinates into the caseinates of either the alkaline earth or the heavy metals. Casein sols are adhesive. By taking advantage of the properties of casein, two types of casein glue have been developed: (1) glues having reversible gels and (2) water-resistant glues. The former are employed for essentially the same purposes as the hide and bone glues, while the latter are used where resistance to moisture is important.

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[1] For a more complete treatment of this subject, see Sutermeister, "Casein and Its Industrial Applications," from which treatise the information given here has been largely derived.

Casein Glues with Reversible Gels.—The glues of this type, unlike the hide and bone glues, do not yield a gel by the mere cooling of a sol; the formation of the gel depends upon the evaporation of water. After the gel has dried, if it is exposed to water, it will go into solution again. In making wood joints, for service where moisture will not be encountered, glues of this type are very satisfactory adhesives. They are cheaper than animal glues, but being alkaline, they stain the wood, and produce a more noticeable glue line than the latter. Like animal glues, they hydrolyze and lose adhesive strength when held in solution at working temperatures. Being alkaline, they are subject also to bacterial decomposition. Because of these facts, the glue should be prepared for use, like the hide and bone glues, just prior to its application.

Preparation of Reversible-gel Glues.—The alkali required to dissolve the casein may be introduced into the mixture in three ways: by employing (1) sodium or ammonium hydroxide as such, (2) calcium hydroxide and a suitable sodium salt in chemically equivalent amounts, (3) the sodium salt of a weak acid.

As recommended by Sutermeister,[1] a suitable proportion for a wood-worker's glue is 100 g. of casein to 600 g. of water. The required weight of water is first stirred thoroughly into the casein, and the mixture is allowed to stand until the casein has become completely swollen. For this purpose 5 or 10 min. may be required. The alkali is then added and the stirring is continued until the casein is dissolved, an operation that may require from 30 min. to 1 hr. Slight warming of the mixture greatly lessens the time needed to effect a solution, but heating the mixture also lessens the time during which the solution will remain suitable for use. The amount of alkali recommended by Sutermeister is 0.1 g. equivalent of sodium hydroxide or 0.2 g. equivalent of ammonium hydroxide. For 100 g. of casein, these equivalencies are represented by 4 g. of sodium hydroxide and 13 cc. of aqueous ammonia having a specific gravity of 0.91.

Because sodium hydroxide is markedly hygroscopic, it is very difficult to prevent it from absorbing water during storage and weighing. Its hygroscopicity also tends to render the weighing inaccurate, especially under the conditions prevailing in the wood-

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[1] *Loc. cit.*, p. 178.

working shop where the operator may be unfamiliar with the properties of the hydroxide. A slight increase in the amount of alkali, moreover, noticeably decreases the viscosity of the solution. Another disadvantage that results from the water-absorbing tendency of the sodium hydroxide is that it cannot be added to the casein by the manufacturer. If this were done the sodium hydroxide would absorb moisture and the mixture would deteriorate during storage. These difficulties may be overcome, however, by the use of dry calcium hydroxide and a sodium salt with which it will react, when wet, to yield sodium hydroxide and a corresponding calcium salt that is practically insoluble in water. Sodium salts that may be employed in this way with calcium hydroxide are the carbonate, oxalate, phosphate, and many others. According to this method, the ingredients can be mixed by the manufacturer, and a working solution can be prepared by the consumer by merely stirring in thoroughly the required amount of water. Such mixtures can remain in storage unharmed as long as they are kept dry. Sutermeister points out that glues of this type can be held in solution for only a limited period. The presence of the calcium salt causes an irreversible gel to form in 15 to 20 hr. These glues are, however, not water-resistant in the sense that this term is used by the wood worker.

As has been indicated, a third method of introducing the sodium hydroxide consists of using a sodium salt that hydrolyzes in water to produce sodium hydroxide and an acid that ionizes only slightly. The sodium hydroxide reacts with the casein, which allows the hydrolysis of the salt to proceed further. The process continues until an equilibrium in accordance with the law of solubility product has been reached. Borax, sodium carbonate, and trisodium phosphate are a few of the sodium salts that may be employed in this manner. The amount of the salt required depends upon its ionization constant. Like those of the second class, mixtures of this type also may be made in the dry state, and then prepared for use by the addition of water.

Water-resistant Casein Glues.—The glues that are described under this topic are, in the literature of the manufacturer, generally called "waterproof," but it is more accurate to say they are water-resistant. As compared to the casein glues that yield reversible gels, which have just been discussed, the water-resistant glues are more important and more widely used. The largest quantity, perhaps, is consumed in plywood and veneered-panel construction.

In all of the commercial water-resistant casein glues, calcium hydroxide is employed to render the gel irreversible. Compounds of other metals, and calcium compounds other than the hydroxide can produce this effect, but calcium hydroxide is cheap and happens to have just the solubility in water that is desired Salts that are too soluble cause the casein hydrosol to coagulate before time has been allowed for the application of the glue. The nature of the change produced by the calcium compound is not entirely understood, but it seems that more than the mere formation of an insoluble calcium caseinate is involved. There appears to be evidence that the irreversibility is partly due to the adsorbtion of calcium compounds as such.

A water-resistant glue for wood-workers' use may be prepared by adding calcium hydroxide to a mixture of the first type described under Glues with Reversible Gels. Sutermeister states that for this purpose 0.54 g. equivalent, or 20 g. of calcium hydroxide to 100 g. of casein are required. The calcium hydroxide must not be added until after the casein has been completely dissolved by the sodium hydroxide. Further, the amount of sodium hydroxide must be slightly increased over that required for the reversible-gel type, or the calcium compound will cause coagulation to occur too soon. With 0.275 g. equivalent of sodium hydroxide, it is reported that the glue will remain workable for 6 or 7 hr. This glue yields wood joints of very good dry strength and acceptable water resistance.

In a similar manner, the reversible-gel glue of Type 2 may be rendered water-resistant by means of calcium hydroxide. In this case, 30 g. of calcium hydroxide' (0.81 g. equivalent) and 0.275 g. equivalent of the sodium salt to 100 g. of casein are recommended. The sodium salts indicated are those that react with the calcium hydroxide to yield sodium hydroxide and an insoluble calcium salt, as previously stated (page 592). Because of the absence of sodium hydroxide as such, the components of the water-resistant sodium-salt glue, like the parallel glue of the reversible-gel type, may be assembled by the manufacturer and the glue may be prepared for use by merely mixing it suitably with water. With regard to its water resistance and working life, *i.e.*, the period during which the solution will remain suitable for spreading, this glue is similar to that described in the preceding paragraph.

When sodium silicate (waterglass) is used as the sodium salt designed to react with the calcium hydroxide in the manner described, the glue exhibits a longer working life with less alkalinity. Because the higher alkalinities promote hydrolysis of the casein, with a resulting loss of adhesive strength, the lower alkalinity of the silicate glues is an important advantage. The silicate glues are able also to carry much higher concentrations of calcium hydroxide without suffering to nearly so great an extent the loss of working life that non-silicate glues show under similar circumstances. It is believed that these important advantages result from the colloidal silica introduced with the waterglass. Since the sodium silicate must not be added to the glue until after the casein and calcium hydroxide have been thoroughly incorporated with each other in the presence of water, glues of this type are not marketed as prepared dry glues.

Each manufacturer of casein glues prescribes the methods for preparing working solutions of his products, and these instructions should be carefully followed. Faulty performance may result from either slight changes in proportions or in methods of procedure. It is their water resistance, of course, that has brought the casein glues into prominence, and although they are not ideal in this respect, they have been found to be acceptable for a great many purposes. According to Sutermeister, plywood panels glued with casein glue have shown a high joint strength after being exposed for months to humid air, or after being submerged for several weeks in water.

ALBUMEN GLUES

Albumen glues also are called "waterproof." The albumen for this purpose is derived from both egg and blood sources. Glue from the latter source, however, is preferred to that from the former. Albumen glues are applied hot in the same way as other glues and the same precautions with regard to their use should be observed.

CHAPTER XVI

RUBBER

Rubber, or caoutchouc, seems to have first become known to Europeans about the year 1525, at which time it was mentioned in the writings of d'Anghiera, a Spanish traveler in Mexico. The name "rubber," as applied to this substance, was not thought of until about two and a half centuries later. In 1770, Priestley, the discoverer of oxygen, recommended it as a substance suitable for the erasing of pencil marks—hence a rubber. Thus from a specific use, its general name was derived.

Source.—Rubber is obtained from a great variety of vines, shrubs, and trees that grow in moist climates of tropical and sub-tropical countries. The best grade has been obtained from a tree of the botanical name, *Hevea Braziliensis*, which is native to the Amazon district of South America. Because the shipments were made from the port of Para, Brazil, this rubber has become known as Para rubber. Comparatively recently, plantations stocked principally with Hevea have been established in various parts of the world, notably in Ceylon and Malaya. A considerable portion of the world's rubber output has been produced by such plantations, but for some rather obscure reason the plantation Hevea does not possess all the excellence of the wild Hevea of the Amazon district. Rubber is also produced by other botanical species in various countries, for example, in portions of Africa, India, Mexico, Central America, etc.

The Latex.—The juice of the plant from which the rubber is obtained is called *latex*. It is not the sap. It is white, resembling an oil emulsion; it is, in fact, a great deal like the juice of the common milkweed. The latex is obtained by the means of incisions made in the bark; the flowing juice is caught in small cups attached to the tree by the means of moist clay or in some similar manner. The amount of fluid collected from a single tapping varies greatly, but it is on the average about 1 oz.; and this is by no means pure rubber. According to Perkin,[1] a typical latex shows the following composition:

	Per Cent
Pure rubber	32
Albuminoid and mineral matter	12
Water	56

Coagulation of the Latex.—In order that it may be exported the latex must be treated so that the rubber globules are caused to coalesce and the albuminoid matter to become immune to fermentation. Also the water must be evaporated to a large extent. To accomplish these results, the latex is subjected to a process known as coagulation; there are many methods by which this is brought about. The latex may be smoked, treated with chemical reagents, boiled, or evaporated, either by spreading on the ground, or as is done in the Congo, by spreading on the human body. In the Para district the latex is coagulated largely by smoking. A paddle is dipped into the latex and then is rotated in the smoke of a smoldering fire; the process is repeated until a large ball or "biscuit" is formed. The methods employing chemical reagents are used largely on plantations where facilities are at hand for carrying them out.

Cleaning.—After coagulation, the rubber is ready for the market. Before it can be used, however, it must be cleaned to remove earthy material, bark, twigs, etc. This is done by slicing and macerating it between rolls and washing it with water. Much loss occurs in the washing process; the amount varies from 10 to 50 per cent. After washing, the rubber is passed through rolls and formed into thin sheets, which because of their appearance are known as *crepe.* These sheets are then carefully dried, frequently in a vacuum drying apparatus.

Vulcanizing.—Pure rubber does not possess the properties that cause the familiar manufactured form to be considered so valuable. At the temperature of very hot summer weather, pure rubber becomes soft and sticky; during very cold weather, it becomes hard and brittle. In either of these conditions it is use-

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[1] PERKIN, F. MOLLWO, *Chemical Eng.*, August, 1913.

less for the purposes to which it is commonly put. It is upon the discovery of the effect of heating the rubber with sulfur that the evolution of the present-time product rests. The sulfur effect was first discovered by Goodyear at New Haven, Conn., in 1839; four years later it was noted independently by Hancock of London. In 1846, Parkes of Birmingham, Eng., observed that the same effect is produced when thin sheets of rubber are immersed in a solution of sulfur monochloride (S_2Cl_2). The process of treating rubber with sulfur is known as vulcanization. It is not necessary to enumerate here all the effects produced by the treatment, but some of the more important are these: the rubber is rendered much less sensitive to changes of temperature; it acquires increased elasticity and tensile strength; it is more durable when exposed to the weather, and more resistant to the action of chemical reagents.

In vulcanizing by the Goodyear process, the crude rubber is very finely divided and intimately and uniformly mixed with the sulfur by continuously passing the mixture through rolls. For ordinary vulcanization, from 5 to 7 lb. of sulfur are used for every 100 lb. of rubber. However, because of other materials that are also used in the mixture as fillers, the amount of sulfur in the finished product does not usually exceed 2 or 3 per cent. After mixing, the mass is heated to about 120°C., usually with steam, which is known as the "steam cure."

The manner in which the sulfur reacts with the rubber is not definitely understood, but the rubber molecule is not broken down in any way; the sulfur unites with it where certain "double bonds" exist to form addition products. All of the sulfur does not combine; a rather small percentage of it remains as a mere mixture.

In the Parkes process, which is known as the "cold cure," thin sheets of rubber are immersed in a solution consisting of 2 or 3 per cent of sulfur monochloride in some one of the more or less active rubber solvents, such as carbon disulfid, benzole, etc. Vulcanization may be brought about also by exposing the rubber to the vapors of sulfur monochloride.

The properly vulcanized product containing 40 per cent of high-grade rubber will stretch to seven times its length and return to its original condition. If, when drawn out, it remains partly stretched, or if a strong indentation leaves a permanent hollow in the solid piece, the rubber has been poorly or incompletely vulcanized.

Accelerators.—When synthetic or artificial rubber (which will be discussed later) was first prepared, it was found impossible to vulcanize it. The difficulty seems to have been that it did not contain certain impurities that were always present in the natural rubbers. Later it was learned that the synthetic product could be vulcanized by adding to the mixture organic compounds which acted as catalysts. When the catalysts were employed in the vulcanization of natural rubber, the results were surprising. In curing automobile tires, for example, the time was cut from 75 to 15 min. As a result, the output for the same equipment was proportionately increased. Because of the increased speed of vulcanization or curing, the catalysts are known as accelerators.

In addition to hastening the process, the accelerators have made it possible to complete the vulcanization with less sulfur. The use of less sulfur has decreased the tendency of the vulcanized rubber to form a "bloom," or efflorescence of free sulfur, on the surface of the article, a condition that was very prevalent with the rubber of an earlier period.

The commercial use of organic catalysts began in 1906, when anilin was first employed. Prior to that time, however, accelerators were known, but they were inorganic materials, such as calcium oxide and hydroxide, magnesium oxide and carbonate, litharge, basic lead carbonate, and the polysulfides of antimony. Since the discovery of the effectiveness of anilin, which is still used to a considerable extent in the manufacture of tires, a great number of other organic catalysts have been developed. Since 1914, their use has been extensive. They are usually complex compounds containing nitrogen. The amount of the accelerator necessary constitutes, as a rule, not more than 1 per cent of the total mixture, but the quantity varies considerably because the percentage, as well as the kind, of the accelerator that serves the best depends upon the other ingredients employed. Zinc oxide, for example, promotes the activity of most accelerators while, on the other hand, carbon black, which is used in large proportions in compounding the mixture for automobile tires in order to increase their resistance to abrasion, cutting, and tearing,[1] influences most accelerators adversely.

Although originally the primary purpose in using accelerators was to shorten the time required for curing, they are now employed for the three-fold purpose of shortening the time, improving the mechanical properties, and lessening the tendency to deteriorate with age. Smith[2] says that the increased strength and elasticity may in many cases be attributed to the fact that a shorter time or lower curing temperature is possible when an accelerator is used. Because of the decreased heat effect, there is less disaggregation and the cured product is therefore stronger. The accelerator improves the aging properties by retarding the slow atmospheric oxidation of the rubber.

Because accelerators allow vulcanization to be brought about at lower temperatures, it has been found feasible to employ organic dyes in the rubber mixture. Thus brilliant-hued products have been made possible. With high vulcanization temperatures the dye would be injured.

Other Materials Used in Rubber.—Even though rubber is greatly improved by vulcanization it does not even then possess the properties required for most of its uses. On this account, at the same time that the sulfur and organic accelerator are incorporated, other materials are mixed with the rubber. These added materials are employed even in high-grade rubber; in fact, pure vulcanized rubber has a very limited use. Of course, it not infrequently happens that many foreign substances are introduced into rubber merely to increase the weight and bulk and thus to cheapen, but if the materials are properly chosen and used, they increase the durability of the rubber by lessening its oxidation, mechanical abrasion, etc. All materials used in this way are admixed in the form of a very fine powder.

According to Schidrowitz[3] the materials employed in the manufacture of rubber articles, aside from the rubber, the organic accelerator, and sulfur, may be classified as follows:

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[1] "Synthetic Organic Chemicals," **3**, no. 3, February, 1930, publ. by Eastman Kodak Co.

[2] "Recent Developments in Rubber Accelerators," *Jour. Ind. Eng. Chem.*, **16**, 1024, October, 1924.

[3] "Rubber; Its Production and Industrial Uses."

a. "Fillers" or "cheapeners" pure and simple.

b. Materials employed for imparting a certain quality or qualities, as hardness, toughness, resistance to steam, etc.

c. Pigments.

a. Fillers.—Powdered chalk, barytes and ground rubber waste may be regarded as typical "cheapeners"; they possess little if any valuable specific quality. In many cases such substances as zinc oxide, lithopone, and oil substitutes are also used solely as cheapeners, but each of these materials may, if rationally employed, serve some useful specific purpose aside from the lowering of cost. Thus zinc oxide hardens and toughens a mixing, and increases its resistance to cutting and abrading forces, if used within certain limits and together with other suitable materials. The same remarks apply to lithopone. The oil "substitute" serves to produce rubber goods in which cheapness combined with a low specific gravity and an absence of hardness are required. Good "reclaimed" rubber is a valuable ingredient in mixings that have to be made at a moderate price and in which a large quantity of "minerals" cannot be employed.

b. Materials Used for Specific Purposes.—1. *For increasing mechanical strength,* or, in other words, for hardening and toughening the material, minerals, such as zinc oxide, lithopone, magnesium oxide, lime, litharge and for special purposes (for instance, for "eraser" rubber) ground glass and talc are used. Certain organic substances, for instance balata—which contains a hydrocarbon similar to that of rubber—also possesses a toughening effect, without, however, speaking broadly, decreasing the elasticity or rather distensibility of the material to the same extent as "minerals."

2. *For making dense,* i.e., *non-porous, mixings for increasing resistance to water and improving the dielectric properties,* organic materials such as asphalt, bitumen, and coal-tar pitch are exceedingly useful.

3. *For softening* harsh mixtures, *i.e.,* for cheap goods containing a large quantity of minerals, such as chalk or barytes, certain oils, and more particularly vaseline are employed.

4. *For hastening vulcanization or improving vulcanizing conditions,* such materials as magnesia, quicklime, and antimony sulfide (golden sulfide) are in many cases essential.

c. Pigments.—The most important white pigments are zinc oxide, lithopone, barytes, and white lead. Antimony pentasulfide and mercuric sulfide (vermilion, cinnabar) are very largely employed as red pigments, the latter chiefly for hard rubber, mainly in dental work. Pigments and dyes other than white and red are employed only for special purposes, as for toys, flooring tiles, imitation mosaics, fancy waterproof cloth, etc.

Manufacture.—In the manufacture of rubber articles of the so-called "mechanical" type—garden hose, for example—the washed and dried rubber is mixed with the desired amount of sulfur, accelerator, and filling materials and the resultant "dough" is rolled out into sheets of the required thickness by means of smooth rolls and attached to cloth to prevent sticking. The sheets are then cut and made up according to the method best adapted to the article being produced. Sometimes strips made from the sheets are wound in a manner suitable to form the article, or they may be superimposed in layers after having been cut to the desired form. After being formed into shape they are vulcanized, or "cured" as it is called, by applying heat and pressure, or heat only. The heat may be furnished by the means of steam or in some other manner, but the best results seem to be produced by steam generally. The article is kept in shape during curing by various methods. Pneumatic tires, heels, washers, hard-rubber pieces, and the like are cured in molds that give them their final shape. Tires are expanded against the mold by a suitable arrangement inside; an inflated air bag, for example, may be employed. Curing in molds is relatively expensive because of the equipment required, but the process is conducive to high quality and attractive finish. If the mold is not used, cloth wrappings may be employed. If wrapped, the finish shows the imprint of the cloth. Hollow articles, such as tubing, bulbs, and druggists sundries may be buried in pans of talc.

Properties of Soft Vulcanized Rubber.—In contact with the air, rubber is slowly oxidized with the formation first of a plastic, sticky substance, which by further oxidation is gradually changed into a dry and readily pulverent form. This oxidizing action is rapidly hastened by the ultraviolet or "chemical" rays of the sun.[1] Hence the better the rubber is protected from light, the longer its life will be. Rubber articles when not in use, should be stored in a cool, dark place. Articles exposed in shop windows may deteriorate more than those in use. Vulcanized rubber that is undergoing oxidation has quite a distinct odor from that which is sound. Rubber that has become hardened by oxida-

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[1] For tests showing the effect produced on rubber by weathering, see Shepard, Krall, and Morris, "Weathering of Vulcanized Rubber," *Ind. Eng. Chem.*, **18**, 615, June, 1926.

tion may be softened again by soaking for several hours in about a 3 per cent solution of carbolic acid (phenol) in water.

All rubber resists in a high degree the passage of heat and the electric current. The changes brought about in it upon being exposed to the atmosphere, however, cause it after a time to become a relatively good conductor of both.

Dilute acids and caustic alkalis affect rubber but little. Concentrated hydrochloric acid, both liquid and gaseous, attacks it. Nitric acid acts feebly when cold but energetically when hot. Sulfuric acid acts in about the same way as it does upon cork; it seems to char it.

Rubber is soluble in benzol, petroleum ether, carbon disulfide, carbon tetrachloride, chloroform, and turpentine, but only the first three mentioned are much used as commercial solvents, as in making solutions for rubber cements. Rubber, being a true colloid, does not dissolve sharply as do salts in water. The solvent is first absorbed by the rubber, whereby it is caused to swell and form a jelly-like mass. In a sense the solvent may be said to have dissolved in the rubber. Finally, when enough of the solvent has been absorbed, the mass assumes the liquid state.

Grease or oil of any kind is decidedly injurious to rubber; it softens and partially dissolves the rubber to form a sticky mass.

It has been observed that copper and its alloys have a destructive action on rubber. Copper oxides and copper salts also affect it in a similar manner. The reason does not seem to be very clear. Of course, copper reacts with the sulfur contained in the rubber, but a rapid hardening also takes place. This has been attributed to oxidation induced by the oxygen occluded or combined with the copper in the form of cuprous oxide, or, in the case of the compounds, by their catalytic action. The action is greatly hastened by grease or any substance capable of exerting a solvent action on the rubber.

Ebonite or Hard Rubber.—In producing this substance, approximately the same materials are used in the mixture as are used for the soft vulcanized rubber, but more sulfur is employed, about 30 lb. of sulfur for every 100 lb. of rubber. Also, the temperature of vulcanization is higher, from 150 to 160°C. Like the soft rubber, ebonite is a non-conductor of electricity, but it is much more resistant to atmospheric action and is acid proof. It lacks extensibility; it is similar to gutta-percha in this respect.

Reclaimed Rubber.—It is possible to recover or reclaim rubber in a usable condition from worn-out articles and rubber waste from the factories. Although usable, it must not be understood that it has been devulcanized and returned to the condition of virgin rubber, for to the present time, no one has been able to accomplish this very desirable result.

There are several processes by which rubber may be reclaimed but that which is most widely used is known as the *alkali process.* In this process, the rubber after having been separated from the metal and fiber as much as possible, is heated in a closed iron vessel with an aqueous solution of an alkali, generally sodium hydroxide. This treatment removes the remainder of the fabric, and all the free sulfur as an alkaline sulfide. Any rubber substitutes present are saponified and dissolved out. The rubber thus treated is then carefully washed and dried and may be incorporated with a lot of fresh rubber.

Reclaimed rubber is sometimes known as "rubber shoddy;" in general, it possesses much lower tensile strength, elasticity, and wearing power than new rubber. Nevertheless, some of it is of extremely good quality; in fact, sometimes it may be superior to some of the poorer grades of crude or virgin rubber. Its value seems to be to a certain extent dependent upon the degree to which the reclaiming process has regenerated its plasticity, but in any event, because the old rubber has already been largely oxidized, its use with the fresh rubber is said to make a product that is less susceptible to oxidation than all new rubber would be. On the other hand, the elasticity of such mixtures must be in the same measure sacrificed.

Synthetic or Artificial Rubber.—Rubber is a hydrocarbon of complex structure; the formula usually ascribed to it is $(C_{10}H_{16})_x$. When rubber is subjected to destructive distillation, its complex structure is broken down and certain liquids result. Among these is isoprene (C_5H_8), a liquid which boils at 32°C. It was early noted that isoprene can be caused to condense or polymerize[1] with the formation of true rubber. Erythrene (C_4H_6), a gas, when cooled with a freezing mixture, can also under

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[1] See footnote, p. 498.

certain conditions be caused to polymerize to form rubber. Therefore, it is necessary only to produce these substances cheaply and in sufficient amounts to produce rubber in commercial quantities.

Isoprene has been made from turpentine, from isoamyl alcohol, which is a constituent of fusel alcohol, and from starch, sugar, and sawdust. Erythrene has been made from acetone, butyl alcohol, and other substances. The polymerization has been brought about by temperature modifications, or by contact under suitable conditions with such substances as acids, alkalis, starch, glycerine, blood serum, albumin, etc. Even the polymerized substance itself can bring about the polymerization of isoprene and erythrene.[1]

Either because of the smallness of the yield, however, or because of the cost of the raw material, as in the case of turpentine, or because of the expense of the processes necessary for conversion, or because of all of these, synthetic rubber has not become a commercial success. Dannerth says[2] that the synthetic-rubber research received its first great stimulus in 1910 when fine quality Para rubber was selling for $2.50 per pound, but now when high-grade plantation rubber is selling at a relatively low price, there is little hope for any laboratory product, unless, of course, it can be made at a price considerably lower than that asked for the natural rubber.

Rubber Substitutes.—A great many substitutes, more or less like rubber, have been prepared, but they must not be confused with the synthetic rubber previously discussed. The most important of the substitutes is known as *factis;* it is made by "sulfurizing" unsaturated fatty oils. There are two kinds of factis: white, and brown or black.

The white modification is made by stirring from 20 to 25 per cent of sulfur monochloride (S_2Cl_2) into linseed, rapeseed, corn, cottonseed, or like oil that has previously been mixed with a little petroleum naphtha. The product is more or less elastic.

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[1] For literature on the synthesis of rubber, see: *Jour. Amer. Chem. Soc.*, p. 165, 1914; *Jour. Ind. Eng. Chem.*, **3**, 279, May, 1911; *Chem. Eng.*, **18**, no. 2, p. 61, August, 1913.

[2] ROGERS and AUBERT, "Industrial Chemistry," p. 720.

The brown or black modification is made of "blown" oil. Linseed or rapeseed oil is heated and a current of air is forced through it until it is quite thick and viscous. This blown oil is then vulcanized by heating with sulfur in a manner similar to rubber. The brown factis is quite elastic and is more stable than the white.

The substitutes are largely used to mix with rubber of a more or less inferior quality, or with some resin, heavy hydrocarbon, asphalt, etc., for cheap compositions. They are assimilated very thoroughly by heated rubber, but can be readily detected when in composition with rubber by treating the sample with alcoholic caustic potash. The substitute is saponified while the true rubber is not.

CHAPTER XVII

ELECTRICAL INSULATING MATERIALS

The range of materials used for electrical insulation is very wide; for, aside from the primary requisite of possessing an insulating value, the material used must also have the necessary physical and chemical properties to enable it to maintain this value under the conditions of use. Obviously, the same material cannot be equally suitable in all locations. In some cases a high flexibility is necessary; in others rigidity and a high mechanical strength are desired. There are, however, some properties that all insulators should possess in common; for example, all must be able to exclude moisture, must not be easily affected by temperature changes, and should be as chemically inert as possible.

In this treatment it will be possible to mention only the more important of the insulating materials. Some of them have been described under the head of other uses and will be but briefly referred to here.

Rubber, in the soft vulcanized state, is used largely as a wire covering, although it is used also for impregnating tapes, and for preparing various insulating compounds.

In the manufacture of rubber-covered wires, a mixture consisting of rubber and sulfur, together with the desired amount of filling materials, is prepared and the whole is kneaded into the form of a "dough." The filling materials include a great variety of substances, and are added for various reasons. To harden and toughen the mass, inorganic materials, such as zinc oxide, lithopone, lime, litharge, magnesium oxide, etc., are employed; while other substances of an organic nature, such as ozokerite, asphalt, and other bitumens, are added to make it more waterproof and to increase its dielectric properties. This mixture may be applied to the wire by either the "seam" or "seamless" method. Since copper reacts with the sulfur contained in the covering, and since this eventually affects its insulating properties, the wire is first tinned. In the "seam" method, strips of rubber are pressed about the wire as it passes through specially grooved rolls. In the "seamless" method, the insulating material, while still plastic, is forced through a die by means of a hollow screw, through the center of which the wire runs. After application, the rubber is vulcanized in a closed chamber by the means of steam.

In the form of hard rubber or ebonite, rubber is used for bushings, parts of switch gear, etc. Curtis says[1] that when hard rubber is exposed to light in the presence of air, complicated chemical reactions are set up, which are equivalent to oxidizing the sulfur of the rubber to sulfuric acid. The acid may then take up ammonia from the air to form ammonium sulfate. Or it may form sulfates by reacting with the mineral fillers of the rubber. Many of the compounds that the acid produces in this way are hygroscopic and form a surface layer of dissolved salts that noticeably lowers the insulating value of the rubber. He says, also, that such rubber can be renovated by suspending it in distilled water for about 2 days to remove the soluble salts, then wiping dry, and coating it with a thin film of light oil. Hard rubber cannot withstand any considerable degree of heat.

Other properties of both the soft vulcanized and hard rubber have been described in the preceding chapter, which see.

Gutta-percha has a high dielectric strength and a better insulating value even than rubber. It is very extensively used for making submarine and subway cables. Like rubber, gutta-percha is obtained from the latex of certain tropical trees. In many respects it is similar to rubber. Unlike rubber, however, it finds its chief use in the natural or unvulcanized state. It can be vulcanized, however, and this treatment renders it harder and less plastic when heated.

Although gutta-percha is plastic, it is not elastic like rubber. When molded by an application of force, gutta-percha retains the shape given it, while rubber returns to its original form when the molding force is removed. At temperatures between 90 and 100°C. gutta-percha is sufficiently plastic that articles may

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[1] "Insulating Properties of Solid Dielectrics," *U. S. Bur. Standards Sci. Paper*, 234, 1915.

be formed of it by pressing it in molds. It melts at about 120°C. In appearance gutta-percha very closely resembles ebonite, but it can be readily distinguished from it by the fact that it is readily softened in boiling water, which property ebonite does not have.

Gutta-percha is soluble in carbon disulfide, carbon tetrachloride, chloroform, and warm benzene. It is not affected by alkalis and dilute acids, nor even by strong hydrochloric, but is attacked by strong sulfuric and nitric acids, as well as by other strong oxidizing agents. It is not very resistant to atmospheric action, but is rather easily oxidized; when oxidized, it is brittle.

A material that is often used in place of gutta-percha for some purposes is *ozocerite*, called also *ceresin* or *mineral wax*. It is a hydrocarbon found upon the earth in the vicinity of oil wells. Upon distillation, it yields about 15 per cent of paraffin oil. It is a good dielectric, and atmospheric and chemical agents have no action upon it. *Nigrite* is another substitute for gutta-percha made by fusing together, at the very lowest temperature, India rubber and the residuum obtained by the distillation of ozocerite.

Bakelite has a high dielectric value and is used either alone to impregnate windings, or as a molded composition with wood fiber, or as a filling material for blotting paper and similar substances. For a discussion of its preparation and general properties see page 538.

Varnishes.—As a rule, the oil varnishes are used to saturate paper and fabrics, while the spirit varnishes are used as a cementing material. Both oil and spirit varnishes are used to a large extent for the insulation of windings. The spirit varnishes dry more quickly, but are less flexible than oil varnishes. Shellac varnish is the most widely used of the spirit-varnish class; it is particularly suitable for low-voltage windings. The composition and general properties of both classes of varnishes have been discussed in Chap. XIII.

Oils.—The use of insulating oils is confined chiefly to transformers, rheostats, and switches. For transformers and rheostats, although the insulating action is very important, the main function is that of cooling. For insulating purposes, mineral oil is generally employed. It should have a high dielectric strength, high flash point, low viscosity, and be free from moisture, acid, alkali, sediment, and impurities.

The insulating value of the oil is less if water is present. A very delicate test for the presence of water consists of shaking a warmed sample of the oil in a test tube with anhydrous copper sulfate. If water is present, the white, anhydrous salt will take up the water and become blue. For this test the sample should be taken from the bottom of the barrel or other container, since if water is present, it will likely be found there.

Paper is used extensively as a cable insulation and in other kinds of electrical construction. For this purpose it may be employed in its familiar form or after being impregnated with oils, varnishes, and similar materials.

The fibers from which paper is made consist essentially of cellulose, which is usually represented by the empirical formula $(C_6H_{10}O_5)_2$. According to source, the chief cellulose fibers employed for papers used in the electrical industry may be classified as follows: (1) fibers derived from wood; (2) seed hairs, as cotton; (3) bast (inner-bark) fibers, such as linen hemp, and Manila fiber.

To prepare wood fibers for paper making, the cellulose must be freed from its encrusting materials, such as the lignin, carbohydrates, proteins, resins, and fats. For this purpose the chipped wood of conifers, particularly the spruces and fir, is heated with a solution of the acid sulfites of calcium and magnesium. The product is known as sulfite cellulose. Soda cellulose is produced by heating shorter-fibered woods, such as those of the poplars, beech, and basswood, with a solution of caustic soda. That which is known as sulfate cellulose is made from coniferous woods by treatment with a hot solution of sodium sulfate containing a little sodium hydroxide or carbonate. The so-called "kraft" papers are made from this fiber. Because of the length of the fibers, papers made from sulfite cellulose are strong, but for equal weight they have less bulk than the softer soda-cellulose papers. Inasmuch as the reagents employed in treating the wood attack the cellulose less than the sulfite or soda liquors, the sulfate-cellulose papers are the strongest of the three. Because the pulp is not bleached, sulfate papers have a dull-brown color.

The cotton and bast fibers have usually served some other purpose before being made into paper. Paper-making material of this class consists generally of rags, old ropes, and cordage. After sorting and cleaning, the material is given a mild alkaline boiling in milk-of-lime or caustic-soda solution, and then it is bleached and thoroughly washed. Because the cotton and bast fibers are longer than the wood fibers, they are generally considered to possess superior paper-making possibilities, but the length of fiber is largely determined by the subsequent beating.

All fibers are beaten after boiling and washing to fray the edges, and thus to increase the matting or felting effect in the paper-making machine. The paper sheet is formed by shaking a dilute suspension of the pulp, containing 98 to 99.5 per cent of water, on a moving wire screen of fine mesh. The water is removed by the aid of suction and absorbent felts. Papers are usually filled or loaded with mineral fillers such as white clay and barytes, and are sized, to render them non-absorbent, by the use of aluminum resinate, casein, gelatin, and starches. For electrical insulation, the paper generally desired is an unbleached paper containing neither sizing nor loading materials. The insulating value of the untreated paper depends chiefly upon the air entrained in its pores.

A special form of semitransparent material, similar to parchment in appearance and toughness, sometimes called "parchmentized" or "greaseproof" paper, is prepared by treating cotton or wood-pulp papers with a sulfuric-acid, zinc-chloride, or caustic-soda solution. The cellulose of the fiber becomes hydrolyzed and semi-gelatinous under this treatment. Because of the difficulty of washing out the hydrolyzing reagents, which are all hygroscopic and active electrolytes, this method of "parchmentizing" paper requires extreme care to avoid the production of an inferior insulation. "Fish paper" and "horn paper" are trade names for products made of hydrolyzed cellulose. A product formed of superimposed layers of parchmentized paper, used for armature wedges and general low-voltage work, is known as *vulcanized fiber.*

Paper coated with varnish, or mica flakes and varnish, is known as *paper micarta.* Cloth, such as duck and muslin, similarly treated is known as *cloth micarta.* The varnish employed may be prepared from shellac or from the synthetic phenol-formaldehyde type of resin (page 538). In addition to a high dielectric value, the micartas have a high resistance to heat and moisture, and the cloth micarta has exceptional mechanical strength.

Mica is one of the most widely used of the solid insulating materials. The variety generally employed is muscovite (page 398). It is obtained from the mines in the form of rough cakes which are split and trimmed into sheets. The harder varieties can be split economically into layers as thin as 0.0005 in.[1]

Mica is unaffected by heat until a temperature of several hundred degrees centigrade is reached. Then the laminae of the harder varieties separate, which makes it very soft and flexible, but which also causes it to disintegrate into scales and flakes. Mica is capable of absorbing a considerable amount of moisture between its laminae; this also increases its flexibility. It will take up oil and other fluids in the same way. The presence of oil seems to lower its insulating value somewhat.

To lessen cost by using waste flakes, and sometimes for the sake of the flexibility that may be secured, that which is known as *reconstructed mica* is prepared. Layers of mica are cemented together by the use of an insulating varnish, as shellac, and are then formed into the desired shape by hot pressure. Stiff, flat plates prepared in this way and milled to uniform thickness are known to the trade as *micanite.* Flexible sheets are prepared in a similar way by using a non-drying varnish, but in this case the hot pressing is omitted.

Asbestos is hydrated magnesium silicate ($3MgO \cdot 2SiO_2 \cdot 2H_2O$). It does not naturally possess very high insulating properties; it is valuable in electrical work, however, because of its noncombustible nature and its resistance to heat. Sheets are prepared by boiling asbestos in a solution of sodium silicate and then subjecting the mass to heavy pressure. Sheets prepared in this way are hard and mechanically durable, but are hygroscopic and have a low insulating value. They have a tendency to disintegrate when wet. Attempts have been made to render the

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[1] Fleming and Johnson, "Insulation and Design of Electrical Windings," p. 81.

silicate binder less soluble and less hygroscopic by treating it with calcium and aluminum compounds, but the reaction products are always left that are hygroscopic in much the same way as the sodium silicate.

Talc, like asbestos, is a hydrated magnesium silicate, but is more acid than asbestos, having the formula $3MgO{\cdot}4SiO_2{\cdot}2H_2O$. It is soft and is easily drilled and machined. After it has been fashioned as desired, it may be rendered exceedingly hard by heating to about 1100°C. Stone prepared in this way is marketed under the name of *lava.* Another product known as *lava composition* is also made from talc by preparing a mixture of the finely powdered stone and a suitable binding material, which is pressed into the forms desired by hydraulic pressure. These forms are dried in air and then heated in kilns until all moisture is removed. The semi-hardened material is now machined to suit the requirements and is then finally hardened by heating to 1100°C., as in the case of the natural stone.[1] Both the natural and the artificial material are heat-resistant and possess good insulating properties.

Marble is used chiefly for switchboard work; it is desirable for this purpose because it is non-combustible, is easily worked, and possesses a pleasing appearance. Its insulating properties may be faulty because of the presence of metallic veins, which are difficult to locate, except by high-voltage tests. Fleming and Johnson say[2] that marble is very hygroscopic and normally contains so much water that it is necessary to bush the holes through which conductors pass. They say further that this is all the more necessary, because the water usually employed for drilling is absorbed by the stone and cannot be effectually removed, except by baking for a considerable time. If the water is allowed to remain, and if it is not suitably bushed, local heating will occur that may be sufficient to fracture the stone. Because marble absorbs dissolved salts produced by the corrosion of metals with which it may be in contact, it becomes stained and discolored. Such stains are practically impossible to remove, because of the distance to which they have penetrated. (For further information concerning marble, see page 406.)

[1] Benson, "Industrial Chemistry," p. 369.

[2] Fleming and Johnson, *loc. cit.*, p. 101.

Slate, like marble, is used for switchboard work and in other locations where a non-combustible material with fair insulating properties is necessary. It is harder and less hygroscopic than marble, but is much more likely to contain metallic veins, so that its insulating value is uncertain.[1] For switchboards slate is very suitable in those locations where marble would be very rapidly discolored. (For a further discussion of the properties of slate, see page 400.)

Electrical Porcelain.[2]—The four general varieties of porcelains used for electrical insulation are the low tension, high tension, spark plug and resistance unit types.

Low tension and high tension porcelains are very similar in composition. The body of the ware in both cases is made of a mixture of China clay, ball (plastic) clay, feldspar and flint (ground quartz). In firing, the feldspar fuses and binds the other materials into a dense vitreous mass. High tension porcelain is fired at about 1285°C. The chief difference between low and high tension wares is that the former is fired at a lower temperature, with the result that it may be less vitreous and more porous. For high tension porcelain the mechanical and dielectric strengths must be greater than for low tension ware. Neither resists thermal shock well.

To provide an insulator with a high dielectric strength at high temperatures, and one which at the same time is mechanically strong and resistant to thermal shock, such as is required for spark plugs, a special hard porcelain, low in feldspar is used. Spark plug porcelain is fired at about 1465°C. and has zero porosity. It is of the same type as that used for chemical laboratory ware.

For resistance units such as are found in small electric furnaces, reflector heaters, flat irons, etc., hard porcelains of the spark plug type may be used, but a special porcelain is generally employed. A porcelain made from steatite ($3MgO \cdot 4SiO_2 \cdot H_2O$) or from periclase ($MgO$) is most common. Being designed for high temperatures but low voltages, it need not be completely vitreous, and its resistance to thermal shock, an indispensable property, is better if it is not.

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[1] Fleming and Johnson, *loc. cit.*, p. 101.

[2] For the discussion of this topic the author is indebted to Charles R. Amberg, Professor of Ceramic Engineering at Alfred University.

CHAPTER XVIII

PRIMARY ELECTRIC CELLS

Definition.—A primary electric cell is a system of elements and chemical compounds so arranged that the energy of the chemical reactions that occur in the system is directly transformed into electrical energy.

Theory of Cell Action.—It has been observed that chemical compounds of only one class react in such a manner that they are suitable for use in electric cells. Such compounds are those that when dissolved dissociate into ions. Ions are considered to be subdivisions of the molecule carrying electrical charges. It is by means of ions that the current is assumed to be carried through the cell. In fact, the whole of the present conception of primary-cell action rests upon the ionic theory; therefore, in order to develop logically this subject, it will be necessary to consider the experimental work by which the ionic theory has been confirmed. This confirmation has been arrived at by a study of various phenomena manifested by solutions, important among which are osmotic pressure and the effect of dissolved substances upon the freezing point and boiling point of water. Because of their significance in this connection, a discussion of these topics will be taken up at this point.

Osmotic Pressure.—If a concentrated aqueous solution of some salt, copper sulfate, for example, is placed in the bottom of a tall cylinder, and then pure water is poured on in such a manner that it floats about the solution, producing a sharply defined layer, it will be found, after a time, that a part of the dissolved salt has passed upward against gravity and entered that which was formerly the pure water. It is apparent that there is some force similar to a pressure driving the dissolved salt from one layer into the other. This pressure is called osmotic pressure. By the use of semi-permeable membranes, the osmotic pressure of dissolved substances may be rendered more evident, and may even be measured. Semi-permeable membranes are such as are permeable to water, but are practically impermeable to the particles of the dissolved substance. Hence, in a sense, the membrane acts as a filter for the dissolved substance and retains it as the water passes through. At first, before better methods were devised, osmotic pressure was demonstrated by filling an animal bladder with an aqueous solution of alcohol, and immersing the bladder in pure water. The water could pass into the bladder, but the alcohol could pass out to only a slight extent. In this way, sufficient pressure was finally developed within the bladder to cause it to burst.

A partial measurement of osmotic pressure may be made in the following manner. A piece of animal parchment is carefully tied over the mouth of a small glass funnel or thistle tube; then the interior of the funnel and stem are filled with a rather concentrated solution of cane sugar. A long piece of capillary tubing is now joined to the stem of the funnel by a sound, well-fitting rubber connection, and the funnel is placed mouth downward in a vessel of pure water; the capillary tube is supported in a vertical position. After standing quietly for several hours, it will be noted that the solution rises in the capillary tube; it may rise 2 or 3 ft. By the use of stronger and generally more satisfactory membranes, prepared artificially, it is not difficult to show a pressure of 30 ft. or more of sugar solution. Pressures as high as 31.4 atmospheres have been measured.[1]

Various hypotheses have been advanced to show what is the cause of osmotic pressure, but it has not yet been satisfactorily explained.

It is worthy of note that osmotic pressure obeys the laws for gases. For example, it has been found that the osmotic pressure of different solutions at the same temperature and of equimolecular concentration, made so by dissolving a number of grams equivalent to their molecular weights in equal amounts of water, exert equal osmotic pressures; this shows that the pressure depends upon the number of molecules in solution. Avogadro's hypothesis for gases states that equal volumes of gases measured under the same conditions of temperature and pressure contain the same number of molecules.

[1] Jones, "Principles of Inorganic Chemistry," p. 103.

In a similar manner Boyle's law applies to osmotic pressure. Boyle's law states that if the temperature remains constant, the volume of a gas varies inversely as the pressure upon it; this is equivalent to saying that the pressure of a gas varies directly with its concentration. Observation has shown this to be true also of osmotic pressure.

The law of Gay-Lussac is applicable because the osmotic pressure of the solution increases in proportion to its absolute temperature; the rate of increase is approximately $1/273$ for each degree rise in temperature.

Osmotic Pressure of Electrolytes.—It was early observed that for equimolecular concentrations, certain substances when dissolved exerted an osmotic pressure far greater than that produced by other substances. In fact, chemical compounds were found to be divisible on this basis into two classes: first, a class in which the pressure was called normal, and second, a class in which it was either *two or more times as great.* In the first class are substances like cane sugar, glycerine, and the alcohols; in general, substances that are not very active chemically. In the second class are the acids, bases, and salts, substances that are chemically the most active. Moreover, it is only the latter class of substances that conduct the electric current, and are decomposed by it; these substances are, therefore, called *electrolytes.* The former do not conduct the current, are not decomposed by it, and hence are called *non-electrolytes.*

The Lowering of the Freezing Point.—When any substance is dissolved in water, the freezing point of the solution is lower than that of the pure solvent. It has been shown that the amount of lowering is dependent upon the ratio between the number of the particles of the dissolved substance and the number of the particles of the solvent, in other words, upon the concentration of the solution. In the case of the electrolytes in water the lowering of the freezing point is either two or more times as great as for a water solution of a non-electrolyte of equivalent concentration, for example, a gram molecule per liter in each case.

Boiling Points Affected.—In a similar manner, the vapor tension of the solution is lowered, or in other words, the boiling point is raised[1] either two or more times as much in a solution of an electrolyte as in a solution of a non-electrolyte of equivalent concentration.

Summary.—All three of these properties of solutions—osmotic pressure, lowering of the freezing point, and raising of the boiling point—have been shown in the case of the non-electrolytes to be dependent upon the number of particles of dissolved substance, *i.e.*, upon the concentration of the solution. Electrolytes behave as though they contain two or more times as many particles as their concentration warrants. This observed difference between electrolytes and non-electrolytes is accounted for by the theory of electrolytic dissociation advanced by the Swedish chemist, Arrhenius. This theory will be explained later.

Solution Pressure and Precipitation Pressure.—Every substance in contact with a solvent has a definite tendency to go into solution. This tendency is spoken of as the solution pressure of the substance. Every dissolved substance has a certain tendency to come out of solution. This tendency may be called the precipitation pressure of the substance.[2] These pressures may be considered to be analogous respectively to the vapor pressure of a liquid that causes it to evaporate, and the back pressure of the resulting vapor upon the liquid. It is well known that if the vapor produced from a liquid is confined above it, there will be developed ultimately, for a given temperature, a definite vapor pressure that will prevent the amount of vapor from increasing. The vapor tension, of course, continues to manifest itself, and to drive molecules from the liquid into the vapor above; but under the influence of the vapor pressure that has developed, molecules pass back into the liquid at the same rate at which molecules from the liquid enter the vapor. That is, there is a constant and equal interchange. The amount of the vapor remains the same but it is not the same vapor. In this manner a condition known as equilibrium is established.

In the same way, when crystals of some salt, copper sulfate for example, are placed in water, molecules of the salt leave the

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[1] Certain exceptions must be noted. With some dissolved substances, as for example, alcohol, a low-boiling-point liquid, the boiling point of the solution is not raised, but lowered below the boiling point of pure water.

[2] Nernst assumes that the osmotic pressure is a measure of this tendency.

surface of the crystals and pass into solution. Because of the salt now in solution, a precipitation pressure is manifested. This pressure increases as the salt in solution increases, until finally, if the temperature remains constant and no water evaporates, the number of molecules of the salt that precipitate upon the crystals in a given period will be the same as the number that pass into solution. Under such conditions, as long as the conditions remain constant, the concentration of the solution will remain constant. The salt in the solid state is now said to be in equilibrium with the salt in solution, in other words, the solution is saturated.

Theory of Electrolytic Dissociation.—According to the theory of Arrhenius, at practically the same instant that the electrolytes dissolve in water, a certain number of the dissolved molecules of the compound divide spontaneously into charged particles, called *ions.* The name means "wanderer" and is applicable because the ions are assumed to be constantly in motion. Both positively charged and negatively charged ions are produced; the total amount of the positive charges equals the total amount of the negative. The positively charged ions are usually the ions of the metals and hydrogen; typical negatively charged ions are such as are formed of the halogens and acid radicals. All acids yield in common the positively charged hydrogen ion, and all bases the negatively charged hydroxyl ion. The other ion in each case depends upon the particular acid or base considered. The plus sign (+) is used to show that the ion carries a positive charge; the minus sign (−), a negative charge. The number of charges carried is equivalent to the valence of the atom or radical; the ions are called monovalent, divalent, etc., as Na^+ and SO_4^{--}.

Ionization may be represented in the following manner; the examples shown are respectively, an acid, a base, and a salt:

$$H_2SO_4 \rightleftarrows H^+H^+ \text{ and } SO_4^{--}$$
$$NaOH \rightleftarrows Na^+ \text{ and } OH^-$$
$$KNO_3 \rightleftarrows K^+ \text{ and } NO_3^-$$

It is very important to keep in mind that dissociation is a reversible process as the equations show. Some of the molecules are constantly dissociating into ions; at the same time a certain number of the free ions are combining to form electrically neutral molecules. In this way an equilibrium is established; the ratio between the charged ions and the undissociated molecules is constant for a given set of conditions.

There are a number of factors that have a bearing on the amount of dissociation. If other factors remain constant, the percentage of dissolved molecules that ionize increases with increase of temperature. The degree of dilution has a greater effect than temperature; the percentage of molecules dissociated is comparatively low in a concentrated solution and increases as the solution grows more dilute. The most important factor, however, in determining the extent of dissociation is the nature of the substance itself. Some acids and some bases, even without extreme dilution, dissociate almost completely; they are called *strong* acids and *strong* bases. Examples are hydrochloric and nitric among the acids, and sodium and potassium hydroxide among the bases. Others that dissociate to only a slight extent are called *weak*, for example, carbonic acid and ferrous hydroxide.

Water itself ionizes to a very slight extent. The products formed are hydrogen and hydroxyl ions, thus:

$$H_2O \rightleftharpoons H^+ + OH^-$$

The reason why electrolytes produce two or more times as much effect as non-electrolytes on the freezing point, boiling point, and osmotic pressure of solutions is now apparent. With electrolytes there may be two or more times as many particles as with non-electrolytes in solutions of equal concentrations. The size of the particles is of no consequence.

Electrolytic Solution Pressure.[1]—The metals themselves, like their salts, have solution pressures; they exhibit a tendency to dissolve in water and aqueous solutions. Although in this respect there is an analogy between metals and their salts, the analogy is by no means exact. When a salt passes into solution, both positive and negative ions are formed simultaneously; the solution remains electrically neutral. On the other hand, when a metal dissolves, it can send only positively charged ions into solution; negative ions are not formed at the same time. As a result, the solution acquires an electrostatic positive charge and

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[1] For a more thorough treatment of this subject see LeBlanc, "A Text-book of Electrochemistry," translated from the 4th German edition by Whitney and Brown, p. 175 ff.

the metal a negative charge. We may conceive of the positively charged state of the ions as being due to the absence of negative electrons, which remain behind on the metal.

The metals vary a great deal with respect to their tendencies to send positively charged ions into solution. With the so-called "noble metals," the tendency is very slight, with copper and lead it is greater, with iron and zinc it is still greater, and with sodium and potassium it is very great, indeed. In this sense, hydrogen acts as a metal; under certain conditions it tends to send positively charged ions into solution. On the hydrogen scale, the following is the order of the more common metals arranged according to diminishing solution pressures:

Potassium
Sodium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Copper
Bismuth
Antimony
Mercury
Silver
Platinum
Gold

The tendency of a metal to dissolve is opposed by ions of the metal already in solution. The dissolved ions are continually impinging upon the surface of the metal where they discharge by removing therefrom negative electrons. When they discharge, they can no longer remain ions but must become electrically neutral atoms. The tendency to precipitate as atoms is greater as the concentration of the dissolved ions is greater; it is measured by the osmotic pressure of the ions.

Then, when a metal is placed in a solution of one of its own salts, if the osmotic pressure of the ions is high, as in a concentrated solution of the salt, and the solution pressure of the metal is low, as in the case of copper, more ions will discharge in a given period than will pass into solution. Consequently, if copper is placed in a concentrated solution of copper sulfate, the metal will become positively charged. On the other hand, when zinc is placed in a solution of zinc sulfate, the solution pressure of the metal, being very great, overbalances the osmotic pressure of the ions and the metal becomes negatively charged. Jones[1] says that the solution pressures of magnesium, aluminum,

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[1] "Outlines of Electrochemistry," p. 82.

zinc, cadmium, iron, cobalt, and nickel are always greater than the osmotic pressures of the ions in any solution of their salts that can be prepared. Hence, they always become negatively charged when put into their own salt solutions. On the other hand, copper, mercury, and silver are likely to become negatively charged when placed in their own salt solutions, because they have such low solution pressures that these pressures are less than the osmotic pressures of the dissolved ions unless the solutions are extremely dilute.

On the basis of the solution-pressure theory, it is possible to account for the replacement of a metal in solution by another metal. If zinc is dipped into a solution of copper sulfate, zinc sulfate is formed and metallic copper is deposited. If copper is placed in a solution of zinc sulfate, no action takes place. The explanation is this. The zinc has a strong tendency to send ions into solution and becomes negatively charged to a high degree. The positively charged copper ions in solution have a strong tendency to discharge; the strong negative charge on the zinc enables them to do so. On the other hand, with copper in a zinc sulfate solution because of the low solution pressure of the copper, the negative charge on the metal is very low. The zinc ions, moreover, have a relatively low discharge tendency; as a result no chemical replacement occurs.

On the same basis, those metals standing above hydrogen in the solution-pressure series replace hydrogen in solution, *i.e.*, the metal will go into solution and hydrogen will be evolved; those standing below hydrogen will not act in this manner.

In brief, the metals standing at the upper end of the series are those that exhibit a strong tendency to go into and remain in the ionic condition; they are those which in nature are never found free, but always in the form of some compound. Those standing at the lower end of the series are easily converted from the ionic to the metallic state, and are those which in nature may be found uncombined.

Electrostatic Attraction between Metal and Liquid.—From the preceding discussion it might be supposed that when a metal is placed in solutions of its salts of varying concentrations, it would either send ions into solution, or ions from solution would precipitate on the metal and discharge until in every instance the concentration would reach a value at which equilibrium is established between the electrolytic solution pressure of the metal and the osmotic pressure of the dissolved ions at the temperature employed. When the case is subjected to test, however, it is found that the passage of ions either to or from the metal interface ceases almost instantly. This apparent discrepancy is accounted for by the very strong electrostatic attraction set up between the charged metal and the oppositely charged liquid. A tension exists at the interface that is measurable as a difference in electrical pressure or potential. We have previously explained how metals with high solution pressures become negatively charged in solutions of their own salts. The negative charges on the metal prevent the positively charged ions that have passed into solution from diffusing away from the metal. At the interface, an *electrical double layer* is formed, negative charges on the metal and positive charges in solution. The condition is similar to that of a charged condenser. Except that the positions of the positive and negative charges are reversed, a like condition is developed when a metal with a low solution pressure is placed in a solution of one of its salts.

The electrostatic attraction always compensates for the difference between the solution pressure of the metal and the osmotic pressure of its ions. There are three cases to be considered:

1. Where the solution pressure of the metal just equals the osmotic pressure of its ions. In this case ions are neither formed nor discharged; an initial equilibrium exists, thus:

$$\text{Solution pressure} = \text{osmotic pressure.} \tag{1}$$

2. Where the solution pressure of the metal is greater than the osmotic pressure of the ions. Under these conditions ions will pass into solution and the metal will become negatively charged. Equilibrium will be reached and ionization will cease when the solution pressure of the metal is balanced by the osmotic pressure working in conjunction with the attraction of the negatively charged metal for the positively charged ions, thus:

$$\text{Solution pressure} = \text{osmotic pressure} + \text{electrostatic attraction.} \tag{2}$$

3. Where the osmotic pressure of the ions is greater than the solution pressure of the metal. A few ions will pass to the atom

form on the metal; the metal will acquire a positive and the solution a negative charge. Equilibrium will be reached and the plating out of the metal will stop when the osmotic pressure is balanced by the solution pressure working in conjunction with the attraction of the negatively charged liquid for the positively charged ions that tend to pass to the metal, thus:

Osmotic pressure = solution pressure +
electrostatic attraction. (3)

It is evident from a study of Eqs. (2) and (3) that the amount of the electrostatic attraction or difference of potential must always depend upon the difference between the solution pressure and the osmotic pressure. It will, therefore, be affected by the kind of metal used and the concentration of the solution employed. It is evident also from the equations that only when some arrangement is made to withdraw constantly the opposite charges from the metal and solution, is it possible for the action to continue for very long. It is upon the principle of constant neutralization of charges that primary electric cells are based.

A Two-metal, Two-fluid, Electric Cell.—The action that occurs in a cell of this type can be very readily shown by the use of zinc and copper in solutions of their salts separated by a porous diaphragm as shown in Fig. 90. Because of the high solution pressure of zinc, it becomes negatively charged by projecting zinc ions into the zinc-sulfate solution [Eq. (2)]. Because of the low solution tension of copper, copper ions precipitate upon the metal and charge it positively [Eq. (3)]. The negatively charged state of the zinc is due to the negative electrons left on the metal when the ions passed into solution; the positively

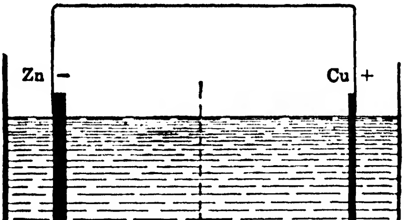

FIG. 90.—A two-metal, two-fluid, primary, electric cell.

charged state of the copper is due to the negative electrons removed therefrom when the copper ions (which lack negative electrons while positive ions) discharged. Because there is an excess of negative electrons on the zinc and a deficiency on the copper, if we connect the two metals by means of a conducting wire, electrons will flow through the wire from the zinc to the copper. There is a tendency to equalize the concentration of electrons on the two metals. Because the electrostatic attraction is now lessened at both metal interfaces [Eqs. (2) and (3)], zinc can send more ions into solution, and the osmotic pressure can cause more copper ions to precipitate and to discharge. The whole process will be continuously repeated. Thus, the latent energy of the dissolving zinc is manifested as a current of electricity passing through the system.

Electrochemical Terms.—Before proceeding further with the discussion of primary cells, it will be necessary to define some of the terms usually employed in connection with them.

As was indicated earlier in the chapter, the chemically active solution used in the cell is called the *electrolyte.* This may be a single solution or, at times, two solutions kept separate in some convenient manner. The metals employed in the cell are generically known as *plates,* although they may not always be in plate form. The *surfaces of contact* between these plates and the electrolyte are known as *electrodes.* The electrode on which ions precipitate and which becomes positively charged in its electrolyte is known as the *positive electrode,* or *cathode.* The electrode where metallic ions enter solution, and which is, therefore, negatively charged, is the *negative electrode,* or *anode.* The ions that move toward the cathode as the current passes through the cell are known as *cations,*[1] and those that move toward the anode the *anions.* Cations carry positive, and anions negative charges. The path by which the current flows from cathode plate to the anode plate, outside the cell, is known as the *external circuit.* The junctions of the external circuit with these plates are known as

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[1] Although we define "direction of current" as the direction in which the cations move, this is only an arbitrarily established convention. As a matter of fact, we now know that the flow of electricity is due to the passing of negative electrons, and that they actually move in the direction opposite to that which is designated as the flow of "the current."

the *poles* of the cell or battery; the junction with the cathode is the *positive pole*, and the junction with the anode, the *negative pole*. The cells themselves are frequently called *voltaic* or *galvanic cells*, in honor of Volta and Galvani, who were pioneer investigators in this field.

The unit of resistance offered to the flow of the electric current is called the *ohm*. It is defined as the resistance at 0°C. of a column of mercury 1 sq. mm. in sectional area, and 106.300 cm. long. The unit of current strength is the *ampere*. It is the current that, when passed through silver nitrate under specified conditions, will deposit silver (see Electrolysis, page 638) at the rate of 0.0011180 g. per second. The unit of potential difference or electromotive force is called the *volt*. It is the driving force or electrical pressure that causes the current to flow. It may be defined relatively as the amount of this force that will cause a current of 1 amp. to flow through a resistance of 1 ohm.

Cathodic Polarization by Hydrogen.—In discussing electrolytic solution pressure, it was pointed out that the metals listed above hydrogen in the potential series, under suitable conditions, are able to replace hydrogen from solution, while those below it will not do so. The position of the elements in this series is an indication also of their discharge tendencies; those with high solution pressures have low tendencies to pass from ion to atom; those with low solution pressures pass from ion to atom more readily.

In the two-metal, two-fluid cell that we discussed, both copper ions from the copper sulfate, and hydrogen ions from the dissociated water were present in the electrolyte about the cathode. Because the discharge tendency of the copper ion is greater than that of the hydrogen ion, when the external circuit between the zinc and copper is closed, only copper ions discharge to the cathode unless the copper-ion concentration falls below a certain value. With a sufficiently low copper-ion concentration, hydrogen ions will discharge; but others will immediately be formed in the electrolyte adjacent to the cathode by the further dissociation of water. The hydroxyl ions and sulfate ions from the dissolved salts are continually being removed from the region about the cathode, because, being anions, they move toward the anode.

The hydrogen ions that discharge under the conditions described cover the cathode with a layer of electrically neutral monatomic hydrogen; the cathode is then said to be polarized by hydrogen. A cathode covered with hydrogen is in effect a hydrogen cathode. Because the solution pressure of hydrogen is above that of copper, hydrogen tends with greater force than that of copper to send ions into solution; thus it has a greater tendency to become negatively charged and to develop a back electromotive force that drives against the current first established. In this way the normal electromotive force of the cell is lessened. It is easily shown experimentally that the loss of electromotive force of the cell due to the polarization of the cathode by hydrogen may be very great.

With a suitable combination of hydrogen-ion concentration, temperature, and electromotive force, hydrogen gas bubbles will be formed. Under such conditions, a new resistance is encountered; the current flow is opposed by the ohmic resistance of the layer of gas bubbles clinging to the surface of the cathode.

Hydrogen Overvoltage.—Instead of zinc and copper in their own salt solutions, let us assume a simple form of cell consisting of the same metals suitably connected dipping into a dilute, aqueous solution of sulfuric acid. Zinc ions will go into solution and hydrogen ions will discharge to the copper. If the acid is sufficiently dilute, however, no hydrogen will escape as gas, although polarization by hydrogen will occur. If we now increase the hydrogen-ion concentration by adding more acid (or an increase of temperature may be sufficient), hydrogen bubbles will eventually be formed on the copper. It is evident that in order to maintain a current of electricity in a cell of this type, a certain amount of electromotive force is required to overcome the back electromotive force developed as a result of the solution pressure of the monatomic hydrogen on the cathode. Careful experimentation has shown that a back electromotive force in addition to that just described must be overcome in order to evolve hydrogen as a gas. This excess back pressure is called hydrogen overvoltage. The hydrogen that is evolved as gas is molecular hydrogen; overvoltage is encountered whenever molecular hydrogen is formed.

Hydrogen overvoltage varies a great deal with the kind of metal employed as cathode and the surface condition of the metal. When arranged according to diminishing overvoltages, the order of some of the common metals is as follows:[1] mercury, zinc, lead, tin, copper, nickel, silver, platinum, and iron. The different metals appear to have some influence in promoting more or less the formation of molecular hydrogen; if the reaction takes place slowly, the overvoltage is high; if it takes place rapidly, the overvoltage is low.

Local Action.—It frequently happens in primary cells that a considerable part of the energy theoretically rendered available by the anode dissolving in the cell is not manifested as a current of electricity in the external circuit. Sometimes more than half of it is used up in maintaining numerous, small currents that flow from part to part of the anode itself. This is due to lack of uniformity in the composition of the metal, in other words, to the presence of impurities. In zinc, which is used in all the common cells, the impurities are lead, iron, and cadmium. These metals have lower solution pressures than zinc, and so function as cathodes. Zinc ions enter the solution at the points where the metal is relatively pure, and other ions, generally hydrogen, precipitate at the impure points, where the solution pressure is low. Thus, local currents are maintained between portions of the metal and electrolyte; zinc is consumed to no purpose. Such action is termed local action.

Aside from the presence of impurities in the zinc, local action may be engendered by the presence in the solution of ions of metals having low solution pressures. For example, copper ions in solution, when they come into contact with zinc, give their charges to the zinc and become atoms of copper, while zinc ions enter solution; for, as has been explained, zinc has a high, and copper a low solution pressure. The deposited copper acts as a discharge point for hydrogen ions.

It has been observed that ordinary zinc, when amalgamated or coated with a layer of mercury,[2] acts like pure zinc in a

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[1] Chapin, "Second Year College Chemistry," p. 293.

[2] The zinc may be coated with mercury by rubbing it with a tuft of cotton moistened with a slightly acidified solution of mercuric chloride, or by rubbing it in the same way in the presence of metallic mercury and dilute hydrochloric acid contained in a tray.

solution of hydrochloric or sulfuric acid; it does not dissolve. The insolubility of the zinc is probably due largely to the high hydrogen overvoltage on mercury. It has been suggested, also, that the effectiveness of the mercury in preventing the zinc from dissolving may be partly due to the formation of a mercury alloy with zinc but not with the impurities. On this basis, as the zinc ions escape from the outer layer, the mercury takes up more zinc from the metal on the inner side. Because the impurities are less soluble in the mercury layer they cannot come into contact with the electrolyte to the same extent. Thus, the amalgam acts as a filter; it passes zinc but holds back the impurities. On the other hand, the effect of the amalgam has been accounted for by assuming that the mercury dissolves even the impurities, both those in the zinc and those that precipitate from the electrolyte. Local action is then prevented because the surface is made uniform and the solution pressure equal at all points. Besides, the amalgam presents a very smooth surface; on this account it is more difficult for hydrogen ions to discharge to it.

Kinds of Cells.—There are many kinds of primary cells, and generally several modifications of each kind, but only those that are the most widely used will be discussed here. They are the Daniell, the Lalande, and the Leclanché, of which the dry cell is a modification.

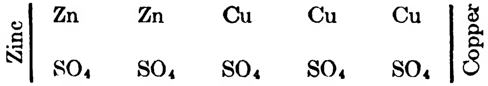
The Daniell Cell

The Daniell cell, which was brought out in 1836, is the oldest of the three types mentioned. In respect to mechanical construction, it may be of either the porous-cup, or gravity type.

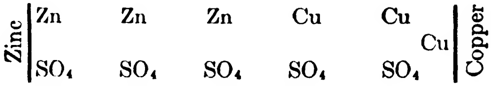
The porous-cup type consists of a jar containing a saturated solution of copper sulfate, in which is immersed a partially closed cylinder of copper sheet. Within the cylinder of copper sheet stands a porous clay cup, which contains either a dilute solution of sulfuric acid or zinc sulfate. In this solution is placed a rather heavy zinc grid. The cup allows ions to travel through its pores, but still prevents a rapid mixing of the two solutions.

The gravity type differs from the porous-cup form in that the two solutions are kept separated only by the difference of the specific gravities of the two solutions. The shapes of the electrodes are modified also.

The *electrochemical action* in the Daniell cell may be sketched graphically. Before the circuit has been closed, the constituents may be considered to bear the following relation to each other:



But immediately after the circuit is closed the following ionic changes occur:



Zinc ions enter solution and copper ions leave it; the latter are converted into metallic copper. In this way electricity is carried through the cell at a slow but definite rate.

As a result of the migration of ions, a change in concentration is brought about in the cell, as sketched in Fig. 91. Since the anode is dissolving, the solution there becomes continually more concentrated in zinc ions, and the osmotic pressure becomes proportionally increased. Consequently, the solution pressure of the zinc meets with more resistance in sending ions into solution with the result that the speed of the cell action is lessened. In a similar manner the osmotic pressure of the copper ions in the copper-sulfate solution becomes less as ions precipitate upon the metal, and the solution becomes less concentrated. In caring for a Daniell cell, attention must be paid to these concentration changes. To keep up the activity of the cell, copper ions must be constantly supplied to the solution by adding more copper sulfate; zinc ions must be removed from the solution by removing the concentrated zinc sulfate solution.

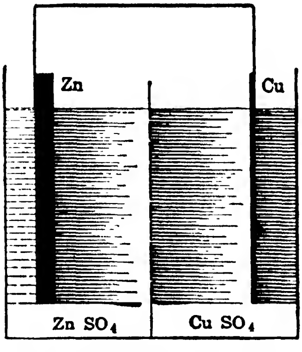


FIG. 91.—Concentration changes in a Daniell cell.

The Electromotive Force of the Cell.—In the Daniell cell, the zinc is about 0.8 volt negative to the zinc-sulfate solution and the copper is about 0.3 volt positive to the solution of copper sulfate; consequently, the electromotive force of the cell is about 1.1 volts. In this cell, as in all cells, the electromotive force is not dependent upon the size of plates but on the amount of solution tension and osmotic pressure. A small battery will produce the same electromotive force as a large one of the same kind, if the solutions used are the same, and of the same concentration. But the current strength depends upon the size of the plates. In the ordinary-sized Daniell cell, the current strength does not usually exceed 0.5 amp.

Depolarization.—In this cell, polarization is prevented by substituting another ion, the copper ion, for hydrogen, so that when the cell is in good condition, the hydrogen ion does not reach the cathode plate.

Defects.—When the cell is allowed to stand idle, the copper sulfate diffuses through the porous cup wall to the zinc. Because of the high solution tension of the zinc and the low solution tension of copper, zinc ions enter solution and copper ions discharge to the metal in exchange. In extreme cases the zinc may be entirely covered with a layer of copper. This replacement of zinc by copper, of course, uses up zinc, but the interchange is especially objectionable because the deposited copper serves as cathodes for local currents. In all Daniell cells, local action is likely to be very great. According to Haber, quoted by Allmand,[1] even under favorable conditions, only 30 per cent of the zinc is electrochemically utilized. When the cell is working, the migration of the cations toward the cathode overcomes the diffusion toward the zinc.

Another objectionable feature is that the porous cup increases the internal resistance of the cell. To aid in keeping this resistance as low as possible, the copper cathode is generally shaped to fit very closely about the cup, so that the distance between the anode and cathode may be as little as possible. This arrangement, however, causes very little copper-sulfate solution to be available, so that its concentration soon becomes low; the internal resistance of the cell increases on this account. To

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[1] "Principles of Applied Electrochemistry," p. 201.

keep up the concentration, crystals of copper sulfate are sometimes packed between the copper plate and the cup, but this is objectionable because the crystals also have a high resistance. Since all of these objections are either directly or indirectly due to the porous cup, a type of cell was devised in which the cup could be omitted. This is known as the gravity type; it is now the most common form of Daniell cell.

The Gravity Type.—In this type the two solutions are kept from mixing merely by the differences in their densities. Such an arrangement decidedly lessens the internal resistance, but also introduces a disadvantage in that the cell cannot be readily transported; any shaking tends to mix the solutions. Further, when standing idle, the solutions are free to diffuse into each other, so that copper ions may reach the zinc. To prevent this diffusion, the gravity cell should always be kept working, even though current from it is not desired for use. In such case, of course, the current taken from the cell should be but a small quantity—enough only that the cationic migration will overcome the diffusion. The current may be regulated by placing a few ohms resistance in the external circuit.

To Set Up a Daniell Cell.—For the cathode electrolyte, a saturated solution of copper sulfate is prepared. At 20°C., which is about room temperature, the crystals are soluble to the extent of 42.3 in 100 parts of water. For the anode electrolyte, either dilute sulfuric acid or a solution of zinc sulfate may be used; there are advantages pertaining to each. With the salt solution, the amalgamation of the zinc is not so imperative, since local action is less pronounced. On the other hand, the internal resistance is less when the acid is used, and the output of the cell is greater. The current strength is less constant with the acid, however, especially during the first 2 or 3 hr. of discharge, or until a considerable amount of zinc sulfate is formed.

If the acid is decided upon, a convenient strength is about 20 per cent. The strength of the zinc sulfate may vary considerably—from 10 to 30 per cent. For short periods of service it is advantageous to use the stronger solution, since its conductivity is greater; up to a certain point, this seems to somewhat more than counterbalance the detrimental effect of the greater osmotic pressure. But on the other hand, the greater the initial concentration, the shorter will be the time during which the cell can work without showing lessened activity due to zinc-ion concentration. In general, for longer periods of service a weaker solution is desired.

THE EDISON-LALANDE CELL

This cell was devised in 1883 by De Lalande, but it has been improved by Edison and others. It consists of a copper-oxide plate between two zinc plates, suspended from a lid, in a 20 per cent solution of sodium hydroxide contained in a porcelain jar. The zinc plates are heavily amalgamated. The copper-oxide plate is made by mixing finely divided copper oxide with sodium-hydroxide solution, and then forming the mass into cakes under heavy pressure. The cakes are then dried and baked at a bright-red temperature. After cooling, the plate is reduced to metallic copper on the surface to give it better conductance at the start.

The electrolyte in this cell is kept covered with a layer of heavy mineral oil, since if it were exposed to the air, it would absorb carbon dioxide and be converted into sodium carbonate, which salt "creeps" badly. There is a disadvantage in having this layer of oil on the electrolyte, since the plates cannot be withdrawn without becoming coated with a film of it, and this film prevents them from being chemically active. In setting up the cell, the elements should be immersed before the oil is poured on.

Electrochemical Action.—The electrochemical reactions that occur in the Lalande cell may be represented graphically as follows:

Before closing the circuit.

Zinc	Na	Na	Na	H	H	Copper oxide
	OH	OH	OH	OH	OH	

After closing the circuit.

Zinc	Zn		Na	Na	Na	Copper oxide
					H_2	
	OH	OH	OH	OH	OH	

Zinc ions enter solution and sodium ions pass over to the cathode, but the hydrogen ions, present as the result of dissociated water, discharge more readily than sodium ions; therefore, hydrogen ions discharge. The zinc hydroxide formed in this way is immediately dissolved by the excess of sodium hydroxide present, with the formation of sodium zincate as follows:

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$$

Depolarization.—The hydrogen separated at the cathode would soon produce polarization were it not that it is oxidized to water by the copper oxide, which is thus reduced to metallic copper, as:

$$CuO + 2H \rightarrow Cu + H_2O$$

The copper oxide is quite active in this way. When it has been reduced to such an extent that its effectiveness is lost, it may be regenerated by heating the plate to incipient redness in the air, over an iron plate to protect it from the direct contact with the flame. Before heating, the sodium hydroxide must be removed from the plate by prolonged soaking in water. In using a regenerated plate, the cell should be short-circuited for a time to reduce the oxide on the surface and increase the conductance. A regenerated plate is never quite as good as a new one.

E.m.f. of the Lalande Cell.—The internal resistance of the Lalande cell is very low; it ranges from 0.03 to 0.05 ohm. The electromotive force of the 500-amp.-hr. type is 0.62 volt per cell, when discharging at the rate of 1 amp. When discharged at a more rapid rate the voltage drops; it is 0.58 volt per cell at 2 amp., 0.55 volt per cell at 3 amp., etc.[1]

Efficiency.—During the action of the cell, practically all of the zinc is utilized electrochemically, *i.e.*, there is very little local action. While standing, the zinc consumption is practically negligible. In this respect, it probably excells any other type of cell. It requires very little attention.

THE LECLANCHÉ CELL

This cell in its original form was introduced in 1868, but a great many modifications have been brought out since that time.

The cell consists of a zinc anode and a carbon cathode, suspended in about a 20 per cent solution of ammonium chloride.

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[1] Information and Directions for Use, furnished by the Edison Storage Battery Company.

To the electrolyte may be added sometimes certain hygroscopic substances, as zinc chloride, calcium chloride, glycerine, etc., to lessen the loss of water by evaporation. The depolarizer consists of manganese dioxide, which is kept in position about the cathode by various devices. In one form, blocks are made of the manganese dioxide, which has been previously mixed with carbon to increase the conductance, and the blocks are then clamped to the sides of the cathode. In another form there are two concentric carbon cylinders, with manganese and carbon packed between them and sealed in. The zinc is placed in the center of the inner cylinder.

Electrochemical Action.—The zinc goes into solution as zinc chloride, and ammonium ions move over to the cathode; but the hydrogen ions of the dissociated water retain their charges less powerfully than the ammonium ions, hence the former discharge, as the following sketches show:

Before closing the circuit.

Zinc	NH_4	NH_4	NH_4	H	H	Carbon
	Cl	Cl	Cl	OH	OH	

After closing the circuit.

Zinc	Zn		NH_4	NH_4	NH_4 H_2	Carbon
	Cl	Cl	Cl	OH	OH	

The result of this action is that undissociated ammonium hydroxide[1] is formed, which in turn furnishes ammonia gas. Some of this gas escapes into the air, but the greater part of it remains dissolved and diffuses into the zinc-chloride solution, with which it reacts to form the compound $Zn(NH_3)Cl_2$.[2] This compound is but slightly soluble and gradually separates out. By the action of the ammonium hydroxide, insoluble zinc hydroxide also is produced. Some of this hydroxide precipitates within the pores of the depolarizer and greatly increases its resistance. The conductivity of the depolarizer of an exhausted cell is very low.

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[1] Ammonium hydroxide dissociates very little, only about one-fortieth as much as potassium hydroxide, for example; see Jones, "Outlines of Electrochemistry," p. 27.

[2] ALLMAND, "Principles of Applied Electrochemistry," p. 207.

Concentration Effect.—Because of concentration changes that take place in the electrolyte, there is a certain amount of local action in this cell. The solution of zinc chloride formed at the anode is heavier than the remainder of the solution and sinks to the bottom, making the concentration of the zinc ions greater here than at the top. It was pointed out in the discussion of osmotic pressure that the concentration of dissolved ions lessened the rate at which more ions could enter solution. In this case, then, the zinc anode can dissolve more readily at the top than at the bottom. In fact, the action is that of a concentration cell. Zinc ions enter solution at the top of the anode and hydrogen ions discharge from solution at the bottom. Sometimes the effect is so pronounced that the rod becomes noticeably "necked" at the top and may even be entirely separated into two parts.

Depolarization.—The depolarizing reaction of the Leclanché cell may be represented by the following equation:

$$2MnO_2 + 2H \rightarrow Mn_2O_3 + H_2O$$

The manganese dioxide does not react nearly so rapidly as the copper oxide of the Lalande cell; in fact, depolarization is very slow. Consequently, but little current can be taken from the cell at a time without the voltage dropping greatly, but depolarization takes place eventually and the cell recovers. Because of this slow action of the depolarizer, Leclanché cells are most suitable where only an intermittent current is desired.

Electromotive Force of the Cell.—Depending upon the form of the cell, the initial voltage may vary from 1 to 1.8. The internal resistance is about 3 ohms. When exhausted, the cell may be renewed with fresh electrolyte, but the electromotive force is not so high as that of a new cell.

"Creeping" of Salt.—Leclanché cells are sometimes troublesome because of the "creeping" of the salt of the electrolyte. This is an effect produced by the evaporation of water and the formation of crystals on the sides of the container. More of the solution rises between the crystals by capillary attraction and evaporates, which leaves more crystals above; the action continues until the crystals may even pass over the edge of the container. The creeping may be prevented by dipping the tops of the jar and the elements in varnish or melted paraffin to which substances the solution does not adhere.

Despite its many objections, the Leclanché cell is widely used, probably because it is easily set up and requires but little attention. It can stand for long periods unused with practically no ill effects, except the local action due to the concentration change. There is but little local action due to other causes.

Dry Cells

Dry cells are cells prepared in such a manner that they are portable and can be used in any position. Although they are called dry cells, it should be understood that they are not really dry, since if such were the case, no action would occur in the cell. In fact, it is a very important consideration of the manufacturer so to construct them that they will remain sufficiently wet.

Dry cells are essentially Leclanché cells; they contain the same elements as the Leclanché, but their electrolyte and depolarizer are in the form of pastes. It is rather difficult to state any definite method of construction, since there are so many different forms. In one form the zinc anode is in the form of a cylinder, which serves as the outer containing vessel. The carbon cathode occupies the interior of the cell, surrounded with the depolarizer—a mixture of finely divided graphite or other carbon and manganese dioxide; the latter must be as pure as possible. The cathode is suitably insulated from the bottom of the cell to prevent internal short-circuiting. Between the depolarizer and the zinc container is the electrolyte, which is about a 25 per cent solution of ammonium chloride, maintained in a layer form against the zinc by being held in some porous material as pasteboard, paper pulp, sawdust, charcoal, infusorial earth, gypsum, magnesium oxide, zinc oxide, etc. The two oxides just mentioned have the disadvantage of setting to a hardened mass by the formation of an oxychloride compound which increases the cell resistance. Hygroscopic substances, such as zinc chloride, calcium chloride, and glycerine, are sometimes added to aid in preventing the cell from becoming too dry. The contents of the cell are kept in place by suitable packing and the whole is sealed in with bituminous material. One or two small openings are left in the container to allow the escape of ammonia gas produced during the working of the cell. When these openings become clogged the cell may burst because of the pressure of the retained gas.

Since dry cells are required to stand idle for long periods, it is very necessary in manufacturing them to see that no defects occur that would lead to local action. The materials used must be very pure. Salts of copper, lead, tin, iron, etc., are very bad, since zinc deposits these metals from their salts, and then they become cathodes for local action.

The voltage of the cells varies according to the brand or type, but may be considered to be equivalent to that of the Leclanché containing the fluid electrolyte, *i.e.*, from 1.0 to 1.8 volts.

The internal resistance increases during the working of the cell; this is due both to the formation of insoluble zinc compounds as explained on page 634, and to the evaporation of water through imperceptible openings in the container or seal. Sometimes the container may be ruptured by the pressure of the gas produced during working. The cell is then likely to fail because the moisture will evaporate and it will become too dry. Such cells may be made to produce several hours' more service by removing the outer pasteboard cover and placing them in water for 1 or 2 hr. The same treatment may be given cells in which no ruptures are apparent if small perforations are made in the case. During soaking a small opening should be left above the water for the escape of air. Deterioration due to drying out may take place even in unused cells, but if well-made, they will remain active for about 2 years.

CHAPTER XIX

SECONDARY CELLS

Secondary cells may be considered to be reversible primary cells. They consist of systems so arranged that when electrolysis is caused to occur in the cell, the electrodes assume such a condition that they may later exercise the same function as the elements of a primary cell. Such systems are also called storage cells, because during electrolysis chemical energy is stored up that may be converted into electrical energy at will. The process of storing up energy in the cell by electrolysis is known as charging, and the taking of current from the cell, as discharging. Since an understanding of electrolysis is of fundamental importance in a study of secondary cells, a discussion of it will be included here.

Electrolysis.—When a current passes through solutions of chemical compounds, or through compounds in the molten state, a chemical decomposition results. This decomposition is known as electrolysis, which means the setting free of combined substances by means of the electric current. When a current is passed through a solution containing a dissociated substance, the ions swarm to the electrodes and discharge. As was explained in the discussion of Electrolytic Dissociation in the preceding chapter, the ions exist in the solution before the current is passed, and begin their migration the instant the circuit is closed. The positive ions travel toward the cathode and the negative ions toward the anode, where they discharge and thus serve to carry the current through the solution. When the ions have reached the electrodes and have discharged, they may separate as elements, or may undergo secondary reactions. When a current passes through an electrolyte dissolved in water, there may be two kinds of ions appearing at both the anode and cathode—ions from the dissolved substance and ions from the dissociated water—but it may happen that only one kind is discharged. For example, when a current is passed between platinum electrodes through a dilute solution of sulfuric acid, hydrogen ions from both the sulfuric acid and the dissociated water will gather about the cathode and give up their charges there. About the anode will gather both SO_4 and OH ions, but because the former give up their charges less readily than the latter, it is only the OH ions that discharge negative electricity to the anode. Two discharged hydroxyl ions unite to form a molecule of water and oxygen, which gas escapes from the solution. The SO_4 ions undergo no change at the anode: they merely carry negative electricity to this electrode, and then form sulfuric acid with the hydrogen ions of the water. Precisely similar actions may occur in the electrolysis of bases and salts.[1]

It is not always hydrogen and oxygen only that are evolved, however. Sometimes the ions of the dissolved substance discharge more readily than the ions from the dissociated water. For example, copper and silver discharge more readily than hydrogen, and chlorine more readily than the hydroxyl ion.

It sometimes happens also that the anode dissolves under the conditions of electrolysis. For example, if a copper anode is used in dilute sulfuric acid, copper ions will enter the solution and produce copper sulfate with the SO_4 ions that collect there. No oxygen will escape as when the insoluble platinum electrodes were used. If a solution of copper sulfate is used in place of the dilute sulfuric acid, the conditions will then be suitable for electroplating. Copper ions will enter the solution at the anode and deposit at the cathode.

Kinds of Secondary Cells.—Theoretically, there are a great many combinations that may serve as storage cells, and much painstaking effort has been expended in attempts to develop various systems into successfully working cells, but practical difficulties have caused all but two to be abandoned. These two are the well-known lead accumulator, produced by Planté about 1860, and modified by Faure about 1880; and the iron-nickel-alkali cell rather recently developed by Edison.

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[1] For a more complete discussion of these cases, see Jones, "Outlines of Electrochemistry," p. 40.

THE LEAD ACCUMULATOR

Construction.—When the accumulator is in a charged condition, *i.e.*, ready to deliver current, it consists essentially of a plate of lead and a plate of lead peroxide dipping into a solution of sulfuric acid that has been prepared to contain 37 per cent of sulfuric acid by weight. This solution has a specific gravity of 1.280. The plate containing the lead peroxide is generally known as the positive plate, and the lead plate as the negative plate. These terms are strictly applicable only half the time, however, for during charging, the current enters at the peroxide electrode, thus making it the anode, and flows through the electrolyte to the lead electrode, now the cathode. On discharging, the current flows through the cell in the opposite direction, leaving the cell by the peroxide plate, thus making it the cathode, and enters the cell by the lead electrode now the anode.

Types of Plates.—The plates of the lead accumulator are of two main types: first, those on which the active lead and lead peroxide are formed from the substance of the plate itself by direct chemical or electrochemical action; and second, those on which the active material is formed of substances applied to the plate. The former are of the type originally produced by Planté, and are known as Planté plates, although the modern plate has been so highly improved that it scarcely resembles the original. The latter type are as modified by Faure; they are generally known as Faure, mass, or pasted plates.

In making the *Planté type*, the surface of the plate is increased as much as possible by scoring with knives or else by casting it in a suitably ribbed or corrugated form. Plates mechanically prepared in this manner are then given a coat of lead sponge or lead peroxide by a process known as "forming." In the earlier methods, the first step in the forming process was to produce on both the positive and negative plate a coating of lead peroxide; this was accomplished by connecting them as anodes in an electrolyte of dilute sulfuric acid. The lead-sponge plate was then produced from a lead-peroxide plate by connecting it as a cathode and reducing it. To secure a sufficient amount of active material the process of oxidation and reduction had to be repeated many times, so that forming was exceedingly slow;

it required about a year. Now the plates are prepared in about one-half day by a process known as "rapid forming." To the dilute sulfuric acid is added some reagent whose negative ion by reacting at the anode tends to produce a lead salt that is at once converted into lead sulfate. In this way a layer of lead sulfate is produced instead of lead peroxide. Since the sulfate layer is more porous than the peroxide, the action proceeds quite rapidly.

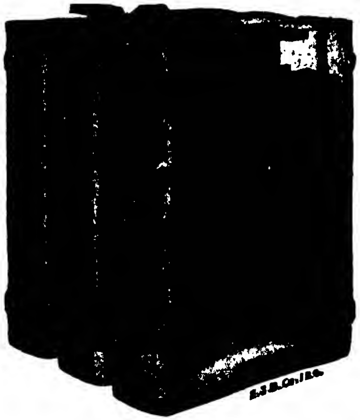

Fig. 92.—"Chloride accumulator."

Fig. 93.—Showing construction of "Iron-clad Exide" cell.

The sulfate can then be converted into lead sponge or lead peroxide as desired by electrolyzing in a bath of dilute sulfuric acid. The substances used as "forming agents" are such salts as the acetates, nitrates, chlorates, chlorides, and their corresponding acids.

In making the *Faure*, or *pasted, plates*, grids containing grooves or pockets are first prepared and filled with a paste containing lead oxide and sulfuric acid, and often other substances. This paste soon sets to a hard mass. It is then changed to lead sponge and lead peroxide by the reactions of electrolysis.

There are two or three noteworthy modifications of the preceding types. They are the plates of the so-called "chloride accumulator," the "box negatives," and the "iron-clad" vehicle plates. The original chloride negative was made in the following manner. Lead and zinc chlorides were melted together and poured into a supporting lead grid. The zinc chloride was then dissolved out, leaving a porous mass of lead chloride, which was later reduced to lead sponge by electrolytic action. The positive plate of this battery was made by the Planté process. Although this chloride method is no longer used,[1] the name is retained. The peroxide plates of the so-called chloride accumulator are now made by inserting in the grid, buttons produced by winding up corrugated lead ribbons in the form of a spiral. These buttons project from the grid a slight distance as shown in Fig. 92. The active material is then formed on the surface of this lead spiral.

In the box negative, the active material is not actually "pasted," but is held loosely in cavities in a grid; it is kept in place by a perforated cover of sheet lead on each side. Because the cover keeps it in place, the active material can be allowed to be very loose and porous, a very desirable feature.

The iron-clad vehicle plate is peculiar in that it depends for support upon an insulating grid or envelope of some substance as rubber, celluloid, porcelain biscuit ware, wood, etc. The envelope of material of this sort surrounds the active material and prevents shedding. Electrical contact is made with a central lead strip or wire.

In the preparation of the Faure-type plates the metal grid used is often made of a lead-antimony alloy containing about 4 to 6 per cent of antimony.[2] This alloy is much harder and more rigid than pure lead, and is designed to resist "buckling"—a warping effect produced in the plate by the volume changes that occur in the active material during charging and discharging. Planté plates are made of soft lead.[3] In assembling the plates in the battery, peroxide plates are not used as end plates because the volume change in the peroxide plate is much greater than in

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[1] Thompson, "Applied Electrochemistry," p. 154.

[2] Allmand, "Principles of Applied Electrochemistry," p. 223.

[3] Watson, "Storage Batteries," p. 21; quoted by Thompson, "Applied Electrochemistry," p. 153.

the lead-sponge plate, and if active on only one side there would be a great tendency toward warping.

Comparison of Types.—Planté and Faure plates each have characteristic advantages and disadvantages. The latter have less weight in proportion to their active mass, and are, therefore, especially suitable where low weight is required. They are mechanically weaker, however, than Planté plates and the active material tends to fall out in time, particularly if the cell is charged and discharged at a rapid rate so that the volume changes are rapid. These detached pieces may lodge between the plates, and short-circuit the battery. The Planté plates are more rugged and are used where ability to withstand heavy service is necessary.

Reactions during Charge and Discharge.—The following explanation is based on the theory developed by Gladstone and Tribe, which is now generally known as the sulfate theory. According to this theory, sulfuric acid reacts with both plates during discharge, producing lead sulfate. During charge, the lead sulfate is converted into lead sponge on the negative plate and into lead peroxide on the positive. The following equations, indicating purely chemical transformations, are used to explain the reactions that occur *during charge.*

At the peroxide electrode:

$$PbSO_4 + SO_4 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4$$

At the lead-sponge electrode:

$$PbSO_4 + H_2 \rightarrow Pb + H_2SO_4$$

Sulfuric acid is set free at both electrodes and the density of the electrolyte increases. During overcharge, oxygen gas is evolved at the peroxide plate as shown on page 639, because when fully charged the plate cannot react with oxygen.

The direction of the current through the electrolyte during charging is from the peroxide plate to the lead, but the direction is reversed during discharge. During discharge, hydrogen ions are set free at the peroxide electrode and sulfate ions at the lead-sponge electrode. The following equations show the reactions that occur *during discharge.*

At the peroxide electrode:

$$PbO_2 + H_2 + H_2SO_4 \rightarrow PbSO_4 + 2H_2O$$

At the lead-sponge electrode:

$$\mathrm{Pb + SO_4 \rightarrow PbSO_4}$$

Water is liberated and sulfuric acid is consumed so that the density of the electrolyte grows less.

The *ionic nature* of the reactions are much more clearly set forth in the following explanation of Le Blanc's theory.[1] The reactions indicated are those that take place *during discharge*. They proceed in the reverse direction during charge.

At the positive electrode:

1. $\mathrm{PbO_2}$ solid $\rightarrow$ $\mathrm{PbO_2}$ dissolved
   $\rightarrow \mathrm{Pb^{++++} + 2O^{--}}$
2. $\mathrm{4H^+ + 2O^{--} \rightarrow 2H_2O}$
3. $\mathrm{Pb^{++++}} + 2\ominus \rightarrow \mathrm{Pb^{++}}$
4. $\mathrm{Pb^{++} + SO_4^{--} \rightarrow PbSO_4}$ undissociated
   $\rightarrow \mathrm{PbSO_4}$ solid

The total of the preceding reactions is equivalent to the following:

$$\mathrm{PbO_2 + 4H^+ + SO_4^{--}} + 2\ominus \rightarrow \mathrm{PbSO_4 + 2H_2O}$$

At the negative electrode:

1. $\mathrm{Pb \rightarrow Pb^{++}} + 2\ominus$
2. $\mathrm{Pb^{++} + SO_4^{--} \rightarrow PbSO_4}$ undissociated
   $\rightarrow \mathrm{PbSO_4}$ solid

The total of these reactions is:

$$\mathrm{Pb + SO_4^{--} \rightarrow PbSO_4} + 2\ominus$$

Density of Electrolyte and State of Charge.—As shown by the equations, sulfuric acid is extracted from the electrolyte by the reactions of discharge and returned to it again by the reactions during charging. Consequently, if we assume that the concentration of the electrolyte in the beginning was correct, the state of charge may be ascertained by determining the density of the electrolyte. With the cell fully charged, the density should be 1.280; it should be recharged when the density falls below 1.160. The syringe type of hydrometer is usually employed for such density determinations.

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[1] For other plausible theories see Dolezalek, "Theory of the Lead Accumulator," transl. by Carl von Ende.

Polarization.—Because of the concentration changes that accompany the reactions of charge and discharge, the voltage of the cell is affected. During discharge the electromotive force decreases because the concentration of the acid is lessened. The amount of acid actually used is but a small fraction of the total amount in the electrolyte, but since it is all abstracted from the solution contained in the pores of the active material, the effect is very pronounced. On standing, this change in concentration is corrected by diffusion between the acid of the pores and that of the main body of the electrolyte. In this way, cells that have been discharged below their normal voltage "recover" upon standing. With a high rate of discharge, the density of the acid within the pores becomes exceedingly low because of lack of time for diffusion; but with slow discharge rates, diffusion may keep pace with the acid consumption.

Self-discharge.—When a charged cell is allowed to stand idle, it slowly discharges spontaneously. This is known as self-discharge; even for a cell in good condition it amounts to 1 or 2 per cent a day. Self-discharge is due to local action. It occurs especially between the peroxide and the lead support of the positive plate; lead sulfate is formed at the surface of contact. This action is more noticeable in the Planté positives than in those of the paste type.[1] On the negative plate the difference of potential between the sponge lead and the solid supporting lead is so small that the self-discharge due to this factor is very slight. In the lead-sponge of many of the negative paste plates, however, are such substances as graphite which are designed to increase porosity and cause the active mass to conduct more readily. With graphite present, the negative plate may discharge itself by local action quite as rapidly as the positive.

Effect of Impurities in the Electrolyte.[2]—It is of greatest importance that the electrolyte be free from impurities, since they may serve greatly to accelerate self-discharge. The impurities that are the most objectionable in the electrolyte may be divided into three classes: first, small amounts of "forming agents," such as the nitric and hydrochloric acids, and other substances mentioned on page 641; second, metals having low

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[1] Morse, "Storage Batteries," p. 207.

[2] Lyndon, "Storage Battery Engineering," p. 52.

solution tensions, as platinum and silver; and third, soluble salts of such metals as iron, whose ions are capable of being oxidized to a higher or reduced to a lower valence.

The forming agents are objectionable because each time the cell is charged they become active in converting more of the lead of the positive plate into lead peroxide, so that in time the lead upon which the plate depends for support may become peroxidized to such an extent that the plate may fall to pieces.

Metals with low solution pressures that may assume the cathodic position to lead are very objectionable because they set up local action that produces self-discharge. Such action is especially likely to occur at the lead plate, because these impurities are present as dissolved salts, and when the metallic ion comes into contact with the lead it replaces the ion in solution; the foreign metal is deposited on the surface of the plate. Lead peroxide is not able to throw the metallic ions out of solution in this manner so they do not deposit on the peroxide plate. Platinum, gold, silver, and copper are objectionable in the order named. Besides being cathodic to lead, it is relatively easy for hydrogen to discharge to these metals, which is a great aid to local action.

Sulfuric acid may acquire traces of platinum during the process of manufacture by being concentrated in platinum retorts. Thompson[1] says that 1 part of platinum in 1,000,000 of acid may produce a rapid self-discharge of the lead plate. The presence of platinum and the similar metals may be recognized sometimes by the continued evolution of gas at the lead plate, after the charging current has been interrupted.

The presence of ions that can exist in more than one stage of oxidation, such as those of iron and manganese, are also aids in bringing about self-discharge. These ions are oxidized to their high valence at the peroxide electrode, then diffuse to the lead electrode where they are reduced; thus they bring about the discharge of both plates.

After commenting on the various factors that bring about self-discharge, Allmand says[2] that a charged cell with a bad

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[1] "Applied Electrochemistry," p. 170.

[2] *Loc. cit.*, p. 227.

electrolyte may lose as much as 50 per cent of its energy in a day through local action.

Sulfating.—When a cell is allowed to stand for some time in the discharged state, the lead sulfate becomes transformed into a dense layer that is very resistant to the action of the charging current. This inert condition is the result of the formation of large-sized, lead-sulfate crystals, which are both poor conductors and inactive chemically because but little surface is exposed in proportion to their masses. In a normal discharged plate, the lead sulfate is finely divided. Besides, it is mixed with lead sponge or lead peroxide, which are relatively good conductors.

The production of the large crystals from the smaller ones, when the cell stands in the discharged condition with lead sulfate on the plates, is due to the constant interchange between the solid and dissolved phases. This interchange occurs even when a substance is in equilibrium with its solution as explained in the discussion of Solution Pressure and Precipitation Pressure on page 617. Because of the greater surface in proportion to their masses, a relatively greater amount of material dissolves from the smaller crystals. On being returned from solution, the dissolved material is received partly by the larger crystals. As a result, the larger crystals eventually absorb the smaller ones.

The effect is promoted also by temperature changes which cause material in solution first to increase and then to decrease.

If this so-called sulfating has not proceeded too far, the cell may be recharged by a long-continued application of the current, but the cell will probably not attain its normal value. If the cell has been allowed to stand discharged for several weeks, the plates may become so badly affected that it is advisable to replace them with new ones. It is very evident, therefore, that when a battery is allowed to stand idle, it should be kept fully charged.

The use of the word *sulfating* in describing this inert condition due to crystal growth is somewhat inapt, since the plates of a discharged cell in the normal condition are also covered with lead sulfate.

Freezing of the Electrolyte.—When completely discharged the electrolyte of the average battery is 1.140. With complete charge it is 1.280. The freezing temperature drops very quickly as the specific gravity increases, somewhat as follows:

Specific Gravity	Freezing Point
1.100	+18°F.
1.120	+14
1.140	+10
1.160	+ 5
1.175	+ 4
1.200	−16
1.225	−36
1.250	−60
1.280	−85

As the preceding table shows, there is no danger of the electrolyte freezing in this climate if the battery is kept in a fair state of charge. It may, however, freeze readily if discharged.

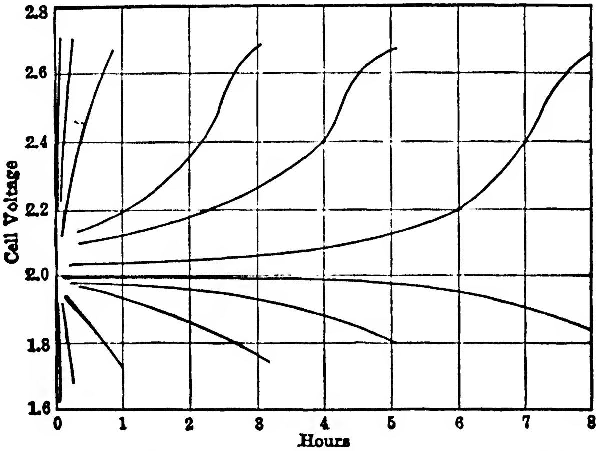

Fig. 94.—Curves of operation of Planté plates at various rates.[1]

Charging and Discharging.—The normal electromotive force of a discharged cell is about 2 volts. As the cell is charged the voltage rises gradually. Oxygen gas is evolved at the peroxide plate at 2.2 volts. The completion of the charge is denoted by the evolution of hydrogen gas at the lead plate, which commences

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[1] Reproduced by permission from "Storage Batteries" by Morse.

at 2.3 volts; but it is good practice to continue the charging current for some time longer.

Batteries should not be charged too slowly, generally not below the 16-hr. rate. If the period required is too long, or in other words, if the current density is too low, lead sulfate instead of lead peroxide is formed on the positive plate.

During charge, a part of the energy of the current is transformed into heat, because of the resistance of the system. Care must be exercised that the temperature does not rise too high.

In discharging, the general rule is to interrupt the current when the drop in voltage has amounted to one-tenth of original voltage of the cell, for example, from 2 to 1.8 volts. This is not invariable, however. Morse says[1] that when discharged at low rates, as in telephone or train-lighting service, the lower limit is about 1.8 volts; in regulating power-plant loads, and in much of the other regular battery work, it is 1.7 volts; at very high rates, as when an emergency battery is called upon to take the entire load of a large station, it may be carried as low as 1 volt. In discharging at the higher rates less total current is available, since but little of the active mass is used due to the fact that the acid has not sufficient time to diffuse into it. The insufficient diffusion brings about concentration polarization as has been explained (page 645).

The effect of variation in charge and discharge rates is illustrated in the following curves and discussion quoted from Morse.[2]

The rates for the curves of Fig. 94 are:

	Amp.
For 8 hr. of charge or discharge	1.0
For 5 hr. of charge or discharge	1.4
For 3 hr. of charge or discharge	2.0
For 1 hr. of charge or discharge	4.0
For 20 min. of charge or discharge	8.0
For 5 min. of charge or discharge	16.0

These are the rates usually specified in practice.

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[1] "Storage Batteries," p. 116.

[2] Pp. 112 and 113.

The capacities corresponding to these rates are:

	Amp.-hrs.
For 8-hr. charge or discharge	8.00
For 5-hr. charge or discharge	7.00
For 3-hr. charge or discharge	6.00
For 1-hr. charge or discharge	4.00
For 20-min. charge or discharge	2.67
For 5-min. charge or discharge	1.33

Morse says further:

> It makes a great difference in the discharge curve of a cell, whether the cell has been charged at a high or a low rate, and just as great a difference in the charging curve, whether the previous discharge has been fast or slow. Take a single case. Suppose a fully charged cell has been discharged at the 5-min. rate. It is evident from the figure that only 1.3 amp.-hr. have been drawn from it. We only need to return a little more than this to the cell to charge it completely. In the same way, if our cell has been completely discharged at a low rate, and then charged at the 5-min. rate, we can only get about 1.3 amp.-hr. into it. It may be fully charged for a 5-min. discharge, but it is by no means charged for a 3-hr. discharge.

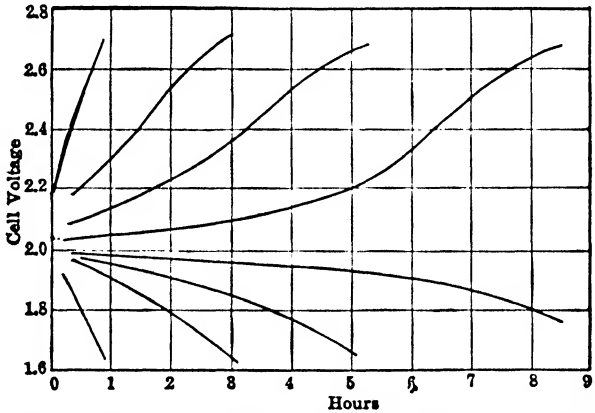

FIG. 95.—Curves of operation of mass plates at various rates.[1]

The following general rules for the operation of batteries are also quoted from Morse.[2]

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[1] Reproduced by permission from "Storage Batteries" by Morse.

[2] Pp. 223 and 224.

For Planté plates:

1. Keep the battery charged.
2. Charge at a fairly high rate. Usually this means at the 8-hr. rate or a little higher.
3. Inspect frequently and remove all possible short-circuits immediately.
4. Keep acid density at the proper point.
5. Keep the acid above the top of the plates.
6. If plates buckle, straighten them out as soon as possible.
7. Do not let the temperature reach too high a point (100°F. is a safe limit).

Discharge at almost any rate does not harm good Planté plates, provided they are charged immediately after the discharge is finished.

For paste plates:

1. Charge at a low rate, 12 hr. or lower.
2. Overcharge occasionally by 10 per cent or so. Once a week is often enough for the overcharge if the battery is in daily service.
3. Use an ampere-hour meter and regulate charge and discharge by that.
4. Try to give a nearly complete discharge before recharging. If the discharge is extended over 2 or 3 days no harm is done.
5. Watch temperature carefully. High temperature is much more destructive to paste plates than the Planté types.
6. Test each cell frequently and inspect at the least sign of trouble.

The most usual trouble arises from continued net undercharge, especially in private installations.

The following further observations have been derived from Lyndon's "Storage Battery Engineering."

If an instrument must be put into the cell for any purpose, never use metal. Use glass, hard rubber or wood.

If batteries are to be put out of commission for some time—say 6 weeks or more—they should not be allowed to stand in the electrolyte unless a small charge can be given them at least once in 2 weeks. When they are to be unused for a considerable period, the elements must be removed from the liquid and dried. But this must be done only after the plates have been specially prepared and they must be dried with the observance of certain precautions.[1]

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[1] For the methods of procedure for such dismantling, see Lyndon, "Storage Battery Engineering," p. 263.

THE EDISON STORAGE BATTERY

In the cells of this battery in the charged condition, the active material on the positive plate consists of hydrated nickelic oxide and peroxide; that of the negative plate is made up of finely divided iron. The electrolyte in new cells consists of about a 21 per cent solution of potassium hydroxide to which have been added 50 g. of lithium hydroxide per liter. During discharge the active material is converted into the nickelous and ferrous hydroxides respectively.

Construction.[1]—For the active material of the positive plate, nickelous hydroxide is prepared and placed in layers in ¼-in. perforated tubes, 4½ in. long. The tubes are made of spirally wound, nickel-plated, steel ribbon. The seam is made spiral to resist expansion. The layers of nickelous hydroxide are about 1/100 in. thick. They are separated by electro-chemically prepared nickel flake. The arrangement is shown in Fig. 96. Each 4½-in. tube contains a total of about 630 layers of nickel flake and nickel hydroxide, pressed closely into contact by a pressure of about 1 ton per square inch. The layers of nickel flake are in metallic contact with the sides of the tube and thus good electrical connection is insured between the active material and the supporting grid in which the tubes are clamped. The tubes are reinforced by eight seamless steel rings.

FIG. 96.—A magnified cross-section of a positive tube of an Edison cell.

For the active material of the negative plate, iron oxide is prepared. This is mixed with a little oxide of mercury (subsequently reduced) to increase the conductivity and capacity, and the mixture is packed into pockets, about 3 in. long by ½ in. wide by ⅛ in. deep, made of perforated, nickel-plated steel. When filled, the pockets are placed in their steel supporting grid and pressed into close electrical contact with it by hydraulic pressure. The dies between which the plates are pressed are

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[1] From Bulletins of the Edison Storage Battery Company.

corrugated; the corrugations are imparted to the walls of the pockets which are thus given greater mechanical strength.

The manner of assembling the plates and the necessary insulating parts, as well as their positions in the container, is shown in Fig. 97. The lid of the container is permanently welded in place, since it is never necessary to renew the parts. The lid is provided with a valve which is designed to allow the escape of the gases produced during charge, but to prevent the entrance of gases from the air. It is necessary to exclude carbon dioxide and oxygen, since the former reacts with the electrolyte, and the latter converts the ferrous hydroxide into the ferric form which cannot be completely reduced again. The valve serves also as a convenient opening for filling.

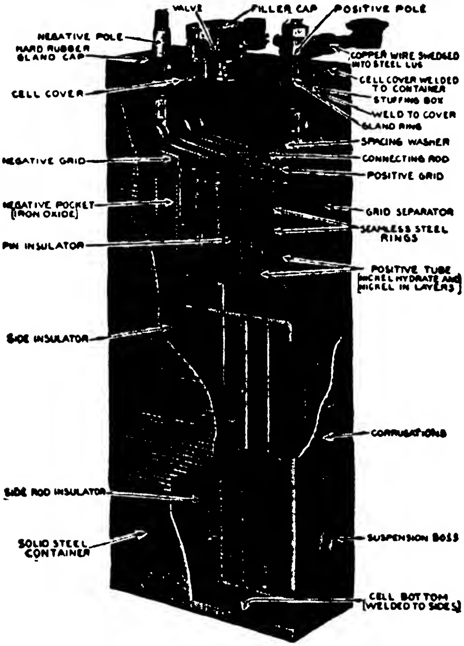

FIG. 97.—Showing parts of the Edison storage cell.

As is obvious from the manner of construction, the Edison cell is of a very rugged type, and well suited for service where an ability to withstand rough handling is essential.

Forming.—The plates are "formed" by repeated cycles of charge and discharge.

Types.—There are two general types of Edison storage cells designed for ordinary service—type A and type B. These differ in respect to the size of the plates. The *type A* positive contains two rows of 15 tubes each; it has a rated ampere-hour capacity of 37.5 hr. The *type B* positive has one row of 15 tubes, and half the capacity of an A plate. The number of *positive* plates in a cell is shown by the numeral following the letter indicating the type. Thus, an A5 cell contains five positive plates and has a rated capacity of 187.5 (5 × 37.5) amp.-hr. A cell marked B4 contains four type B positives, and has a rated capacity of 75 $\left(4 \times \frac{37.5}{2}\right)$ amp.-hr., etc. The number of negative plates in any cell is always one greater than the number of positives.

Both type A and type B cells are made in a "high" form. They are designated by the letter H, as B6H. The high forms are identical with the others in all respects, except that the container is deeper. This permits an excess of electrolyte to be carried so that water need not be added so often.

Reactions during Charge and Discharge.[1]—The active material in the tubes of the positive plate, when it is in the discharged condition, is the green nickelous hydroxide. During charging, this is converted partly to nickelic oxide and partly to nickel peroxide. It has been found that when nickelous hydroxide is oxidized chemically, it is always first changed into nickel peroxide; it is reasonable to assume that the same result is brought about by the oxygen liberated electrolytically at a nickelous hydroxide anode. This assumption, moreover, is borne out by the facts. Thompson says[2] that a freshly charged nickel plate contains more oxygen than is required by the formula Ni_2O_3; the amount of the excess is sufficient to correspond to at least 8 per cent of nickel peroxide. The nickel peroxide formed in this way, then reacts chemically with the nickelous hydroxide to produce hydrated nickelic oxide.

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[1] The explanation given here is based on Allmand's and Thompson's discussion of Foerster's researches. See Allmand, "Principles of Applied Electrochemistry," p. 239; and Thompson, "Applied Electrochemistry," p. 178.

[2] P. 178.

It has been shown[1] that the colloidal hydroxides of nickel and iron are not definite compounds, but rather oxides containing more or less occluded water; therefore, in writing the equations for the reactions in this cell, these substances are not always shown as definite hydrates, or as containing integral molecules of water. The following equations show the reactions that take place *during charge.*

At the positive electrode:

$$NiO \cdot H_2O + 2OH^- \rightarrow NiO_2 + 2H_2O + 2\ominus \qquad (1)$$

By a secondary, non-electrochemical reaction, this peroxide is changed as follows:

$$NiO_2 + NiO \cdot H_2O \rightarrow Ni_2O_3 \text{ hydrated} \qquad (2)$$

Reaction (2) takes place only during the first part of the charge, when much nickelous hydroxide is present. Toward the latter part of the charge, when the nickelous hydroxide has been largely used up, the peroxide, being unstable, decomposes spontaneously, thus:

$$4NiO_2 \rightarrow 2Ni_2O_3 + O_2 \qquad (3)$$

Because the peroxide is dissolved in the nickelic oxide, Reaction (3) does not proceed as rapidly as it otherwise would, but it runs to completion on standing. During the same period of the charge when Reaction (3) takes place, some oxygen is liberated directly from the electrolyte, thus:

$$4OH^- \rightarrow 2H_2O + O_2 + 4\ominus \qquad (4)$$

Reaction (4) is due to the same condition that brought about Reaction (3), *i.e.*, the gradual using up of hydrated nickelous oxide, which when it was present in sufficient quantity united with all the discharged oxygen. By Reaction (4), current is used up to no purpose; thereby, the efficiency of the cell is decreased.

At the negative electrode:

In the pockets of the negative plate when the cell is in the discharged state, the active material is ferrous hydroxide. This is reduced to metallic iron as is shown by the following equation, which represents the reactions *during charge:*

$$FeO \cdot H_2O + 2H^+ + 2\ominus \rightarrow Fe + 2H_2O$$

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[1] ALLMAND, *loc. cit.*, pp. 239 and 240.

Water is thrown off at the negative plate, as well as at the positive [Eq.(1)], so that the electrolyte becomes more dilute on charging. During discharge the process is reversed and the electrolyte becomes more concentrated. The reduction of the iron oxide does not proceed readily. Hydrogen is given off in the gaseous state from almost the beginning of the charge; the amount gradually increases as the charge proceeds. In this way considerable current value is lost, even much more than at the positive electrode. It is perhaps needless to remark that since hydrogen and oxygen are escaping simultaneously during charging, lighted matches or similar sources of ignition must be kept away from the cells.

On *discharging*, the reactions are the reverse of charging and may be represented by the following equations:

At the positive plate:

$$Ni_2O_3 \cdot 1.2H_2O + 1.8H_2O + 2\ominus \rightarrow 2Ni(OH)_2 + 2OH^- \quad (1)$$

But if the discharge takes place soon after charging, the nickel peroxide present is first reduced, thus:

$$2NiO_2 + H_2O + 2\ominus \rightarrow Ni_2O_3 + 2OH^- \quad (2)$$

At the negative plate:

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2\ominus$$

Charging.—The following curves and data relating to charge and discharge are taken from bulletins issued by the Edison Storage Battery Company.

The length of the charge is determined by the extent of the previous discharge. If totally discharged, the cells are charged for 7 hr. at the normal rates shown in Fig. 98; if only half discharged, for only half of 7 hr., etc. If the extent of the previous discharge is unknown, they are charged until the voltmeter shows a constant reading for 30 min. of about 1.8 volts per cell with normal current flowing. In charging it is essential that the rate of charge be not less than the specified normal rate, or, if a tapering charge is given, that the *average* rate be not less than normal. The capacity of any cell is determined by the number of plates and can be calculated as shown on page 654. The temperature during charge should not be allowed to exceed 46°C.

Discharging.—The normal discharge rates for the various cells are the same as the charging rates, which are shown in Fig. 98. The discharge voltage for any type of Edison cell is about 1.2.

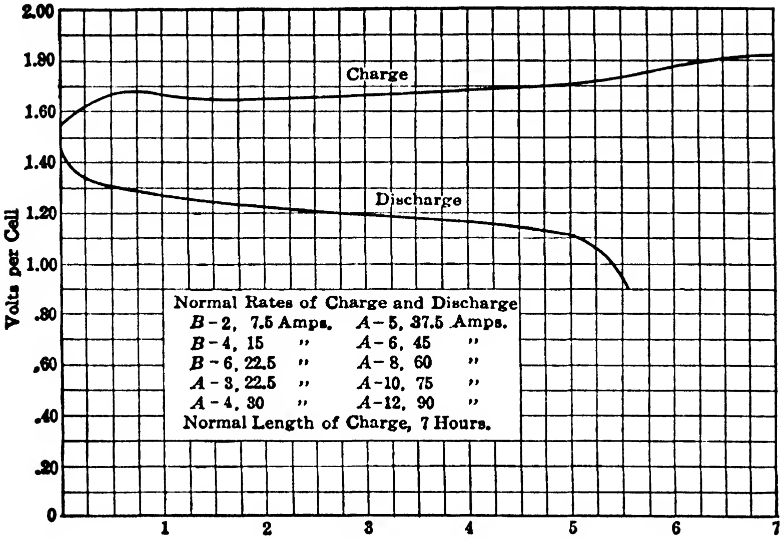

FIG. 98.—Curves showing a discharge at the 5-hr. rate and a normal 7-hr. charge A and B type Edison cells.[1]

The discharge may be considered complete when the voltage has fallen to about 0.9.

Self-discharge.—On standing, the Edison cell undergoes a certain amount of self-discharge; it is more pronounced during the first 24 hr., when it may amount to as much as 10 per cent. This is due to the evolution of oxygen by the decomposing nickel peroxide, thus:

$$4NiO_2 \rightarrow 2Ni_2O_3 + O_2$$

After the peroxide has decomposed, the self-discharge proceeds much more slowly, so that it reaches 15 per cent only after several weeks.[2]

A noteworthy feature of the Edison cell is that it may stand idle indefinitely, either charged or discharged, without injury.

[1] From Bulletin of the Edison Storage Battery Company.

[2] ALLMAND, *loc. cit.*, p. 238.

This is a marked contrast to the lead accumulator, which must never be allowed to stand discharged.

Addition of Water.—During each charging of the cell, water is lost through electrolytic decomposition, as was explained in discussing the reactions that take place during charge. Since the total amount of the electrolyte is not large in proportion to the size of the cell, this loss must be replaced by the addition of distilled water. Enough water only must be added to bring the electrolyte to its normal level as shown in Fig. 99. In the bulletins of instruction issued by the Edison Storage Battery Company, the proper heights of the solution above the plate tops are indicated as follows:

Type A3, A4, A5, A6, A8, A10, and A12........	½ in. above plate tops.
Type A3H, A4H, A5H, A6H, A8H, A10H, and A12H....................................	3 in. above plate tops.
Type B2, B4, and B6..........................	½ in. above plate tops.
Type B1H, B2H, B4H, and B6H...............	2¼ in. above plate tops.

The height of the solution may be determined by inserting a glass tube at least ¼ in. outside diameter (it must be sufficiently large to prevent a false indication due to capillary attraction) and with straight-cut end, until it rests upon the plate tops. Then the upper end is closed tightly with the finger and the tube is withdrawn. The height of the liquid in the tube indicates the height of the electrolyte above the plate tops. The cells should not be filled above the levels indicated, since the bulk of the electrolyte increases during charging, due both to the liberation of water at the plates as shown by the equations, and to the expansion caused by the rise in temperature. If the cell is too full, the electrolyte will flow out.

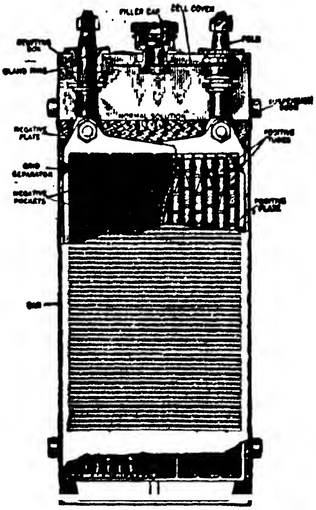

FIG. 99.—Showing normal level of electrolyte in Edison cell.

Renewing Electrolyte.—It is necessary to renew the electrolyte periodically; the frequency of renewal depends upon the extent to which the battery has been used. During use, the density of the electrolyte is reduced gradually by the slight amounts of potassium hydroxide thrown out by the escaping gases during charge. The time between renewals varies from 1 to 3 years or even longer; it is determined by the specific gravity. If the gravity falls below 1.160 with the battery fully charged and the surface of the electrolyte at the proper height, it is an indication that the solution should be renewed.[1] The cell should be completely discharged before removing the electrolyte, and it must not be allowed to stand empty, but must be filled at once with the fresh solution. If the moist negative electrode is allowed to stand in contact with the air, the iron is oxidized to the ferric state and this cannot readily be completely reduced. The renewal solution consists of about a 25 per cent solution of potassium hydroxide to which has been added 15 g. of lithium hydroxide per liter. The renewal electrolyte differs from that carried by a new cell; the electrolyte in a new cell is a 21 per cent solution of potassium hydroxide with an addition of 50 g. of lithium hydroxide per liter.[2]

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[1] Recommended by the Edison Storage Battery Company.

[2] TURNOCK, "Active Materials and Electrolyte of the Alkaline Storage Battery," *Met. Chem. Eng.*, September, 1916.

CHAPTER XX

HYDROMETRY

The Principle of a Hydrometer.—When a body floats in a fluid, the weight of the fluid displaced is equal to the total weight of the floating body. Upon this principle hydrometers are constructed. These instruments are usually of glass so designed and made that when floating, the long axis is in the vertical position; the required displacement is secured by a bulbous middle portion beneath which a weight is fixed. The upper portion consists of a slender stem, which in the most common forms is graduated.

General Classes.—Hydrometers are of two general classes:

a. Those of Constant Volume.—In using an instrument of this class, the amount of fluid displaced is the same for each determination, since the hydrometer is weighted until a fixed mark on the stem sinks to the level of the surface of the liquid. From the weight required the specific gravity is determined.

b. Those of Variable Volume.—In using instruments of this class the determination is made by noting to what point on the graduated scale the instrument sinks when placed in the fluid being tested. For liquids, hydrometers of this sort are used almost entirely. There are two kinds in general use in the United States:

1. *The Baumé* (bō-may′) *Hydrometers.*—These instruments are used most in industrial operations and for checking specifications in mercantile transactions.

2. *The Direct-reading Specific-gravity Hydrometer.*—This hydrometer is used for most laboratory work, although it is employed for those purposes mentioned in the preceding paragraph as well.

The Baumé Scale.—There are two Baumé scales, one for liquids lighter and another for liquids heavier than water.

For liquids heavier than water, the scale begins at zero. This zero point was determined by floating the instrument in pure water at 60°F. and marking the stem at the surface of the water for 0°Bé. A solution of common salt (NaCl) containing 15 parts of the pure salt and 85 parts of pure water, was then prepared. The instrument was floated in this solution at 60°F., and marked 15°Bé. at the surface of the liquid. The space between the two marks thus determined was divided into 15 equal parts, and the scale was completed by continuing these divisions along the stem of the hydrometer.

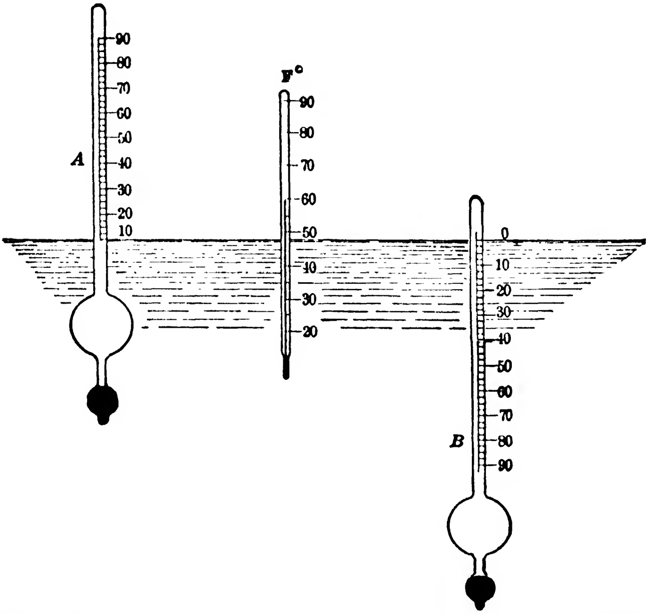

Fig. 100.—Showing (*A*) Baumé hydrometer for light liquids, and (*B*) Baumé hydrometer for heavy liquids in pure water at 60°F.

For liquids lighter than water, the scale begins at 10. It was constructed according to the same arbitrary plan as the preceding. The point of the scale level with the surface of the liquid when the instrument was floated in a 10 per cent solution of common salt (NaCl) at 60°F. was marked zero. The point to which it sank in pure water at 60°F. was marked 10. The intervening space on the stem was then divided into 10 equal parts, and these graduations were extended along the scale.

It will be observed that the numbers from 10 upward appear on both Baumé scales, and when speaking of an unfamiliar liquid it should be stated whether it is lighter or heavier than water.

The Direct-reading Scale.—The scale on the direct-reading specific-gravity hydrometer begins at *one* for liquids both heavier and lighter than water. The instrument reads 1.000 when floated in pure water at 15.5°C. (60°F.). For liquids heavier than water the scale reads one plus a decimal; for liquids lighter than water, a decimal only. The decimals are usually shown to the third place.

Comparison of Hydrometers.—Because the scale divisions are equally spaced, the Baumé hydrometer is very easy to read. When it is desired to determine actual weights per unit volume, however, its readings are cumbersome to apply. The readings, moreover, do not enable one to compare the densities of liquids directly, which can easily be done with the direct-reading, specific-gravity instrument.

On the other hand, since the scale divisions on the direct-reading, specific-gravity hydrometer are not equally spaced, it is more likely to be imperfectly made. Besides, its accuracy cannot be readily checked. The great advantage of the direct-reading instrument lies in the fact that it is so easy to convert the specific-gravity ratios into weight per volume.

The Use of Hydrometers.—The density of a liquid is most conveniently measured when it is contained in a tall, narrow, glass cylinder, known as a hydrometer jar. The best type is that which bears an enlarged top as shown in Fig. 101. This enlargement prevents the upper part of the hydrometer stem from floating near the edge of the jar; if this should happen, capillarity would render an accurate reading impossible.

When making a reading on any hydrometer, the eye must be on a level with the surface of the liquid, as shown in Fig. 101, and the scale must be read where it touches the lower curve of the meniscus. If the eye is not held in the proper position, the readings will be incorrect as shown by the dotted lines.

Since the specific gravity of a liquid changes rapidly with changes of temperature, if accurate determinations are desired, the temperature of the liquid being tested should be brought to exactly the temperature for which the density is being ascertained (generally 60°F.), and the temperature should be uniform throughout. Sometimes, rather than actually to modify the temperature of the liquid, *corrections* in the readings are made for temperature differences. On the Baumé scale the correction generally used is 1°Bé. for every 10°F. In using the instrument for liquids lighter than water in a liquid that is too warm, *i.e.*, too much expanded, the instrument will sink too far and read too much, because the larger numbers are at the top of the scale and signify the lighter liquids. Consequently, the correction must be subtracted in this case. With the instrument for liquids heavier than water, the larger numbers are at the bottom of the scale; hence, in an over-warm liquid the instrument will read too little, and the correction must be added. With liquids that are too cold, the reverse is true in each case. Since the degree of expansion varies with the kind of liquid, and is not the same per degree at all temperatures, no sufficiently accurate, generally

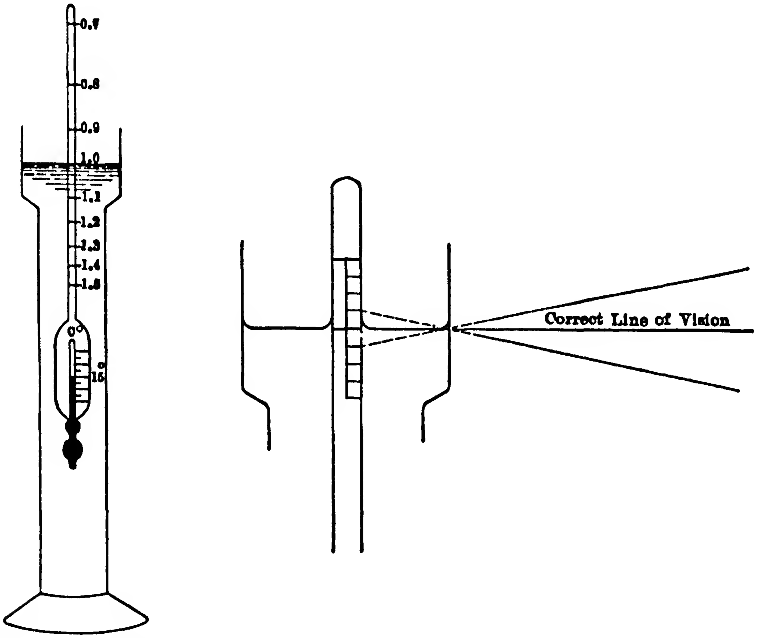

FIG. 101.—Direct-reading hydrometer in pure water at 15.5°C. (60°F.). Enlarged section indicating correct method of reading scale.

applicable correction can be assigned for the direct-reading scale, where small decimal differences are important. Corrections may, however, be worked out for a given liquid within specified ranges of temperature.

The hydrometer should always be allowed to remain in the liquid several minutes before the reading is made—as much as 15 min. in viscous liquids, as in some oils for instance. It should be noted that the accuracy of the hydrometer increases with the thinness of its stem or spindle.

I. Instruments in Liquids Lighter than Water

The Baumé scale begins at 10.

The direct-reading scale begins at 1.

To convert the values of one scale into the corresponding values of the other. The known value is substituted in the following formulas and the expression is solved algebraically.

For liquids lighter than water:

$$\text{Bé.} = \frac{140}{\text{Sp. gr.}} - 130$$

$$\text{Sp. gr.} = \frac{140}{130 + \text{Bé.}^\circ}$$

II. Instruments in Liquids Heavier than Water

The Baumé scale begins at 0.

The direct-reading scale begins at 1.

To convert for liquids heavier than water:

$$\text{Bé.} = 145 - \frac{145}{\text{Sp. gr.}}$$

$$\text{Sp. gr.} = \frac{145}{145 - \text{Bé.}^\circ}$$

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