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A MANUAL FOR THE STUDENT AND MANUFACTURER

SIXTH EDITION—IN TWO VOLUMES

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METALLURGICAL PRODUCTS

The use of metals marks the beginning of civilization. Without a plentiful supply of these materials the whole structure of our society would collapse. Winning the metals from the ores and maintaining them in the free state involves many aspects of the chemical industry.

CHAPTER 23

THE METALLURGY OF IRON AND STEEL

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Iron is the second most plentiful metallic element on the earth's surface. From the magnetism of the earth we may also infer that its interior is probably an iron ball, and that the supply is limitless, provided we can get at it. The most important chemical properties of iron from a practical standpoint are: First, its liability to oxidation in damp air (i.e., rusting); second, the ease with which its oxides (ores) are reduced at all temperatures above 500° F. (260° C.); and third, its very powerful chemical affinity for carbon.

Its most important physical properties are its strength, magnetism, and ability to become hardened and to retain a durable cutting edge after appropriate manufacture and treatment. In these three properties it can be made to excel almost all other substances. Add to them its cheapness, and we can understand the importance of the ferrous metals to industry and to civilization. Another characteristic of iron which is of almost equal importance is its very unusual adaptability. To illustrate this briefly: Iron or one of its alloys can be made either the strongest or one of the weakest of metals; either the most magnetic or one of the non-magnetic metals; one of the hardest or one of the softest; one of the toughest or one of the most brittle; it may have a coefficient of expansion with changes in atmospheric temperature varying from almost zero to a maximum; it may rust easily or it may be non-corrosive; and it may be given a combination of some of these different properties at will, according to the purpose for which it is to be fitted in service. And most of these variations are brought about by changing the amount of foreign elements by less than 5% of the mass, or by giving it a different heat treatment, or by both together.

ECONOMIC TRENDS IN IRON AND STEEL

Quantity Produced—The production of iron from its ores antedates recorded history and the spreading use of iron and steel has been one of the principal factors in the rise of civilization. However, the quantities used in earlier years seem almost insignificant in comparison with the use in recent decades. The real growth in the iron and steel industry began about the middle of the nineteenth century with the development of the Bessemer process of steel making. This was quickly followed by the open hearth process. Increases in size and improvements in the blast furnace came in response to the increased demand for pig iron, brought on by the relatively cheap steel making processes. As a result iron and steel production, in the United States as well as in other industrial countries, began accelerating tremendously about the time of the Civil War. The trend of this increased production is shown in Figure 1.

Because of its impurity and therefore its friability, pig iron cannot be worked or wrought. In America, about one-quarter of it is used in the form of iron castings, and the remainder of it is purified into steel. The data for pig iron production include that which is used in castings and that which goes into steel production. Total steel production is appreciably higher than that for pig iron, because a large amount of scrap steel is always returning to the producing plants.

Prices—The trends in the price of iron ore, pig iron and steel are shown in Figure 2. It will be noticed that with the exception of the World War years the price of pig iron remained approximately constant. However, during the same period the purchasing power of the dollar decreased considerably so, in

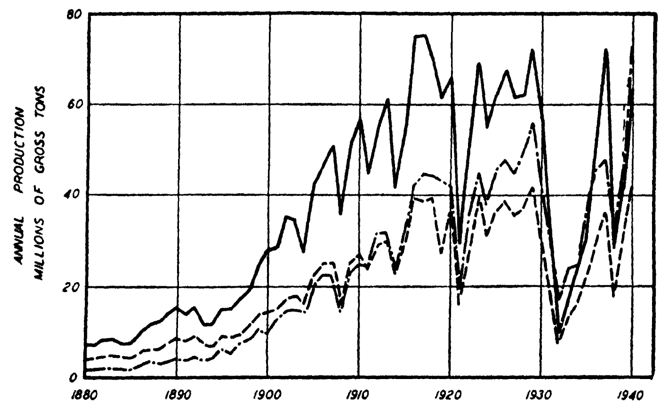

Fig. 1. Trends in the Production of Iron Ore, Pig Iron, and Steel in the U. S., 1880-1940.

terms of equivalent commodities, the cost of pig iron really decreased materially. This is in keeping with the general trend of the chemical and related industries, that improved methods bring lowered costs and greatly increased production. (See Chapter 1, "The Economic Pattern.")

The cost of steel, on the other hand, shows an apparent significant rise in the past 50 years (Figure 2). Two factors have contributed to this. (1) The quality of the average steel produced has been markedly improved and (2) the finished steel has gone more and more into the more expensive forms—thin plate, for instance. A given quality and form of steel is actually considerably less expensive, in terms of other commodities, than it was a few decades ago.

The difference between the height of the curves of Figure 2 is a graphic illustration of the familiar "value added by manufacture."

Recent Production Trends—After having climaxed a steady five year production climb by turning out 36,145,095 gross tons of pig iron and 50,568,701 gross tons of steel in 1937 the iron and steel industry tumbled precipitously in 1938. Although the total world figure shows a drop from the 1937 record level, the bulk of the decline took place in the United States. World output of pig iron and steel fell 20% from 1937; American production fell off 48%, the rest of the world only 4 to 5%. This smaller decline in the other countries was due to the artificial stimulation of wholesale armament production. Foreign producers, stimulated by war conditions, heavy armament activities, and frantic attempts at self-sufficiency, continue operations on a scale only slightly below the 1937 record figures. In fact, new production peaks are being established in Germany, Italy, Japan, and the U.S.S.R. This trend in foreign production will undoubtedly have significant repercussions in the American iron and steel circles.

Distribution of Consumption—The automotive industry has long been the chief consuming outlet for steel in the United States, taking on an average from

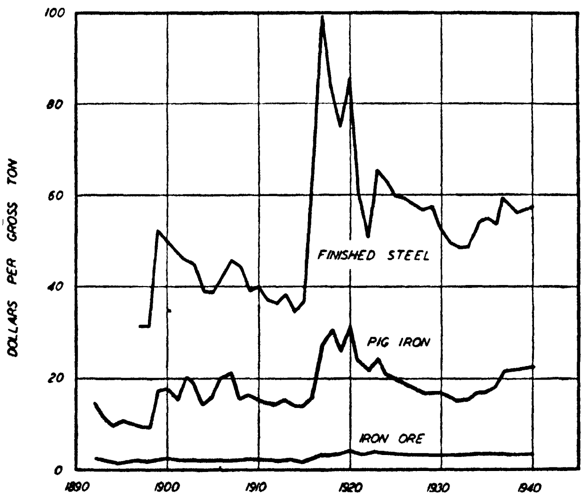

FIG. 2. Trends in Prices of Iron Ore, Pig Iron, and Finished Steel, 1890-1938. (Minerals Yearbook U. S. Bureau of Mines, Washington, D. C., and Iron Age, January, 1941)

The prices of iron ore and pig iron are the averages f.o.b. mines and furnaces, respectively, as reported to the Bureau of Mines; the price of finished steel is an average composite computed by American Metal Market.

Note: Top Curve = Finished steel
Middle Curve = Pig iron
Bottom Curve = Iron ore

⅕ to ⅙ the annual output. The amount of steel moving into agriculture depends mainly on crop production, and in good years this quantity is quite large. Steel consumption for containers represents an increasing and significant outlet. Industrial building is another activity which uses considerable steel. Buying by railroads has been in a decline, which is partially due to new light-weight rolling equipment designed for higher speeds. This trend which is more evident in the passenger branch, also applies to freight-moving equipment. With so many variables at play it is to be expected that the iron and steel industry may have frequent and occasionally severe fluctuations. However, viewing the situation broadly it is reasonable to expect that American industrial production will continue to increase in the long run and that iron and steel will follow the trend.

Consumption of Coke by the Iron and Steel Industry—Since coke is a necessary raw material for the blast furnace in the iron and steel industries, it is to be expected that there is a close connection between these industries and coke plants. This connection is for the most part quite apparent as regards plant location. Coke plants are generally located near iron and steel plants. However, where cheap and efficient transportation is available the hauling distance for coke supply sometimes approaches 500 and even 700 miles. It is of interest to note that European practice considers 200 miles a maximum transportation radius from coke plant to blast furnace.

The close relationship between coke production and the iron and steel industry is quite evident from considerations of the financial affiliations of coke plants. The number of these plants which have direct financial affiliation with or direct ownership by an ironworks, or an assured coke outlet through long term contracts has always been over 50% of the total coke plants in operation. Designating these plants as "furnace" plants, the latest available figures (1938) show that of 83 coke plants 43 were furnace plants. Furthermore, the furnace plants produced 65% of a total 1938 production of 31,795,892 net tons.

ORES

The ore of iron most usually smelted is hematite, Fe_2O_3, which is sometimes relatively pure, as originally in the Lake Superior region, and is sometimes combined with water of crystallization, when it is known as limonite. Magnetite, Fe_3O_4, is the next commonest and exists in abundance in many parts of the earth's crust. In some localities, siderite, the carbonate, is important but is often low in grade. The United States is blessed with many and large deposits of iron ore and has the largest iron-smelting industry in the world. Pyrite, FeS_2, occurs in America and many other parts of the world, but must be freed from its sulfur before smelting and is not often treated.

Iron Ore Reserves—Estimates of ore reserves for Minnesota, furnished by the Minnesota Tax Commission, and for Michigan, furnished by the Michigan Board of Tax Commissioners, appear in Table 1 and cover developed and prospective ore in the ground and ore in stock piles. These reserves constitute the bulk of the U. S. iron ore reserve with the exception of reserves in Wisconsin which have recently been estimated at 5,500,000 tons.

Over 1 billion gross tons of iron ore (which is reserved on the Mesabi range in Minnesota) has served to stabilize the total reserve at a figure approximating 1,400,000,000 gross tons.

TABLE 1—IRON ORE RESERVES (1935-1938)

Gross Tons

	1935	*1936*	*1937*	*1938*
Minnesota	1,237,833,228	1,257,108,283	1,248,974,440	1,225,773,389
Michigan	162,213,481	158,424,248	154,032,944	148,607,346
	1,400,046,709	1,415,532,531	1,403,007,384	1,374,380,735

The data on ore reserves are always somewhat deceptive because they imply a certain quality of ore and there may be tremendously greater quantities of lower grade material available. At the present time acceptable ore in the United States must contain approximately 50% of iron. The data of Table 1 refer to ore of this grade. But it has been estimated [1] that in this same Lake Superior Region there are 276 billion tons of ore containing 36% or more of iron, enough to last for thousands of years. Thus, it is evident that the size of our ore reserves depends very largely on the techniques available for handling the lower grade resources.

THE BLAST FURNACE

The Operation of the Blast Furnace—Over 95% of all the iron ore treated goes into the blast furnace, where it is smelted with coke and preheated

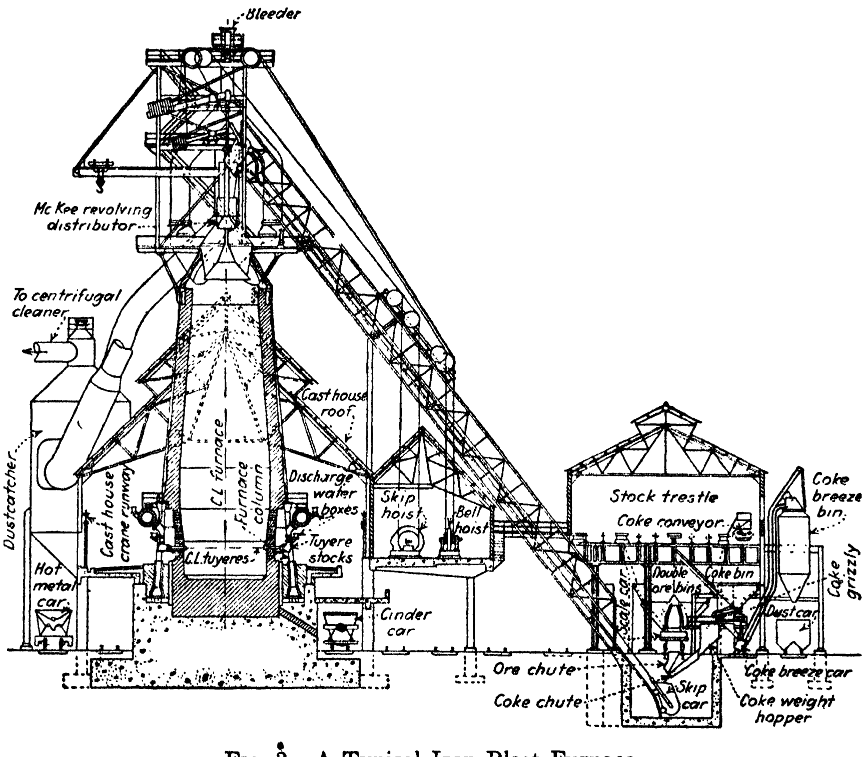

FIG. 3. A Typical Iron Blast Furnace.

air, and a relatively impure grade of metal, known as pig iron, is produced. Rarely, charcoal fuel and cold air are employed. The modern American blast furnace conforms in a general way to the lines of Figures 3 and 4. A column of coke fills the body of the furnace from the bottom of the hearth to the top of the bosh (see Figure 5), and above this alternate layers of coke and iron ore, together with an appropriate fluxing material, generally limestone.

The preheated air, at a temperature of usually 1300 to 1400° F. (705° C.)

[1] The Iron Ore Resources of the World, Eleventh International Geological Con-, Stockholm, 1910, Vol. 2, p. 777.

and at a pressure of about 15 to 30 lbs. per square inch, enters through the tuyere pipes at the top of the hearth, combines with the fuel and creates a volume of intensely hot reducing gases, which pass up through the interstices of the charge, melting, heating, and reducing the ore which it meets, and finally passing out at the throat of the furnace. The temperatures at different points in the furnace and the various reactions which take place are shown in a general way in Figure 7. Below the top of the bosh, the fuel is the only material not in liquid form. The iron, containing about 3.50 to 4.50% of carbon and varying amounts of silicon, sulfur and other elements, according to the reactions of the smelting zone, collects in the bottom of the hearth, and on top of it the cinder (liquid slag), consisting of the impurities in the ore together with the ash of the coke and the lime, magnesia, and impurities of the flux. All sulfur which is brought to the condition of CaS goes into the cinder, and all that in the form of FeS goes into the iron. With this exception the cinder contains all the oxidized materials and the metal all those in reduced condition.

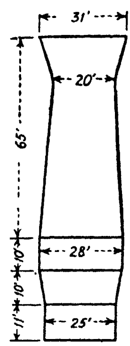

FIG. 4. Approximate Dimensions of an Iron Blast Furnace.

The cinder, because of its low specific gravity, floats on top of the metal and is drawn off about 15 times in twenty-four hours and disposed of. The metal is tapped out of the bottom of the furnace about every six hours and is either cast in the form of pigs or transported to a nearby steel mill in the liquid form.

The gas received at the throat contains about 22 to 27% of CO and has a calorific power of 85 to 105 B.T.U. per cubic foot. About one-third of it is used for combustion in the four hot blast stoves (brick regenerators) which preheat the air used for smelting, and the remaining two-thirds is consumed under boilers or in gas engines, for the generation of power. The most modern furnaces have only three stoves. The reason for this is that exhaust gas is now freed more completely than formerly of dust particles; therefore, it does not "glaze" the checker-work of the stoves so much when it is burned therein and they do not require so frequent cleaning. The stoves are used alternately for storing heat from the exhaust gases, and then giving it out again to preheat the blast which is driven into the furnace.

The proportions of a modern furnace are shown in Figure 3, in which the hearth diameter is extended as far as seems possible in view of the necessity of the blast penetrating uniformly throughout the column of coke at the tuyeres and minimizing the so-called cone of CO_2 which exists at the center of every blast furnace hearth with its base at about the level of the tuyeres and its point a few feet above it. The dimensions at the widest part of the furnace are limited by the dimensions of the hearth, and the height of the furnace is limited by the circumstance that there must be a slight narrowing as the shaft extends upwards in order to compensate for the swelling of the charge due to the chemical reactions. A 20-foot diameter is necessary at the top, in order that the raw materials may be distributed evenly when charged.

Individual blast furnace production now runs as high as 1200 or more tons of molten pig iron per twenty-four hours and is achieved by having large hearths of the furnace in which there can be rapid combustion of the coke by the hot blast, whose temperature is commonly 1400° F. and whose volume is as great as the volume of the hearth will permit, namely 70,000 to 75,000 cu. ft. per min. Obviously this large tonnage contributes to reduced overhead and reduced labor costs.

CHEMISTRY OF THE BLAST FURNACE

Prior to the date of recorded history primitive man discovered, perhaps partly by chance, that when certain brown stones, which were doubtless oxides of iron,

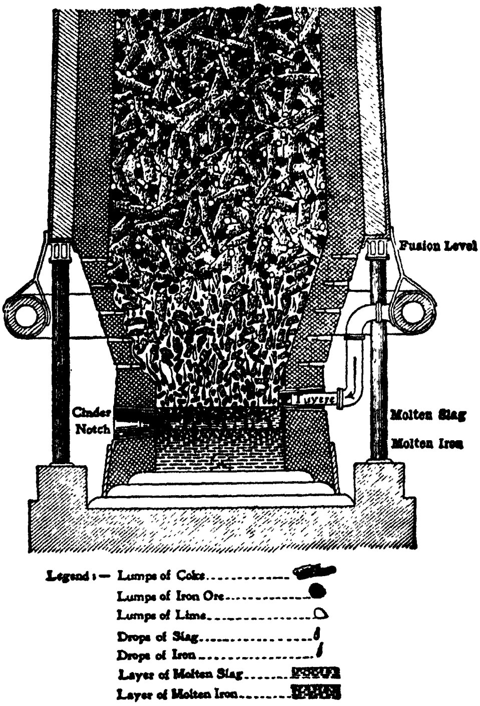

FIG. 5. Distribution of Materials in Lower Part of Blast Furnace.

It has been demonstrated that the column of coke rests upon the very bottom of the furnace, but it would confuse the illustration of the layer of molten iron if this were indicated.

were heated in a charcoal fire, there was produced a pasty malleable substance which could be used for spear heads, arrow tips, or could be pounded together at a high heat and welded into larger masses for various structures or implements that might be of service to him. The chemical reaction of this ancient operation is still used today in the upper half of the modern blast furnace. This basic chemical reaction is the reduction of iron oxide by CO gas and the formation of relatively pure iron.

The reduction of iron oxide is quite complicated, as it proceeds in three steps, each of which requires different concentrations of CO. For instance at 400° C., ferric oxide, Fe_2O_3, is reduced to the magnetic oxide, Fe_3O_4, if only a trace of CO is present in a mixed gas composed of CO and CO_2. The next step is the reduction of the magnetic oxide to ferrous oxide, FeO. This requires that about 38% of the carbonaceous gas shall be CO. The last step is the reduction of FeO to metallic iron, Fe. This requires that about 60% of the carbonaceous gases shall be CO.[2] The reduction equilibria become even more involved when carbon is introduced in the metal in the form of iron carbide.

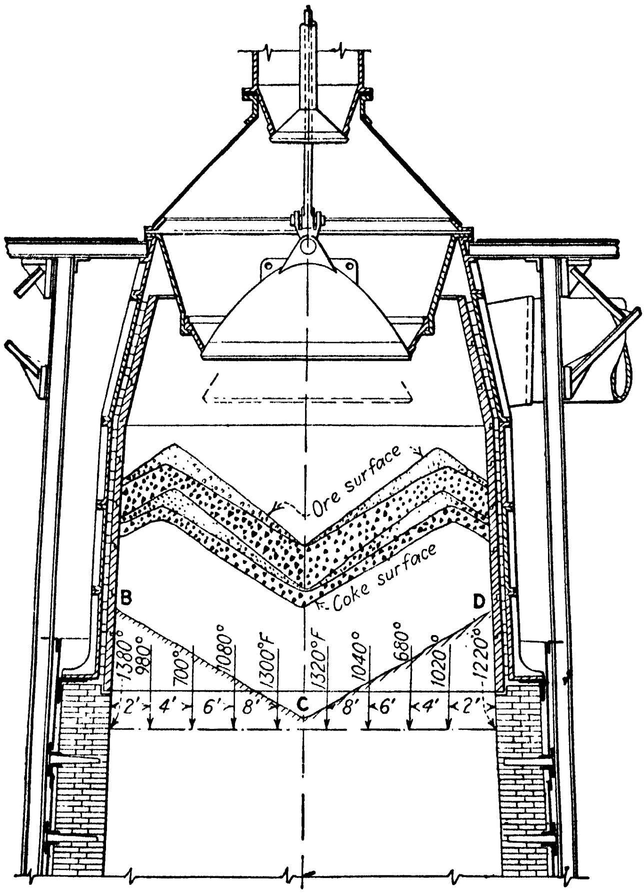

FIG. 6. Distribution of Materials at the Top of a Blast Furnace.

In blast furnace operation, no attempt is made to control conditions for the individual steps of reduction for the reaction

$$CO_2 + C = 2CO$$

which occurs immediately after coke is burned in front of the tuyeres, gives ample CO to cause the final reduction to metal to proceed rapidly. However, adjustment of the temperature in the hearth of the furnace is very important as it indirectly controls the completeness of reduction and the elimination of im-

[2] Matsubara, A., Trans. Am. Inst. Min. & Met. Eng. *68*, 3 (1922).

purities (particularly sulfur) from the pig iron. Temperature of the hearth is controlled by the temperature of the preheated air, and the "burden" (ratio of ore to coke) of the charge fed into the top of the furnace. It is also largely dependent on the "free running temperature of the slag," because a viscous slag will demand a higher hearth temperature than will a fluid slag.

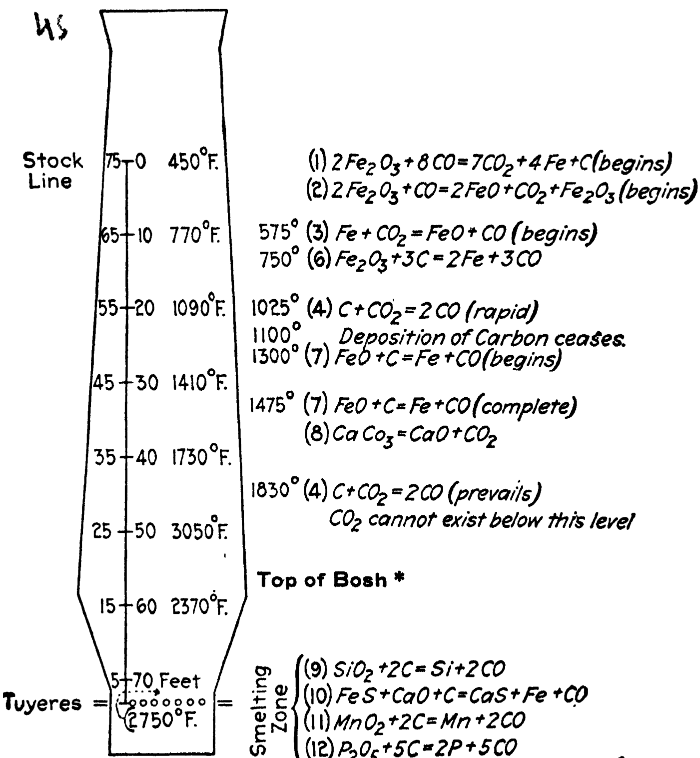

FIG. 7. Reactions in the Iron Blast Furnace. HF

* In normal operation fuel is the only material which descends below the top of the bosh without melting. It is also a criterion of good practice that no unoxidized ore, or oxide in any form in the iron, shall pass below this point.

The purity of the pig iron produced depends upon the contaminating elements, such as phosphorus, sulfur and manganese, which may be present in the iron ore and coke, and also the temperature of the operation, which reduces impurities in accordance with the well-known table of chemical strengths in relation to the affinity of CO for oxygen at the temperature in question. The iron oxide is reduced in the upper half of the furnace and then the materials are subjected to higher and higher temperatures until the iron is melted and saturates itself with carbon and with other reduced impurities which it encounters as it trickles down and collects in the bottom of the furnace. The silica, the clay, and the ash of the coke unite with the flux, usually limestone, added for that purpose and form a liquid slag mass which floats on top of the iron. The impurities in the pig iron depend chiefly upon the temperature of the furnace and, therefore, upon the extent to which the hearth reactions take place.

With the exception of the production of pig iron in liquid form instead of the old, comparatively pure, wrought iron in pasty form, the basic principles of the product of the smelting operation are the same today as they were a few thousand years ago. Recent developments have been in the direction of producing greater tonnage, greater uniformity in composition and quality, and greater efficiency in the use of fuel per ton produced, etc. Figure 8 represents in a graphical way the chemical reactions taking place in the furnace and, al-

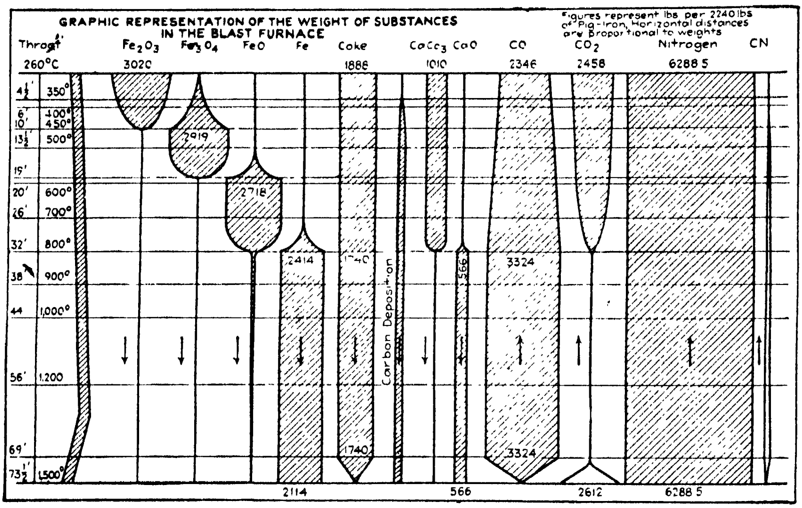

Fig. 8. The Flow of Material Through the Blast Furnace.

though this is an old fashioned furnace, which was common in earlier days, the same principles apply to a furnace of modern dimensions.

Blast Furnace Efficiency—Uniformity in chemical reactions, and therefore in production, is achieved by the minimum variation in the composition of the raw materials and in the charging of them. This latter is dependent upon the size of the raw materials and the height of the stock line, as will be evident from study of Figure 6. It is obvious that uniformity in temperature is an important consideration and that regularity of charging, good distribution of the various raw materials when charged, and approximate uniformity in the volume of gases formed in the hearth of the furnace and their contact with all raw materials in the stack are important considerations. Much attention has been given to these factors and it is unfortunate that limitations of space here forbid our discussing them as extensively as their importance warrants.

The proportion of raw material used in a modern American furnace to one ton of iron produced is roughly 2 tons of iron ore, slightly less than 1 ton of coke, approximately half a ton of flux (limestone), and 4 to 4½ tons of air. The necessity for the uniformity of air requires no comment and when we consider that from 2½ to 15 gallons of water vapor are blown into a modern furnace per minute, depending upon the humidity of the atmosphere, it will be obvious that the constant moisture content in the supply of air to the blowing engines is one of the most important considerations. The water vapor dissociates in the hearth, robbing the furnace of temperature at this point where it is most needed and returning it to the cycle in the upper part of the stack, where, however, it does not contribute materially to uniformity in operation. Several attempts have been made to dry the blast to an approximately uniform minimum by cooling and, tentatively, by chemical and adsorption methods, but the results to date have not justified the cost. In late 1941 this was changed by "air conditioning" the blast in several furnaces.

The efficiency of the iron blast furnace depends largely upon the tonnage produced, the uniformity of operation, and the heat radiated. Probably the

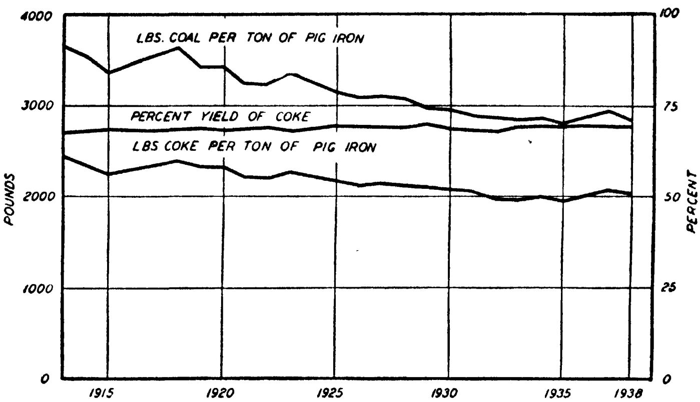

FIG. 9. Trends in the Consumption of Coking Coal, Yield of Coke from Coal, and Consumption of Coke in Blast Furnaces, 1913-1938. (Minerals Yearbook, U. S. Bureau of Mines, Washington, D. C., 1938-9)

Note: Upper Curve = Pounds of coal per gross ton of pig.
Middle Curve = Per cent yield of coke per ton of coal.
Lower Curve = Pounds of coke per ton of pig.

most important factor under the control of the blast furnace operator is contact with every particle of the descending solid materials by a proportionate part of the ascending gaseous materials. In this connection it should be noted that the solid materials require about 17 hours to descend from the charging apparatus to the hearth, while the ascending gases are believed to require approximately 20 seconds to ascend from the tuyeres to the throat.

The efficiency of American blast furnaces has been steadily improved, both because of increased size and because of close attention to the control of the operating variables. This trend toward greater efficiency is shown in Figure 9, which gives data on the average coke consumption per long ton of pig iron, over a period of 25 years.

THE MAKING OF STEEL

The pig iron produced by the blast furnace contains 3½ to 4% of carbon and smaller though varying percentages of such elements as silicon, sulfur and phosphorus. This material is too brittle and possesses insufficient strength and ductility for most of the modern ferrous metal requirements. Hence, most of the pig iron is converted into steel. Steel is usually classed as the material which contains less than 1.7% of carbon and relatively small amounts of other impurities; though the alloy steels may contain relatively large proportions of other metallic elements. If the carbon content is very low and no other metals are present the material is sometimes classed as "wrought iron" or sometimes "dead soft" steel. Wrought iron always contains intermingled slag.

The Older Refining Processes—By rule of thumb, at least, iron smelters have long reckoned with the basic chemical law of fire metallurgy, namely: uncombined elements dissolve in hot metal; oxidized elements leave the metal. For centuries, the soft iron, produced in nearly-pure form by low-temperature reduction of ore (which iron would not harden on heat treatment), was converted into steel (which would harden) by heating it for many hours in contact with carbon. This heating resulted in the solid carbon dissolving in the solid iron. But, obviously, the oxidizing or de-oxidizing of elements could best be accomplished in the liquid state. And so, in England, towards the end of the eighteenth century, Henry Cort initiated the puddling process. The puddling process involves melting pig iron on a hearth lined with iron oxide. The impurities in the pig iron—carbon, silicon, manganese, phosphorus, and some sulfur—react with the iron oxide, are converted to oxides, and leave the iron until the latter, rendered more infusible by increasing purity, "comes to nature," as it is called; that is, it becomes pasty and has to be pulled out of the furnace and worked to free it as much as possible from intermingled slag. In other words, we now obtain by an indirect process the same type of product which the ancients used to produce by direct reduction from the ore. This was always, and is, called "wrought iron."

Even when chemical reductions or oxidations do not occur, liquefaction is now employed. For example, instead of "cementing" solid iron with solid carbon in the ancient way, the crucible process consists of dissolving carbon in iron which has been liquefied in a crucible. This proceeds much more quickly. But this crucible process, in America at least, has been practically superseded by the electric steel process. Furthermore, wrought iron is steadily giving place to "soft" open hearth or Bessemer steel (i.e., these kinds of steel when relatively low in carbon). Therefore, we do not give more space here to a discussion of either of these once-important processes.

Other Processes for Purifying Pig Iron—About the middle of the nineteenth century, Henry Bessemer oxidized the carbon, silicon, and manganese in pig iron by blowing cold air through a liquid bath of the metal. A little later, William Siemens, in association with the Martin brothers of France, developed the Siemens-Martin, or "open hearth," process. This deviates in two chief respects from the old puddling process: The temperature is much higher by virtue of the so-called "regenerative process" (for which see Figure 10), and, therefore, the purified metal does not "come to nature," but is tapped from the furnace in the liquid condition; and, second, the impurities are oxidized by iron oxide charged with the raw materials, or added to the slag, or both, instead of forming the lining of the furnace. Finally, toward the end of last century, the electric steel process was developed. This may be either a mere melting and chemical-adjustment operation, as in the old crucible process, or else it may be a process for the removal of impurities, as the open hearth process. In either case, the source of heat is electric current instead of combustion.

The Removal of Phosphorus—Phosphorus can readily be oxidized out of liquid iron, and is removed in the puddling process, where the richly-basic slag (high in Fe_3O_4) readily dissolves it. But, when a slag runs high in a strongly acid radical such as SiO_2, the latter drives the phosphorus back into the metal, for

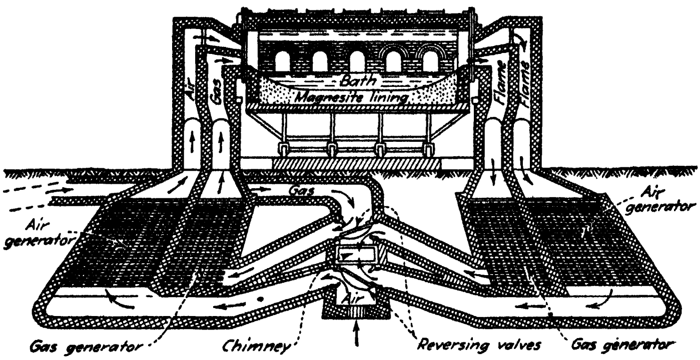

FIG. 10. Schematic View of Regenerative Furnace.

The four regenerators are shown in plan view. They are chambers standing in front of the furnace, which is shown here in vertical section. Each regenerative chamber is filled with a checkerwork of brick, except that there is a space above and below the checkerwork which serves for the distribution of the gaseous materials. Before the furnace is started, the bricks of the regenerators are heated by means of wood fire. Following now the direction of the arrows shown on the drawing, the air and gas enter the appropriate regenerative chamber, are heated by the hot brick, travel to the furnace chamber, unite and burn. Then the products of combustion pass out to the regenerators on the right. Every 15 minutes or so, the direction of gas and air is reversed. The result is that the air and gas enter the furnace in a preheated condition, which promotes combustion efficiency and high temperature, and the products of combustion leave the apparatus at a comparatively low temperature, which promotes fuel economy.

the strongly acidic phosphoric oxide requires a basic radical to be kept out of the metal. Two English chemists, Thomas and Gilchrist, modified the Bessemer process by charging a goodly percentage of lime and thereby producing a highly-basic slag. They found that, by this means, phosphorus, after being oxidized, could be permanently removed from iron. This practice was then applied to the newly-introduced open hearth process, and the "basic open hearth steel process" is now the world's predominant steel producer. It operates with a basic slag and a basic lining, whereas the original Bessemer process uses an acid slag and an acid lining. This is the only type of Bessemer process which has been extensively used in America.

The Removal of Sulfur—Sulfur stands so far below iron in the table of chemical strengths that its removal by oxidation is practically impossible. It is distributed between metal and slag in the form of sulfides; namely, FeS, MnS, CaS, Na_2S, etc. FeS is very soluble in iron, and CaS and Na_2S almost completely insoluble.

A good deal of the sulfur in pig iron is removed in the blast furnace hearth by the following reaction:

$$\underset{\text{Soluble in metal}}{FeS} + CaO + C = Fe + \underset{\text{Soluble in slag}}{CaS} + CO.$$

This reaction takes place as the metal droplets pass through the slag layer and also at the interface between the metal and slag layers. The equilibrium for sulfur removal is favored by an increase in temperature, so maintenance of high temperature in the hearth of a furnace is a very important feature of operation.

Sulfur is also eliminated to a considerable extent in the blast furnace ladle by adding soda ash, Na_2CO_3, to the liquid metal. The sulfur in the metal is then converted to Na_2S which is insoluble in the metal but soluble in the slag.

A like procedure is followed in the electric arc furnace, where CaC_2 is formed at the arc, and then the following reaction occurs:

$$\left.\begin{matrix}3FeS\\3MnS\end{matrix}\right\} + 2CaO + CaC_2 = \left.\begin{matrix}3Fe\\3Mn\end{matrix}\right\} + 3CaS + 2CO.$$

The more fluid the slag and the higher the temperature, the more sulfur dissolves in the slag, especially when in the form of MnS. With the very fluid slag of the puddling furnace, more than 50% of the sulfur can be removed from the iron; perhaps this is aided by a slight oxidation of sulfur by the highly-oxidizing and fluid puddling slag. In the production electric furnace it is inadvisable to push the temperature up to the point where the reaction $FeS + CaO + C = CaS + Fe + CO$ prevails, but a slag rendered very fluid by CaF_2, for example, high in CaO and low in FeO, will desulfurize the iron effectively, and this is common practice in Europe.[3]

Bessemer Steel—The Bessemer process is illustrated in Figures 11 and 12, in which cold air is blown through a bath of liquid pig iron. The oxygen of the air oxidizes the silicon, manganese, and carbon and these oxidized materials separate in the form of a slag, with the exception of the latter, which passes off as gas (chiefly CO). The complete purification of 10 to 25 tons of liquid pig iron requires only seven to ten minutes of blowing. The heat produced by the oxidation of the impurities is sufficient not only to keep the bath in the liquid condition during the operation but also to raise its temperature more than 575° F. (300° C.). The liquid metal, however, dissolves some iron oxide, which has a very harmful effect upon its qualities, but is nearly all removed by the addition of manganese at the end of the "blow." Traces of nitrogen are also absorbed in the "bath."[4] The addition of manganese, with carbon and silicon, is called "recarburizing."

The appearance of the "converter" flame gives an index by which the operation may be followed and controlled. When the oxidation of impurities is completed, the flame shortens, or "drops," and the blowing is discontinued. Then a predetermined amount of manganese is added to remove absorbed oxygen; silicon to remove oxygen and to prevent gas bubbles of "blowholes"; and carbon to give the desired degree of strength or hardness, or both. Advocates of the

[3] See Campbell, D. F., Iron & Steel Institute, 1930, pp. 85-109 (Fig. 4); No. II, Robertson, S. L., "Metal Treatment"; Palmer, F. R., 1936 (Am. I. & S. I.), pp. 4 and 6.

[4] See "The Absorption of Nitrogen by Steel," by R. S. Dean, U. S. Bureau of Mines, 1931.

Bessemer process maintain, perhaps with good reason, that if extensive and considered attention to the manufacture of Bessemer steel had been given to it recently in the same degree as that expended on basic open hearth steel, the former would occupy a much more important relative position than it now does. Attempts in this direction are being made. For example, instead of controlling the operation by the pressure of blast at the different periods, it has been shown that the volume of blast is a better criterion; also the photo-electric cell is being used to indicate and record the intensity of light emanating from the flame, and a process of dephosphorizing the finished steel by churning it up in the ladle with a fluid slag rich in lime and iron oxide, is in operation.

Messrs. Thomas and Gilchrist developed a process of producing a basic slag (rich in CaO) in a Bessemer converter, by which phosphorus was kept out of the metal after once it (the phosphorus) had been oxidized. This "basic" process is important in England and Europe, but is not in use in America.[5] The principle, however, is that employed in the so-called "basic open hearth" process.

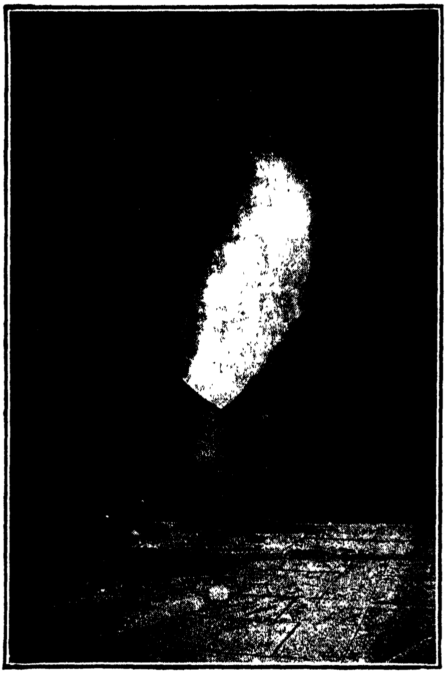

FIG. 11. A Bessemer Converter Blow.

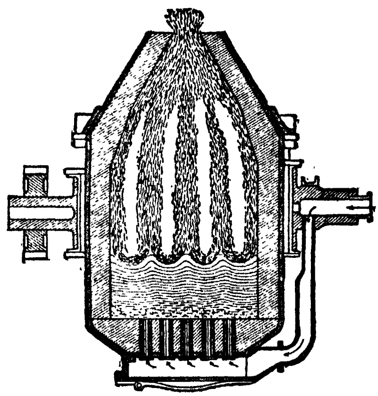

FIG. 12. Cross Section of Bessemer Converter.

Open Hearth Steel—The open hearth process really consists in remelting old steel scrap with varying amounts of pig iron. During and after melting,[5] the impurities are oxidized by the addition of iron oxide, usually in the form of ore or mill scale. It takes from three to four hours to melt and about an equal length of time to complete the purification and adjust the final temperature. Frequently the pig iron is added in liquid form, having been stored in large reservoirs, known as "mixers," between blast furnace production and use in open hearth. Also steel scrap equivalent is sometimes used in liquid form, being pig

[5] See "The Thomas-Gilchrist Basic Process, 1879-1937," by F. W. Harbord, Journal Iron & Steel Institute, *II*, 1937.

iron purified of silicon, manganese, and most, or all, of its carbon in a Bessemer converter, and then brought molten to the open hearth furnace.

Except in England, where a large amount of acid open hearth steel is made for ships, bridges, and other structural purposes, the basic process is predominant. In this process, the slag is rich in lime, and therefore the furnaces are lined with magnesite or dolomite. As a result, phosphorus as well as silicon, manganese, and carbon are removed to as low a point as may be desired. An important, although somewhat uncertain, amount of sulfur is also carried into the slag in the form of calcium sulfide, CaS, or manganese sulfide, MnS.

Manganese and silicon must be added to the metal at the end of the open hearth process, as in the Bessemer process, but even under these conditions basic open hearth steel may contain dissolved oxide, some intermingled oxides (called "inclusions"), and it also may be impregnated with gas bubbles or "blow-holes." For the best grades of structural steel and steel castings, the acid open hearth process therefore maintains its importance, in spite of the higher cost of manufacture which results from the price of low-phosphorus pig iron and steel scrap.

Recent innovations in the manufacture of open hearth steel comprise, (1), an intensive study of the "physical chemistry of steel making," especially equilibrium relations between the proportions of iron oxide dissolved in the slag and in the bath, with consequent speed of oxidation of the impurities and also less oxygen left dissolved in the metal when the heat is tapped; (2), insulation of almost all parts of the furnace and regenerators, with consequent decrease of heat radiation, and also decrease in air infiltration from the outside, with its resulting dislocation of fuel-to-air ratio in combustion, and, finally, slower cooling down, and therefore less spalling, of the furnace refractories when the furnace is shut down; (3), automatic control of several operations formerly adjusted manually, such as: desired ratio of fuel to air even in wide variations in amounts of fuel used; reduction of the fuel being burned when the roof reaches a dangerous temperature; maintenance of a slight pressure in the furnace chamber, so that whatever leakage occurs through the walls, etc., will be from within outwards, instead of from without inwards; reversing of regenerators when the temperature of the regenerator on the outgoing side becomes about 200° F. higher than that of the regenerator on the entering side; (4), continuous recording of the CO_2 content of the furnace gases to check the fuel-combustion efficiency; (5), the use of a "viscometer" and/or "slag pancakes" to guide slag control and thereby improve the physical chemistry of the operation; (6), the use of a "carbometer" or else a "carb-analyzer" for rapid determinations of the carbon content of the bath.

Summary of Iron and Steel Processes—The reason for the existence of the various steel making processes is found in the differences in cost of product, degree of freedom from certain impurities and therefore usefulness in different types of service. For example: Wrought iron is low in carbon and contains particles of intermingled slag; therefore it has a market amongst those who think the slag reduces rusting, though this market is steadily decreasing. Bessemer steel sometimes costs less to produce than does open hearth steel; it seems to excel in machining qualities, but it is thought to be less amenable to manufacturing control, and it is often higher in phosphorus. Basic open

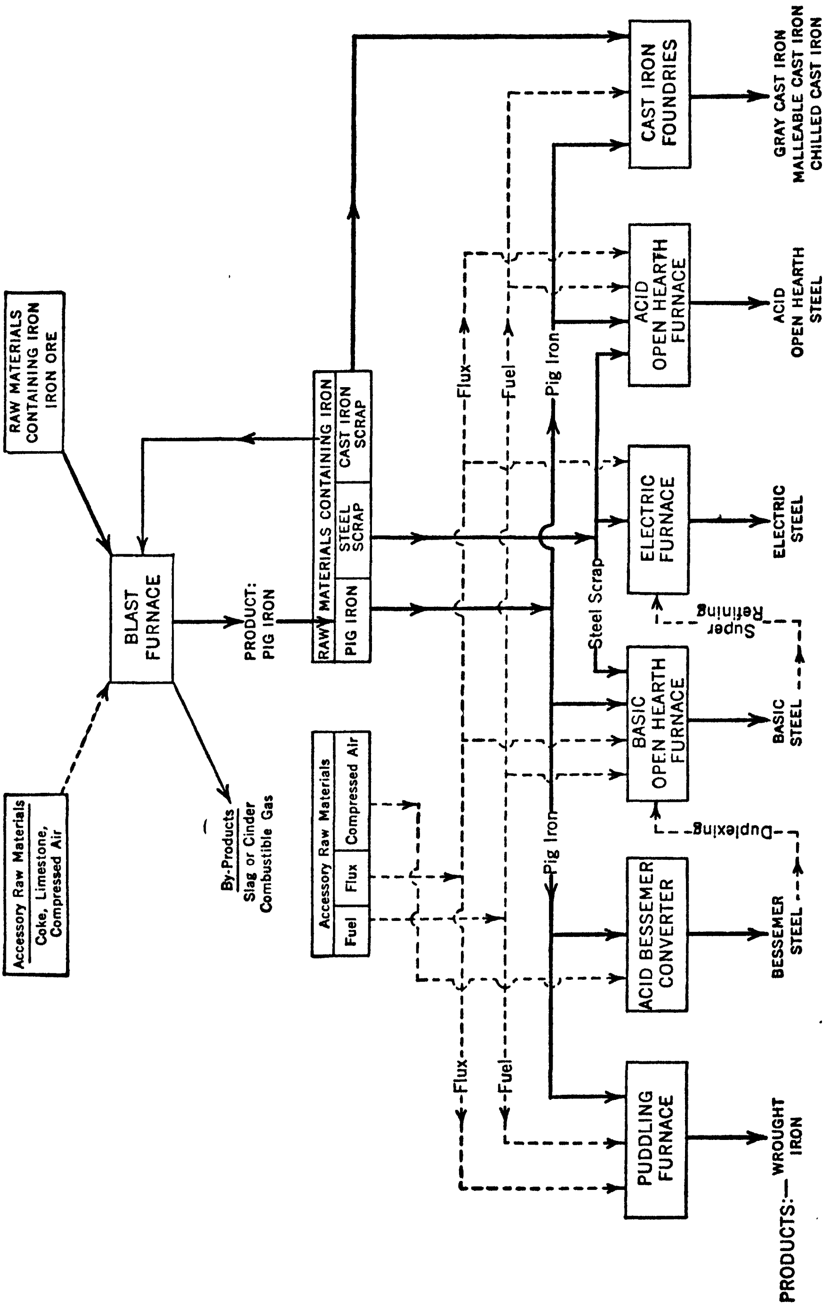

FIG. 13. The Principle Modern Processes in America for Iron and Steel Manufacture.

hearth steel is not high in price, it is tough and reliable, but acid open hearth steel is preferred to it by many, especially for resisting "fatigue" stresses and for relative freedom from "blowholes" (which are especially objectionable in castings) and from "inclusions" and from dissolved oxygen. Where very high quality is demanded, as in cutting tools, special machine or airplane parts, etc., and therefore a higher cost is justified, electric steel is used. This is especially free from dissolved oxygen, "inclusions," and sulfur. The electric furnace can remove dissolved oxygen, occluded oxides (so-called "inclusions") and sulfur from basic open hearth steel. Therefore, a process of "super-refining" the latter is sometimes practiced. Likewise, the basic open hearth furnace can reduce phosphorus and sulfur in acid Bessemer steel, and this is often accomplished. The "blown" metal from the Bessemer converter is used as a liquid steel scrap to form part of the charge of the basic furnace. When this is done, solid steel scrap is not used in the open hearth furnace.

ELECTROMETALLURGY IN THE IRON AND STEEL INDUSTRY

(Most of the material in this section was contributed by W. S. Landis, Vice President of The American Cyanamid Company.)

Electric Smelting of Iron Ores—Electricity may be used as a source of heat in the smelting of either iron or steel, and in localities remote from fuel supply and adjacent to other cheap sources of power experiments of this nature have been made with commercial success. Thus, in Norway, Sweden, Italy, and Japan the electric smelting in furnaces shaped originally somewhat like the ordinary blast furnace has met with success. Electric energy is used to supply the necessary heat and almost any form of carbon, usually charcoal, is used for the reducing agent. By this combination of reducing agent and electric energy the quantity of carbon required in the operation can be reduced to only about one-third of that consumed in the modern fuel-fired blast furnace. That is, the fuel-fired blast furnace consumes about two-thirds of its coke charge for supplying heat and about one-third in effective reduction. Where the heat is supplied by the electric current only the reduction carbon need be added. The pig irons produced in this process are of exceptionally high grade and command a premium over pig iron produced in the coke furnace.

The power requirement of a modern electric pig iron furnace amounts to about 2500 K.W. hours per ton of pig iron produced, when operating on high grade iron ore and charcoal.

Electric Melting or Purifying—Furnaces heated by arc (carbon electrode furnaces) or by the resistance offered by the molten metal to the passage of an eddy current (induction furnaces), are widely used for the production of the highest quality of steel. The two chief characteristics in which this process differs from a process in a combustion furnace are: (1) The very high temperature obtainable, and (2) the possibility of working in a neutral or reducing furnace atmosphere. These enable the operator to produce deoxidizing slags, very high in CaO, low in iron oxides, and containing (in arc furnaces) from 1 to 3% of calcium carbide. This makes it possible to deoxidize and desulfurize steel to a somewhat greater degree than is possible in combustion furnaces.

Electrolytic Iron—The production of pure iron by the electrolysis of a ferrous or ferrous ammonium sulfate solution in a manner similar to that used in the electrolytic refining of copper has been carried out on a limited scale. The product is used for the production of special alloys and steels, but since high-grade iron and steel can be made much more cheaply by electrothermic processes, the electrolytic process offers little possibility of large development. A recent modification of the electrolytic process plates out pure iron objects such as tubes, and cylinders on mandrels. The soft pure iron can be drawn and spun much like copper and brass, and after suitable surface treatment for the protection against rusting, is proving an acceptable substitute for these more costly metals.

Ferro-Alloys—A great expansion in the use of alloy steels has been the cause of a marked increase in the production of the materials known as the "ferro-alloys." In general, the ferro-alloys may be said to be relatively low in iron and relatively high in other metal constituents. They are nearly all prepared in the electric furnace. They are used in the production of alloy steels which contain relatively small amounts of the nonferrous metals.

Ferro-silicon is made by charging a mixture of coke and siliceous iron ore into a simple electric furnace with open top, the iron content depending upon the grade of material to be made. The product is tapped out into sand beds and broken up for market.

Three standard grades of this alloy are produced in the electric furnace, 50% silicon, 75% silicon, 90% silicon. The size of the furnaces used for this work varies considerably, the smaller ones running as low as 2500 K.W. and the larger to 12,000 K.W. In general, these furnaces are much the same as those used in producing calcium carbide (See Chapter 12, "Electrochemical Industries"), but because of the higher conductivity of the charge, a lower voltage is used. In an average furnace the energy consumptions for 50% ferro-silicon are 6000 K.W. hours per ton of product; for 75% alloy 10,000 K.W. hours per ton of product, and for the 90% alloy 14,000 K.W. hours per ton of product.

Ferro-Chrome—Ferro-chrome is today of great importance because it is the basis of the stainless steel production. There are two merchantable grades, the high carbon alloy carrying 60-80% chromium with 6 or 7% carbon, and the low carbon ferro-chrome carrying approximately the same amount of chromium but with a carbon content of less than 0.2%. The high carbon alloy is used for production of tools and the harder alloys.

The high carbon ferro-chrome is made by the reduction of selected types of chrome ore in an open top electric furnace. These ores are generally self-fluxing, but if not, suitable additions are made to produce a highly basic slag.

Because of the very great affinity of chromium for carbon it is very difficult to produce low carbon alloys by direct reduction of chrome ore with carbon. One process produces first a high carbon alloy and then resmelts this in the presence of chromium oxide. A much improved process is to reduce a selected chrome ore in the electric furnace by the use of silicon or high-analysis ferro-silicon. This method produces ferro-chrome of extremely low carbon content.

The power requirements for the high carbon ferro-chrome run about 6000 K.W. hours per ton of alloy. For the low carbon alloys which involve a double smelting operation (in one case silicon production) this power consumption runs as high as 12,000 K.W. hours per ton of product.

Ferro-Manganese—The electric furnace is not needed for the production of manganese iron alloys of less than 40% manganese content. For material containing between 40 and 70% manganese, local conditions govern choice of furnace, and for the high grade alloys running up to 80% the electric furnace is frequently used. Open top furnaces smelt down a mixture of manganese ore, carbon and fluxes to produce the high grade ferro-manganese of commerce. The manganese oxides are relatively volatile as compared with most products treated in the electric furnace and in the production of these alloys there is a very considerable volume of fume discharged from the furnace. It is readily recognized by its reddish-brown color. The power consumption for the production of an 80% manganese alloy (5-6% carbon) is about 2500 K.W. hours per ton of product.

Miscellaneous Alloys—The electric furnace is also called upon to produce ferro-molybdenum, ferro-vanadium and ferro-titanium used in the formulation of the strong steels. Similarly ferro-tungsten is produced for the tool steel manufacture.

A process available for the production of some of these rarer metals and at least indirectly belonging to the electro-metallurgical industry is that developed by Goldschmidt in which oxides of the metals to be reduced are mixed with aluminum powder and the mass raised to reaction temperature by an ignition cartridge. The strong affinity of the aluminum for oxygen results in a very energetic reaction with production of quite high temperature. The contents of the crucible at the close of the reaction are a molten mass of the metal on top of which lays a slag of molten alumina. The aluminum powder is produced by grinding aluminum which in turn is an electrochemical product.

HEAT TREATMENT OF STEELS

Constitution of Iron and Steel—The most recent diagram of equilibrium conditions, or phase changes occurring in the freezing and cooling of alloys of iron and carbon is shown in Figure 14. Above the lines *AC* and *CD* there are liquid solutions of carbon in iron. The line *CD* terminates at about 6.5% carbon and a temperature of about 1800° C. (3272° F.). This limit results from the volatility of iron. The compound Fe_3C would apparently occur at 6.67% of carbon if the metal could be heated to a high enough temperature to take that much carbon into solution.[6]

SLOWLY-COOLED STEEL

From zero up to 1.7% carbon, any alloy which freezes consists of a solid solution of iron with carbon, the percentage of carbon being, obviously, that percentage which was present in the liquid solution. It should be noted that any alloy of iron and carbon containing 1.7% or less of carbon is defined as steel; any alloy with more than 1.7% carbon is defined as pig iron (when this is in the form of castings, or is being melted preparatory to pouring into castings, it is called "cast iron"). With the exception of the small corner near zero carbon

[6] Those unfamiliar with the principles of such diagrams should refer to the material under "Iron-Carbon Equilibrium Diagrams" in Reading List at end of the chapter.

and 1535° C. (2800° F.), all the iron in these solid solutions is in the so-called "gamma" allotropic form—that is, it has a face-centered space lattice and is paramagnetic. Only in the left-upper corner is a small area of solid solution in which the iron is in the body-centered space-lattice form. It also is paramagnetic.

Considering pure iron which is cooling slowly: From the temperature of 1400° C. (2555° F.) to 910° C. (1670° F.) it exists as gamma iron; below

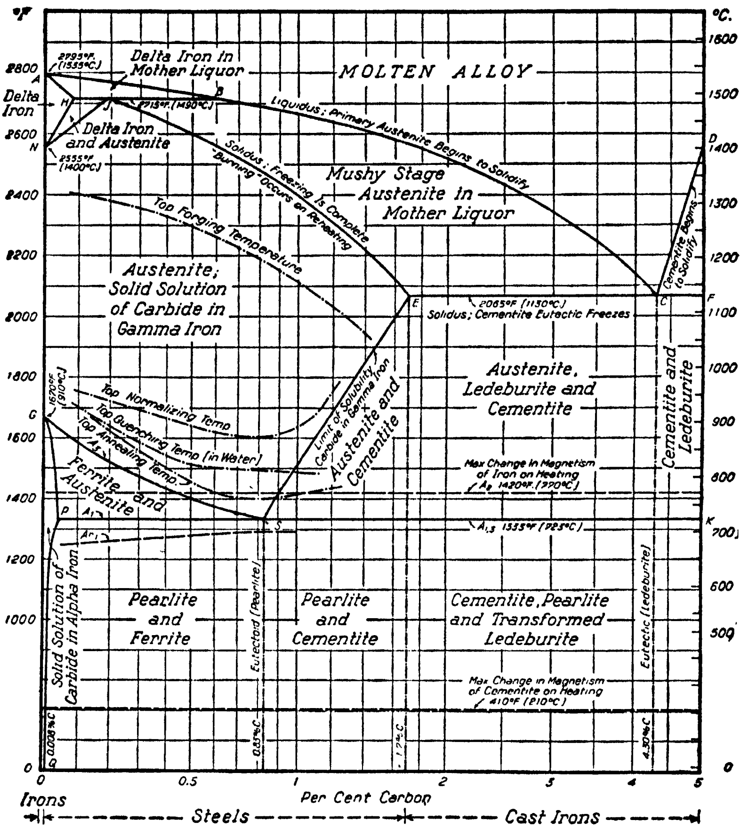

FIG. 14. Equilibrium Diagram of Iron and Carbon. (Courtesy the American Society for Metals)

910° C. it has a body-centered lattice and is called "alpha" iron. Below 760° C. (1400° F.), alpha iron is ferromagnetic. In the gamma form it will dissolve carbon up to 1.7%; in the alpha form it will dissolve only traces of carbon (0.03% at 700° C., and 0.008% at 0° C.).

At the temperature of 723° C. (1333° F.) every steel consists in part of a solid solution containing 0.83% carbon and 99.17% iron. But as the temperature drops slowly, the solid solution decomposes completely, within a few degrees into crystals of Fe and Fe_3C. Assembling these data, the lines *GS, SE,* and *PSK* represent the decomposition of the solid solutions into crystals of Fe and Fe_3C. With less than 0.83% of carbon, alpha iron will begin to separate from a slowly-cooling solid solution at an appropriate temperature between 910° C. and 723° C. (1670 and 1333° F.). With more than 0.83% of carbon, Fe_3C will begin to separate from a cooling solid solution at the indicated temperature on the line *SE*. In either event, when the solid solution cools to 723° C. it will contain 0.83% of dissolved carbon and will have intermingled with its structure whatever crystals of Fe or Fe_3C, as the case may be, which separated from it to bring its composition to 0.83% carbon. Obviously, it can never have *both* Fe and Fe_3C mixed with it at this point. But when it cools slowly across the line

FIG. 15A. Crystals of Ferrite (Fe) in a Matrix Consisting of Relatively Small Crystals of Ferrite and Cementite (Fe_3C). This matrix is known as "pearlite." This steel contains 0.34 per cent carbon. 100×. (Micrograph made by Sadun S. Tör at Lehigh University)

PSK, it decomposes completely into relatively-small crystals of alpha Fe and Fe_3C. (For the sake of accuracy, we must repeat that the Fe contains traces of dissolved carbon, but these traces only alter secondarily the principles prevailing here.) Therefore it is clear that all steels which have been slowly-cooled to atmospheric temperature will be composed of crystals of alpha Fe and Fe_3C, the proportion of each depending on the percentage of carbon present in the steel. These facts are illustrated in Figures 15A, 15B, and 15C. Since Fe is relatively soft and ductile, and Fe_3C is very hard and brittle, the corresponding properties of the steel will depend primarily on the percentages of Fe and Fe_3C crystals contained therein. They will also depend in an important way on the sizes of the Fe and/or Fe_3C crystals.

Rapidly-Cooled Steel—If the steel is cooled rapidly from the area of solid solution to atmospheric temperature, there is no decomposition into crystals of Fe and Fe_3C; neither is there an undecomposed solid solution. So far it has never been possible to cool steel rapidly enough to prevent some decomposition

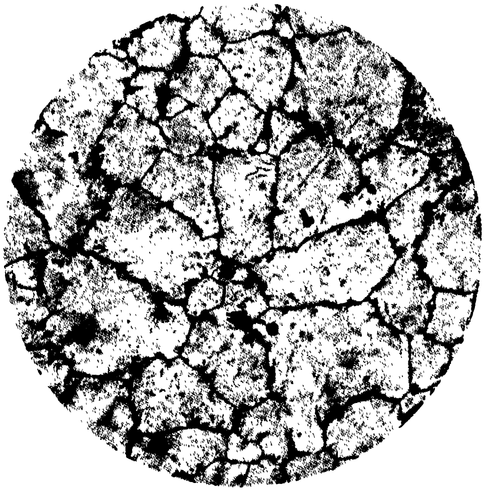

Fig. 15B. Crystals of Cementite (Fe_2C) in a Matrix of Relatively Small Crystals of Ferrite and Cementite. This steel contains 1.5 per cent of carbon. 100×. Etched with sodium picrate. (Courtesy Francis F. Lucas)

Fig. 15C. Pearlite. Being a matrix consisting of crystals of ferrite and cementite. These crystals separate when the solid solution cools slowly across the line PSK in Fig. 14. This steel contains 0.83 per cent of carbon. Original magnification 3500 diameters. Reduced to 1750? diameters in reproduction for publication. (Courtesy Francis F. Lucas) of the solid solution. On the other hand, it must be cooled relatively very slowly to achieve a complete separation into crystals of Fe and Fe_3C. We have all gradations of slow and accelerated cooling from quenching in iced salt solutions, to cold water, hot water, oil, heavy oil, a blast of air, still air, hot ashes, cool-

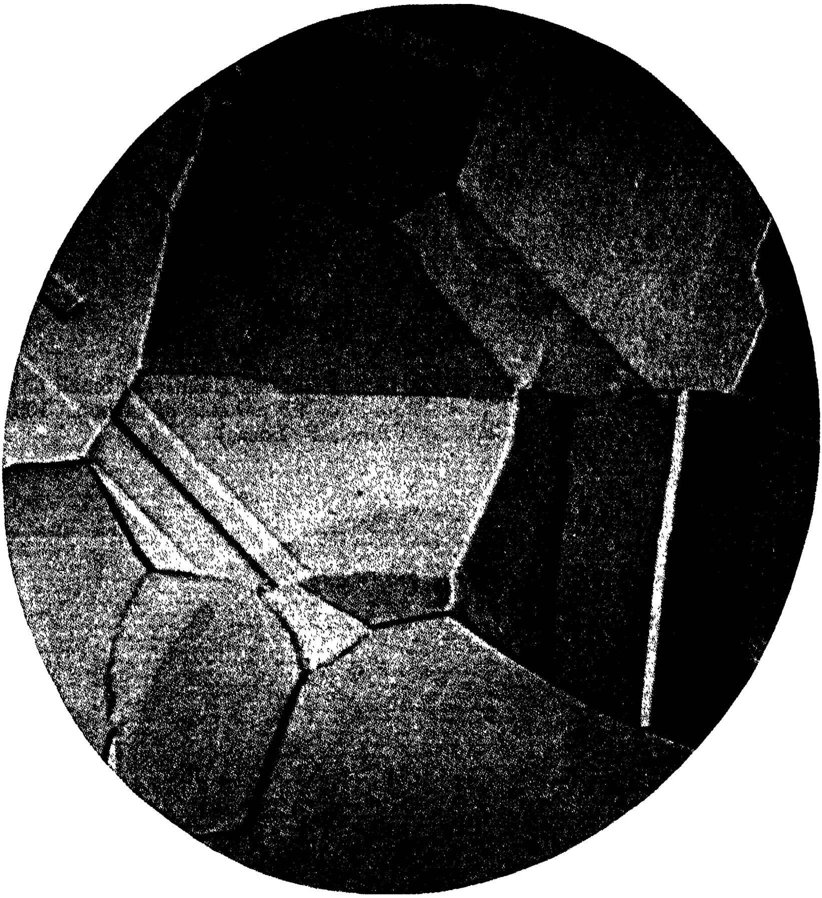

FIG. 15D. Crystals of Austenite = the Solid Solution of Iron and Iron Carbide. This is the structural normal to, and stable in, the area NGSEJ in Fig. 14. 500×. (Courtesy Joseph R. Villela)

ing in the furnace, etc. These and other techniques comprise the operations of "heat-treating of steel."

(4) **Heat-Treating for Hardness**—Assume steel of 0.83% carbon and heat it to 750° C. (1380° F.). Its structure will be, presumably, similar to that shown in Figure 15D. This structure is called "austenite." To cool it slowly from 750° C. will produce a structure similar to that shown in Figure 15C. This structure is called "pearlite." But if we cool it rapidly, it will consist of a hard, unstable structure like that shown in Figure 15E. This is called "martensite." It is thought to be a metastable solid solution of carbon, or carbide, in alpha ferrite,

and many believe that one of the chief causes of its hardness is the presence in it of Fe_3C crystals in a size known as the "critical dispersion size"—that is, the size which gives the maximum wedging action of the slip planes so as to oppose deformation, or ductility. Such crystals, if present, are perhaps the result of

FIG. 15E. Martensite = the Hard Structure Produced When Austenite is Cooled at What is Called "the Critical Cooling Rate." 2000×. (Contrast this with Fig. 15C = the structure which results when austenite is cooled very slowly. The steel in this micrograph and that illustrated in Fig. 15C both contain 0.83 per cent of carbon.) (Courtesy Joseph R. Villela)

incipient precipitation from the solid solution. They may be colloidal. For centuries the procedure of hardening steel by quenching has been practiced without its exact nature being understood. Martensite is very strong, very brittle, has an abnormal tetragonal form of space lattice, and is burdened with many unequalized, internal stresses. If its rigidity be relaxed, as, for example, by "tempering" it to some temperature between 200° and 300° C. (400° to 575° F.), its lattice changes from tetragonal to cubic. It also loses most of the unequalized stresses, decreases in strength and hardness, but materially decreases its brittleness. It then becomes suitable for a cutting tool, provided it has sufficient carbon (0.70 to 1.50%) to give it cutting hardness.

Heat-Treatment for Toughness—Steel to be tough must not contain as much carbon as that which is to be hard. The upper limit for carbon in tough steel is 0.50%. If a steel of 0.45% carbon is heated until it becomes wholly a solid solution—say to 800° C. (1472° F.)—and is quenched in oil, it cools to atmospheric temperature with a structure somewhat like that of Figure 15E. The vital criterion is that it shall cool without separating large crystals of Fe, as shown in Figure 15A, because these crystals move easily along their slip planes and yield without offering much resistance. But the structure shown in Figure 15E is indicative not only of strength, but also of internal stresses and brittleness. It is therefore materially relaxed, for which purpose it is heated to at least 400° C. (750° F.), and perhaps as high as 650° C. (1200° F.). This causes the solid solution to decompose into crystals of Fe and Fe_3C, but, the decomposition having taken place below the normal phase-change temperature, the crystals are all small. The strength is decreased by this decomposition, but it is always greater than it would be if large crystals of Fe were present. The more it is heated, the more the strength is reduced, but also the more the ductility is increased; therefore, it makes a tough steel; excellent to resist impact (shock) and fatigue (i.e., alternating stresses, varying stresses, vibration, etc.).

CAST IRON

Constitution of Cast Iron—The equilibrium diagram of iron and carbon is a Type III diagram with which all metallurgists are familiar. Up to 1.7% carbon the alloys freeze as solid solutions; above 1.7% carbon there is the usual eutectiferous system in which the two components are the saturated solid solution and (ordinarily) Fe_3C. The word "ordinarily" is used advisedly because equilibrium seems to rule that, when the carbon in the liquid solution is in excess of 1.7%, the excess should precipitate as graphite; and also that carbon precipitating from solid solution should appear as graphite, even though it is perhaps in solution as Fe_3C. But the affinity of iron for carbon is so great that Fe_3C is the usual precipitate unless chemical or heat-treating means are taken to cause graphite to appear. For example, silicon in proportions of about 0.75 to 2.50% will promote the separation of graphite instead of Fe_3C from the liquid, as well as from the solid solution. This shows the importance of reaction (9) in Figure 7, and of producing a high temperature in the hearth of the furnace, which promotes reaction (9). Pig iron is intentionally produced so as to have a predetermined percentage of silicon; then the relative amounts of graphite and Fe_3C which separate on the freezing of the metal will depend on the silicon and the speed of freezing. Thus cast iron may occur as gray iron, with appreciable amounts of graphite (Figure 15F), or white iron, or mottled iron, which is mostly white with some gray spots, or "chilled" iron, which is white on the outside, where freezing was relatively rapid, and gray in its interior portions.

Properties of Cast Iron—White cast iron is hard and brittle, sharing in part the properties of Fe_3C. It has almost no engineering uses. Gray cast iron is a complex material, containing crystals of graphite and ferrite and sometimes also metastable crystals of Fe_3C in the pearlite matrix, and even relatively large crystals of Fe_3C. It is obvious that its properties will depend upon its constituents. Graphite is flocculent and weak. When it occurs in flakes, its presence causes gray cast iron to be unreliable in tension and to break without deformation. But if the crystals of graphite are small and well distributed in an iron matrix, the cast iron may have a strength of 65,000 lb. per sq. in., or even higher,

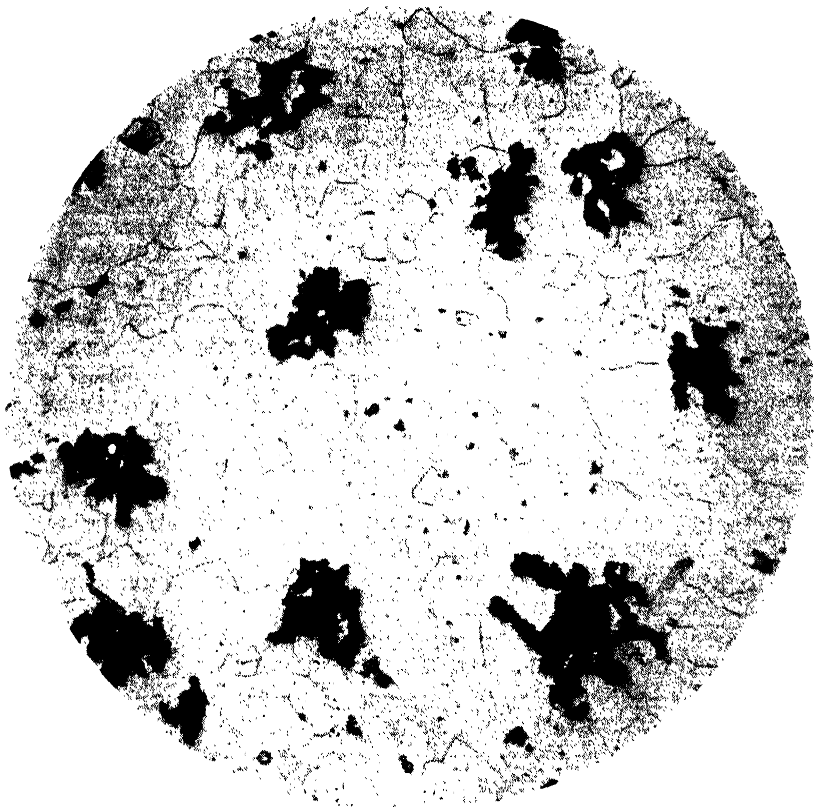

FIG. 15F. Graphite in Cast Iron. This is a malleable cast iron. 200×. (Courtesy Roy M. Allen)

and may have a moderate ductility. This is the basis of so-called "high strength cast iron," in which small graphite particles are well distributed in a matrix which may be partly or wholly pearlite. "Alloy cast irons" may consist of small graphite particles in a matrix of pearlite and ferrite, in which the ferrite is strengthened and/or toughened by nickel or molybdenum, etc. Chilled cast iron as used in rolls has a hard exterior which will take a high polish, and an interior which will give the rolls a backing of protection against breaking under shock.

Malleable Cast Iron—If cast iron be frozen so that it is all white, as, for instance, if it be cast in thin sections so that it cools rather rapidly, and if, then, it be reheated for several hours to about 900° C. (1650° F.) and cooled slowly therefrom, it may consist of crystals of graphite in widely-distributed and small particles, and crystals of ferrite. This can be accomplished if the silicon, the speed of freezing, and the heat treatment applied in the final operation are properly coordinated. It is also customary to reduce the amount of carbon to a relatively small amount—say, not more than 2.30%—by melting and slight oxidation in an "air furnace." The result is a cast iron having tensile strength of 50,000 lb. per sq. in., or better, with an elongation of sometimes 18% in 2 in., an impact value of 16 ft.-lb., or better, and a fatigue endurance limit of 25,000 lb. per sq. in., or better. Sometimes the heating and other operations are adjusted to produce a metallic matrix of pearlitic structure (Figure 15C), and sometimes alloying elements such as molybdenum, copper, chromium, etc., are used to produce the desired result. Not a large tonnage—less than a million tons per year—is consumed, but the material finds usefulness in automotive, agricultural, and other machinery, pipe fittings, household hardware, railroad rolling stock, and toys.

ALLOY STEELS

Alloy Steels in General—Either singly or in multiples, the following elements are commonly added to steel to produce specific effects which exceed the properties of straight carbon steel: Nickel, chromium, silicon, manganese, molybdenum, vanadium, tungsten, copper, and sometimes others. Nickel is added to about one-half of all kinds of alloy steels made; chromium is added to a goodly tonnage, especially to make the so-called "stainless" steels. The art of deciding between different alloy steels, or of formulating an analysis to provide desired properties, is a very complex one and requires life-long study. We can here only postulate a few simple rules for guidance. In general, alloying elements are added for two predominant purposes: First, to affect the characteristics of the individual crystallographic constituents. These are ferrite and cementite in annealed steels at atmospheric temperatures, and austenite and martensite in steel at other temperatures and in heat-treated, or metastable, steels. The second chief purpose is to alter the speed of, or the position of, the equilibrium phase changes which occur as indicated in Figure 14.

Nickel—Most of the nickel added to steel forms a solid solution with the ferrite crystals, which it renders more tough. Nickel does not exert as much of a direct strengthening effect on ferrite as does dissolved phosphorus, silicon, and manganese, but steels rich in ferrite,—that is, steels having less than about 0.60% carbon,—are most commonly toughened by from 1% to 3.50% nickel. They then exhibit a high impact resistance, especially at sub-zero temperatures, and an improved resistance to "fatigue." Nickel steels are used for structures (bridges, buildings, crankshafts, etc.). In combination with chromium, nickel is used for a great variety of steels. Besides toughening the ferrite, nickel promotes the separation of a relatively small size of ferrite crystal between the lines *GS* and *PS* in Figure 14, and also tends to increase the proportion of ferrite normally occurring in pearlite; in other words, to decrease the proportion of excess ferrite which will separate between the lines *GS* and *PS*. For example, steel containing 3.5% of nickel, will have the point "S" located at 0.68% carbon, instead of 0.83%. Since a larger size of ferrite crystal tends to make it yield more to strain, it is obvious how the two latter influences promote strength and toughness.

Nickel has a face-centered space lattice, as has gamma iron. Therefore, nickel tends to delay, on cooling, the change from face-centered to body-centered iron (the line *NH* in Figure 14), and to delay the decomposition of austenite. When iron contains as much as 20% of nickel, the lines *GS* and *PSK* occur below atmospheric temperature, so that the steel is normally austenitic.

Low Chromium—Chromium makes sluggish all the phase changes indicated in Figure 14. Therefore, chromium of from 0.50% to 1.50% has been used for years to facilitate the heat-treatment of steel. For example, if it is desired to create the hard structure shown in Figure 15E, it is necessary to heat steel until austenite is produced and then quench an ordinary carbon steel in water. But, if the steel contains, besides carbon, a small amount of chromium, the desired result may be obtained by quenching in heavy oil, which does not produce so rapid a cooling, and consequently so severe stresses in the steel. Furthermore, the effect of rapid cooling will penetrate deeper into the surface of the piece when chromium is present. This latter effect is expressed by saying that "chromium promotes depth hardening." The same principle applies, of course, in heat-treating for toughness, and steels containing nickel and chromium are greatly valued for their toughness and uniformity when the section is not very thin. There are many other important effects of chromium on steel which we have not here space to discuss. Chromium has a body-centered space lattice; therefore, it lowers the temperatures at which the line *NH*, Figure 14, occurs, and raises the temperatures of the lines *GS* and *PSK*.

High Chromium—Steel becomes really stainless when it contains at least 11.5% of chromium, and increasingly so as the proportion of chromium is raised. This result is apparently due to the formation of an adherent, continuous, thin (practically invisible) film of chromium oxide on the surface of the metal, which resists attack by oxidizing agents, such as nitric acid, the atmosphere, etc. It is essential, however, that the steel be in the condition of a solid solution, or at least that there be no separated crystallites which cause differences of electropotential, even if only microscopic in size, because it is known that these differences are the driving force which determines the tendency of reaction to occur. A few hundred thousand tons of stainless steel are now made annually.

A popular type of stainless steel is that which contains 18% chromium and 8% nickel (so-called 18-8), because it is not only stainless and strong, but it lends itself readily to deep-drawing. This alloy owes its characteristics chiefly to the circumstance that it is austenitic at atmospheric temperature. Therefore, it is tough, ductile, and strong, like most austenites. Like them, it also has a rather low yield strength compared to its ultimate strength. This demonstrates a new principle: Whereas it takes about 20% of nickel to make steel austenitic at atmospheric temperatures, and whereas no proportion of chromium will produce this effect, nevertheless 18-8 is austenitic. This anomaly is explained as follows: Nickel lowers the temperature at which gamma iron changes to alpha (austenite to pearlite); chromium increases the sluggishness and inflexibility. So 18-8 cools as austenite until it arrives at a temperature where it should change according to equilibrium, but now it has become so inflexible that it cannot change. This same principle is observed in the case of other steels containing at least two alloying elements.

Miscellaneous Alloying Materials—Both manganese and silicon are used for the deoxidation of steel following a heat in the Bessemer, the open hearth, or the electric furnace. However this is not thought to constitute an alloy. When manganese plus silicon equals at least 2 to 3%, the point "S" in Figure 14 is pushed well to the left. In other words, a structural steel containing 0.40% carbon will contain very little, if any, ferrite in excess of the pearlitic ratio. This makes for a stronger steel, because the excess ferrite crystals of relatively large size yield to strain more readily than do the ferrite crystals in the pearlite. Several American bridges have been built of so-called (miscalled) "silicon steel," containing roughly 1% or more silicon and somewhat less manganese, with about 0.40% carbon. In other cases the manganese is raised to 1.50 to 1.90% and the silicon lowered to less than 1%, or may even be as low as 0.20%. The silicon in these steels is so minor they are often called "pearlitic manganese steels." With carbon of 0.50 to 0.70% this is favored for railroad rails, because it resists "shatter cracks," and with carbon of 0.30 to 0.40% it resists fatigue cracks in automobile axles. There are many silicon-manganese spring steels used, particularly for automobiles, containing about 2% silicon, less than 1% manganese, and 0.50% or more carbon. These are heat-treated to give resilience.

Manganese—Manganese, being face-centered, lowers the change from gamma to alpha iron. With more than 7% manganese, austenite persists to atmospheric temperature. In order to be truly austenitic, this steel must be cooled rapidly from about 1000° C. (1800° F.), because it contains 1% or so of carbon which would separate as $(Mn \cdot Fe)_3C$ as the steel cools across the line *SE* in Figure 14. Unless fully austenitic, it is brittle. "Austenitic manganese steel," containing about 13% manganese, quenched in water, has high resistance to abrasion, is strong, tough and ductile.

Silicon—Silicon dissolves in ferrite as FeSi. It increases the electrical resistance of the ferrite and decomposes the solid solution of alpha iron with carbon, for which see the line *GPO* in Figure 14. For the first reason it decreases the eddy currents in the armatures of alternating-current machinery, and, for the second reason, it increases the magnetic permeability thereof. Very pure iron containing 4.75% silicon is preferred for "silicon transformer steels," of which there is a goodly tonnage made each year.

Molybdenum—Molybdenum creates great sluggishness in steel. It seems to function as a "stabilizer," or "fixer," of the constitution of pearlite, austenite and martensite, and molybdenum carbide dissolves in, and precipitates from, solid solution with difficulty. It may form a carbide, or may form a double carbide with Fe, or may merely dissolve in Fe_3C. It definitely associates with cementite rather than with ferrite, but may form the compound Fe_3Mo_2, which dissolves in ferrite. It promotes depth hardening more powerfully than any other alloying element. It prevents, or lessens, "temper brittleness," i.e.: brittleness in certain steels (particularly NiCr and pearlitic manganese steels) which have cooled slowly from about 450° C. (800° F.). This is thought to be due to the precipitation of carbides in the grain boundaries. Even as little as 0.30% molybdenum produces a molybdeniferous carbide which does not readily dissolve in solid steel, nor precipitate in the grain boundaries except with extremely slow cooling, or else long sojourn at high temperature. Considering stabilization of martensite, i.e., resistance to softening of hardened steels, straight carbon steel is hardened by heating it until it becomes a solid solution and then cooling at a "critical cooling rate" which produces the hard, martensitic structure (Figure 15E). Its brittleness must then be relieved by warming it (called "tempering"). But, if it is warmed above about 300° C. (575° F.) it loses too much of its cutting hardness. However, if it contains, say, 9% molybdenum, usually with 4% chromium, the carbide does not fully dissolve until the steel is heated to 1150 to 1250° C. (2150 to 2250° F.); it then acquires a cutting hardness after a moderately accelerated cooling, and this hardness is retained thereafter even when the steel is reheated above a red heat, say, 1100° C. (2000° F.). Such steel can be used for a cutting tool, even when the friction of work heats the edge to red heat. It is therefore called "high speed steel." Molybdenum shares with tungsten and cobalt this capacity of "stabilizing" martensite, but it seems to possess uniquely its ability to lessen "temper brittleness." Molybdeniferous carbide exists as a minute, undissolved precipitate which interferes with grain growth of austenite by mechanically interfering with grain absorptions, and increases "creep" resistance by mechanically interfering with slip and yielding. It increases strength at elevated temperatures, although this has not as yet been coordinated with its "constitution-stabilizing" function. Also we should consider the insolubility of molybdeniferous carbide independently of the stabilizing influence of molybdenum. From what precedes it is evident why molybdenum is added to steels and alloy steels which are to be used for welding, heat-treatment, high-temperature service, tools, etc.

Vanadium—Vanadium has a powerful affinity for oxygen and for carbon. It is used for deoxidizing steel. Above 0.30% it induces brittleness, but is used in small amounts to form a carbide which is not easily soluble in austenite and therefore mechanically opposes grain growth. Vanadium steels are small in grain size and therefore tough and impact-resistant. The element helps to confer "high speed" qualities. Chrome-vanadium, manganese-vanadium, nickel-vanadium, and other combinations are used for toughness, and/or hardness, resilience, etc.

Tungsten—Instead of 9% molybdenum, 18% of tungsten is used in high speed steels, because of the tendency of molybdenum steels to decarbonize when heated.

Copper—For many years steel containing about 0.25% copper has been used because it does not rust as rapidly as plain carbon steel. It strengthens ferrite, and toughens it somewhat like nickel. Recently it has been used to produce "precipitation hardening" effects.[7]

READING LIST

ORE RESOURCES AND METAL PRODUCTION

Eleventh International Geological Congress, "Iron Mines and Mining," Stockholm (1910).

Roush, G. A., "The Mineral Industry," McGraw-Hill Book Co., New York. Published annually.

"Minerals Yearbook," U. S. Bureau of Mines, Washington. Published annually.

Ries, H., "Economic Geology," seventh edition, Chapter 14, J. Wiley & Sons, New York (1938).

[7] See Bullens, *op. cit.*, Vol. I, pp. 203, et al.; Vol. II, pp. 100, et al.

Roush, G. A., "Strategic Mineral Supplies," McGraw-Hill, New York (1939).
Leith, C. K., "World Minerals and World Politics," McGraw-Hill, New York (1931).

MANUFACTURE AND TREATING OF IRON AND STEEL

Clements, F., "Blast Furnace Practice," three volumes, Ernest Benn, Ltd., London (1929).
Sweetser, R. H., "Blast Furnace Practice," McGraw-Hill, New York (1939).
Camp, J. M. and Francis, C. B., "The Making, Shaping, and Treating of Steel," fifth edition, Carnegie Steel Corp. (1940).
Thum, E. E., "Modern Steels," Am. Soc. for Metals, Cleveland (1939).
Stoughton, B., "The Metallurgy of Iron and Steel," fourth edition, McGraw-Hill, New York (1934).
"Metals Handbook," Am. Soc. for Metals, Cleveland (1939).

THE BESSEMER PROCESS

McCaffery, R. S., "The Bessemer Process and Its Products," Am. Iron & Steel Inst. Preprint, pp. 1-17 (October, 1931).
Henning, C. C., Trans. Am. Inst. of Min. & Met. Engrs. *116*, Iron and Steel Division 137 (1935).
Graham, H. W., "The Acid Bessemer Process of 1940," Am. Inst. Min. & Met. Engrs. Tech. Publication No. 1232 (1940).

OPEN HEARTH STEEL AND STEELMAKING

"Symposium on Steel Making," Iron and Steel Inst., London, Special Report No. 22 (1938).
Herty, C. H., et al., "The Physical Chemistry of Steel Making," Carnegie Inst. of Tech., Pittsburgh, Mining & Met. Investigation (1934).
Cook, E., "Open-Hearth Steel Making," Am. Soc. for Metals, Cleveland (1937).
Buell, W. C., "The Open Hearth Furnace," three volumes, Penton Pub. Co., Cleveland (1936, 1937, 1939).
Reinartz, L. F., "The Development of Open-Hearth Steel Making Processes in the U. S. A.," Blast Furnace and Steel Plant *26*, 995-9, 1011, 1093-6 (1938).

ELECTRIC FURNACE PRACTICE

Dean, R. S. and Von Bernewitz, M. W., "Smelting Ores in the Electric Furnace," Information Circular No. 6955, U. S. Bureau of Mines (October, 1937).
Christianson, H., "The Production of Iron in Norway," Metals and Alloys (September, 1936).
Farnsworth, W. M. and Johnson, E. R., "American Electric Furnace Practice," J. Iron & Steel Inst., No. 7, 15 pp. (1938).
Moore, W. E., "Present Status of the Electric Arc Furnace in Industry," Trans. Electrochem. Soc. 77, Preprint (1940).

MALLEABLE CAST IRON

"Malleable Iron," Cast Metals Handbook of the American Foundrymen's Assoc., Chicago (1940).

ALLOY STEELS

Bullens, D. K., et al., "Steel and Its Heat Treatment," Vol. II, J. Wiley & Sons, New York (1939).
"Metals Handbook," Am. Soc. for Metals, Cleveland (1939).
Bain, E. C., "Functions of Alloying Elements in Steel," Am. Soc. for Metals, Cleveland (1939).
Cleaves, H. E. and Thompson, J. G., "The Metal Iron," issued by Alloys of Iron Research Committee of the Engineering Foundation, McGraw-Hill, New York (1935).
Epstein, S., "The Alloys of Iron and Carbon," ibid. (1937).
Sisco, F. T., "The Alloys of Iron and Carbon," ibid. (1937).

Marsh, J. S., "The Alloys of Iron and Nickel," ibid. (to be published).
Kinzel, A. B. and Crafts, W., "The Alloys of Iron and Chromium," ibid. (1937); revised Kinzel, A. B. and Franks, R., ibid. (1940).
Thum, E. E., "The Book of Stainless Steels," second edition, Am. Soc. for Metals, Cleveland (1935).

IRON-CARBON EQUILIBRIUM DIAGRAMS

Doan, G. E., "The Principles of Physical Metállurgy," Part II, McGraw-Hill, New York (1935).
Marsh, J. S., "Principles of Phase Diagrams," McGraw-Hill, New York (1935).

REDUCTION OF IRON OXIDE

Ralston, O. C., "The Reduction of Iron Oxide," U. S. Bureau of Mines, Washington, Bull. 296 (1929).

CHAPTER 24

NONFERROUS METALLURGY

PART ONE

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The "bronze age" in human history followed the "stone age" and preceded the present "age of steel." Whether this in turn will be succeeded by an "age of plastics" remains to be seen. At present the tonnage of iron and steel produced so far exceeds the total tonnage of all other metals combined, that it is customary to speak of all metals other than iron as non-ferrous. All attempts to develop a more positive nomenclature have failed and thus an important group of materials continues to be spoken of in a negative way.

ECONOMIC CONSIDERATIONS

Sources of Production—Since the metallic resources of a nation or continent are highly important in its domestic economy and world trade, Table 1 will be of interest. This table lists in order of present output the two or three countries (in the case of Africa and Australia, continents) which produce the principal amounts of the metals or, in cases where the ore is at present largely shipped out of the country for treatment, the ore is designated.

Two decades are covered in the table and the figures require little comment. Although the order of production changes in a few cases, it is seldom that a country, once listed as a leading producer, is relegated to a minor position. Some of the figures given for 1939 are abnormal because of preparations for war.

It will be noted that the United States is in a favorable position with respect to most of the important metals, but in the cases of tin, platinum and nickel it should be stated that only insignificant ore deposits are known in the country. There is also some deficiency in manganese, chromium, antimony and mercury as well as some of the minor metals.

Comparative Values of Metals—Table 2 gives a list of some of the common metals arranged in order of the value of the world's output during 1937. Included in the table for reference is the weight and value of a cubic foot of each metal, the value being based on average United States prices in 1937. This table shows clearly that although the tonnage of nonferrous metals is far below that of pig iron, the value is much greater.

BASIC PRINCIPLES OF SMELTING AND REFINING

It is probable that the first metals used by primitive man were those which occur in nature in the metallic state, viz.: gold, silver, platinum, copper, bismuth

TABLE 1—LEADING PRODUCERS OF METALS IN ORDER OF TONNAGE OUTPUT

	1920	*1930*	*1939*
Aluminum Ore	U. S., France, Guiana	France, Guiana, U. S.	France, Guiana, Hungary
Aluminum Metal	U. S., Switzerland, Germany	U. S., Canada, Germany	Germany, U. S., Canada
Antimony Metal	China, Germany, Mexico	China, Mexico, France	Bolivia, Mexico, China
Beryllium Metal		Germany, U. S.	Germany, U. S.
Bismuth Ore and Metal	Bolivia, Australia, U. S.	Bolivia, U. S., Spain	Peru, Canada, Mexico
Cadmium Metal	U. S., Germany	U. S., Australia, Canada	U. S., Belgium, Canada
Calcium Metal		France, Germany	Germany, France
Chromium Ore	New Caledonia, Rhodesia, India, Turkey	Rhodesia, Russia, New Caledonia	Turkey, Rhodesia, S. Africa
Cobalt Ore	Canada	Congo, Canada, India	Africa, Canada, Burma
Copper Metal	U. S., Chile, Japan	U. S., Chile, Africa, Canada	U. S., Africa, Chile, Canada
Columbium Ore			Nigeria
Gallium Metal		Germany	Germany
Gold Metal	Transvaal, U. S., Mexico, Canada	Transvaal, U. S., Canada	Transvaal, Canada, U. S.
Indium Metal			Belgium, Japan, U. S.
Iron Metal	U. S., Gt. Britain, Germany	U. S., France, Germany	U. S., Germany, Russia
Lead Metal	U. S., Spain, Mexico	U. S., Mexico, Australia	U. S., Australia, Mexico
Magnesium Metal	Germany, U. S., France	Germany, U. S., France	Germany, Gt. Britain, U. S.
Manganese Ore	India, Brazil, Russia	Russia, Gold Coast, India	Russia, India, S. Africa
Mercury Metal	Italy, Spain, U. S.	Italy, Spain, U. S.	Italy, Spain, U. S.
Molybdenum Ore	U. S.	U. S.	U. S., Norway, Mexico
Nickel Metal and Ore	Canada, New Caledonia	Canada, New Caledonia	Canada, New Caledonia, Russia
Platinum Group Metals	Colombia, Russia, Japan	Colombia, S. Africa, Canada	Canada, S. Africa, Colombia
Silver Metal	Mexico, U. S., Canada	Mexico, U. S., Canada	Mexico, U. S., Canada
Tantalum Metal		Australia, U. S.	Africa, U. S., Australia
Tin Ore	Malaya, Bolivia, China, E. Indies	Malaya, Bolivia, Siam, E. Indies	Malaya, Bolivia, Siam, E. Indies
Tungsten Ore	China, Burma, Bolivia	China, Burma, U. S.	Burma, China, U. S.
Uranium Ore	U. S., Canada, Africa	Africa, Canada, U. S.	Africa, Canada, U. S.
Vanadium Ore	Peru, U. S.	Peru, U. S., Africa	Peru, U. S., Africa
Zinc Metal	U. S., Belgium, Poland	U. S., Belgium, Poland	U. S., Germany, Belgium

and mercury, followed by metals which could be easily extracted from oxide minerals occurring near the surface of the earth. Tin and lead are important among this group; followed by iron, the high melting point of which delayed its general use until after the "bronze age."

Through all history the most common method of removing oxygen from combination with a metal has been to heat the oxide with carbon. This was undoubtedly first discovered by accident, perhaps when an aboriginal ancestress of the race collected some beautiful azurite ($2CuCO_3 \cdot Cu(OH)_2$) or malachite ($CuCO_3 \cdot Cu(OH)_2$) minerals to adorn the family fireplace and discovered after

TABLE 2—COMPARATIVE VALUES OF METALS

Calculated from Production Tables in the Mineral Industry, 1937

	Wt./Cu. Ft. Lb. Avoirdupois	*Approximate Value Cu. Ft. Dollars*	*Approx. World Vol. Prod. 1937: Cu. Ft.*	*Approx. World Value Prod. 1937: Dollars*
Pig Iron	450	4	500,000,000	2,000,000,000
Gold	1,208	616,560	1,960	1,208,000,000
Copper	557	72	9,000,000	648,000,000
Zinc	437	30	8,400,000	252,000,000
Tin	460	248	1,000,000	248,000,000
Lead	708	42	5,340,000	224,280,000
Aluminum	163	33	6,610,000	218,000,000
Silver	654	7,343	28,800	211,478,000
Nickel	550	121	450,000	54,450,000
Platinum	1,344	999,600	18	17,993,000
Cadmium	543	678	17,000	13,526,000
Mercury	849	1,019	11,900	12,126,000
Magnesium	109	33	198,000	11,880,000
Cobalt	533	1,012	11,000	10,132,000
Total for the nonferrous metals listed			31,068,678	3,129,865,000

a particularly hot fire that they had disappeared and in the embers was found a strange substance which we know as copper. Its ductility enabled it to be worked into many useful shapes.

The recovery of metals from sulfide minerals probably followed many hundreds of years after the treatment of oxide minerals by simple reduction was established practice. Again it was probably by accident that some metallic sulfide minerals were ignited and burned until converted to oxides, which in turn were reduced by the coals of the fire which ignited them. It was only after the Bessemer process was applied to the metallurgy of copper near the close of the last century that metals were recovered from sulfide minerals by any fire method other than roasting followed by reduction.

The difficulty of reduction of a metal compound to the metal is measured by the free energy change of the necessary reaction. This takes one into the field of chemical thermodynamics and the values of the free energy changes in the various metallurgical processes have not yet been accurately measured, except in a few instances. However, the familiar electromotive force series, found in any elementary chemistry text book, is a semiquantitative listing of a property of metals, which is roughly the same as their reducibility. That is, the further up the electromotive series a metal is found, the more difficult it is to reduce. This is not necessarily true for adjacent members of the series but it does serve as an approximate guide for the visualization of the relative difficulty of reduction.

Since the reducibility of metallic oxides varies, by varying the temperature and the amount or character of the reducing agents certain metals of varying purity may be obtained while other metallic constituents in the charge may remain as unreduced oxides or silicates. However, in producing a given metal by reduction it usually happens that one or more other metals are simultaneously reduced and contaminate the primary metal, thus making a subsequent refining operation necessary.

The converse of the reducing operation is fire refining which is, in most cases, selective oxidation. During this treatment a metal containing various amounts

TABLE 3—TYPES OF NONFERROUS MINERALS

METALS EXTRACTED PRINCIPALLY FROM SULFIDE MINERALS	METALS EXTRACTED PRINCIPALLY FROM OXIDE MINERALS
Copper *	Iron
Lead *	Aluminum
Zinc	Tin
Nickel	Magnesium
Antimony	Manganese
Cadmium	Tungsten
Molybdenum	Chromium
Vanadium	Beryllium
Mercury	

* Copper and lead are recovered to a minor extent from oxide minerals and in the Michigan district copper is recovered from ore where it exists in the native or metallic state.

of impurities is exposed to the action of free or combined oxygen and such of these impurities as are more readily oxidized than the principal metal will be converted to oxides and usually float on top of the bath. Where the impurities have a low affinity for oxygen, they cannot be removed by direct oxidation. For example, antimony is readily removed from lead by oxidation but bismuth and the precious metals cannot be thus removed and require special treatment.

Since the procedure used for extracting the various metals from their ores depends to a considerable extent on whether their important minerals are oxides or sulfides, it will be of interest to classify the common metals in these two groups as a basis for further discussion. This is done in Table 3. The term oxide is here used in a broad sense and covers carbonates, silicates and hydrated oxides.

PRELIMINARY TREATMENT OF ORES

Character and Richness of Ore Deposits—With few exceptions the nonferrous minerals occur either in relatively narrow veins necessitating the simultaneous removal of large quantities of waste rock during the mining operations, or widely disseminated through valueless rock. In either case the metallic content of the rock as mined is low. In other cases, particularly with copper, lead and zinc, the sulfides may be associated with iron sulfide minerals which have little value. In some cases precious metals may be associated with the base metals but usually in very small amounts. The copper content of the ores mined in the United States is seldom over 1.5 per cent, and in the case of the great Utah Copper Company mine the average copper content of the ore is a slight amount under one per cent.

The metal content of a usable ore obviously must depend on the unit value of the recovered metal and the available technique for enriching and smelting the ore. Table 4 summarizes the information on range at concentration of metals in various ores.

TABLE 4—USABLE CONCENTRATIONS AND RESERVES OF ORES IN LIGHT OF PRESENT KNOWLEDGE AND AVAILABLE TECHNIQUES

Ore	*Low Grade* [1]	*Average* [1]
Lode Gold $/ton	$ 1.00	$ 5-12
Silver oz./ton	10	15-30
Platinum dwt./ton	3	5-8
Iron % Fe	30	50-60
Copper %	0.8	1.5-5
Lead %	5	6-10
Zinc %	3	10-30
Tin %	1	1.5-5
Aluminum % Al_2O_3	30	55-65
Antimony %	40	50-60
Bismuth %	..	40-60
Beryllium % B_2O	10	10-12
Manganese % Mn	35	45-55
Mercury %	0.5	1-3
Molybdenum % MoS_2	0.4	1-3
Titanium % TiO_2	3	4-8
Tungsten % WO_3	..	60-70
Vanadium % V_2O_5	2	3-8

In some copper, lead and zinc mines each metal exists uncontaminated by the other and the problem of extraction is simple. In other cases, two or more metals exist together and the processes of extraction are complicated. The precious metals, if present in ores being treated for copper or lead, fortunately follow one or both of the metals during the extraction process and are recovered during the refining operations.

Preliminary Concentration of Minerals—It is obvious that if it were necessary to fuse ores containing only one or two per cent of base metal preparatory to reduction, the extraction would be low and the cost prohibitive. Fortunately, however, methods have been developed whereby most of the valuable minerals may be separated from the waste rock at only moderate expense and collected as an enriched product or concentrate. For example, a low-grade copper ore thus treated may yield a large percentage of its copper in a concentrate which may contain 25 to 30 per cent copper and a low-grade lead or zinc ore may be treated to give a concentrate containing 50 to 65 per cent of lead or zinc. The treatment of such concentrates by fire methods is sufficiently inexpensive so that the resulting metals may be produced at a profit within the normal price ranges.

Hand Picking—The earliest form of concentration was hand picking whereby waste rock was picked from metallic minerals or the metallic minerals picked

[1] From Bateman, A. M., "Economic Mineral Deposits," J. Wiley & Sons (1941).

from waste rock, depending on which predominated. Later, with the development of finer crushing devices, various methods were used for separating minerals in accordance with their specific gravities. It is comparatively easy by these methods to separate sulfide minerals from the lighter silicate minerals, but the difference in specific gravity between some of the sulfide minerals is so slight that clean separation is difficult. Nevertheless, the process has merit and is used where conditions are favorable.

Flotation—The most common method of concentration at present is the flotation process. In using this, the ore must be crushed and finely ground to

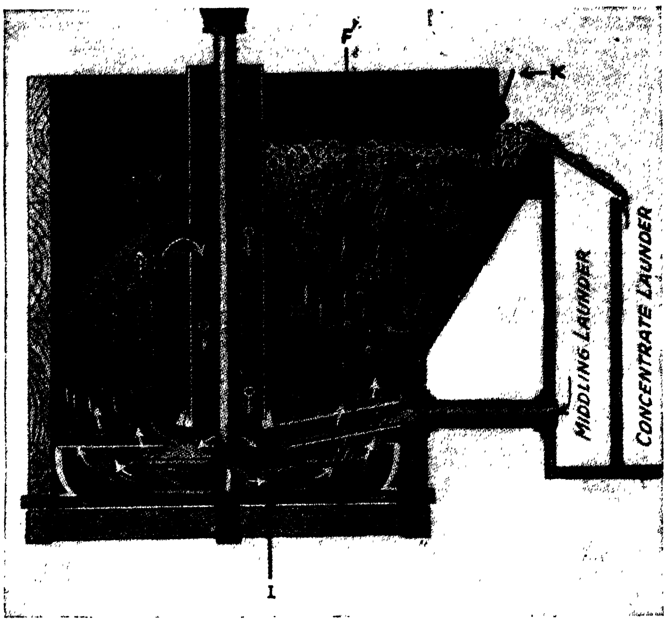


FIG. 1. Impeller Type Flotation Machine.

separate the different minerals completely from each other. The ground material is then agitated and aerated in water to which small amounts of flotation reagents have been added. Among these agents are (1) a frothing agent (e.g. pine oil, cresylic acid, amyl alcohol); (2) a collecting agent (e.g. potassium ethyl xanthate, sodium diethyl dithiophosphate, oleic acid) which films the particles of valuable mineral so that they will adhere to air bubbles; and (3) a variety of inorganic chemicals (e.g. lime, soda ash, copper sulfate, sodium cyanide) which may be used to prevent or assist the filming of specific minerals. When the reagent treatment and aeration are properly carried out, the valuable mineral particles are carried by bubbles into a froth layer and are skimmed off, while the gangue particles remain suspended in the water. One type of flotation machine is shown in Figure 1.

The flotation process which at first merely separated sulfides from other minerals has been developed over a period of years to a point where by slight variation of reagents or procedure, the sulfides may be separated from each other and even concentrations made of non-metallic minerals. Because of these developments, the grade of concentrates has been gradually improved and the percentage of recovery increased, resulting in lower costs of subsequent smelting operations and more total revenue. The net effect is a lower cost per pound of metal recovered.[2]

Roasting and Sintering—Before smelting zinc concentrates, it is necessary to remove nearly all the sulfur and this is only slightly less true in the case of lead. With copper concentrates a considerable amount of sulfur is present in the feed to the smelting furnace and the sulfur is removed subsequently from the molten sulfide produced during smelting.

The operation whereby sulfur is removed by oxidation from a concentrate without heating to fusion is known as "roasting" (e.g. $2ZnS + 3O_2 = 2ZnO + 2SO_2$). The product is pulverulent. In some cases the operation is carried out in such a way that the heat of oxidation raises the temperature to a point where incipient fusion takes place and the product is agglomerated. This procedure is known as "sintering."

Where the desulfurized product is to be smelted in a shaft furnace sintering is desirable, for the porous lumps assist in keeping the charge open and easily penetrated by reducing gases.

Apparatus for Roasting—The apparatus used for roasting nearly all ores is essentially the same as that discussed in Chapter 7, Sulfuric Acid. In plants where market conditions justify it, the gases from roasting the sulfide concentrates of zinc or copper ores are used for acid production.

Apparatus for Sintering—The usual equipment for sintering is the Dwight-Lloyd machine shown in Figure 2. It consists of a series of "pallets" or moving cast iron grates of varying size (frequently about 2 ft. × 4 ft. to 6 ft.) with ends about 6 inches high. These are moved over the wind or suction box shown in the figure, forming what is essentially a continuous close-fitting trough above it. At the right-hand end of the machine is a heavy motor-driven sprocket wheel which engages the pallets, lifts them from the bottom to the top of the machine and pushes them across the wind box. As they pass under the feed-hopper, the pallets are covered with moistened sulfide charge, the depth of which is regulated by an adjustable scraper attached to the lower left edge of the feed-hopper. The pallets then pass under a burner or ignition stove, the hot gases from which are drawn down into the charge by the suction fan for a sufficient length of time to ignite the surface. This acts as kindling and as the pallets proceed over the suction box the air drawn through the charge causes oxidation of the sulfides at such a rapid rate that incipient fusion and sintering take place. The speed of pallets and other obvious variables is adjusted in such a way that the oxidation proceeds completely to the bottom of each pallet by the time it reaches the end of the suction box.

At the left-hand end of the machine there is a gap of 2 feet or more in the train of pallets which allows each pallet to fall sharply against the one which preceded it, thus discharging its load of sintered ore. The pallets then proceed

[2] For further discussion of the principles involved in beneficiating ores see the section on solid-solid separations, Chapter 2, The Unit Operations. For sources or details see the titles under Beneficiation of Ores in the Reading List at the end of this chapter.

in an inverted position by gravity until they reach the sprocket wheel at the right-hand end of the machine.

The pallets are equipped with two rollers at each end which ride on guide rails during the fall at the left-hand end of the machine and their passage from that point to the sprocket wheel.

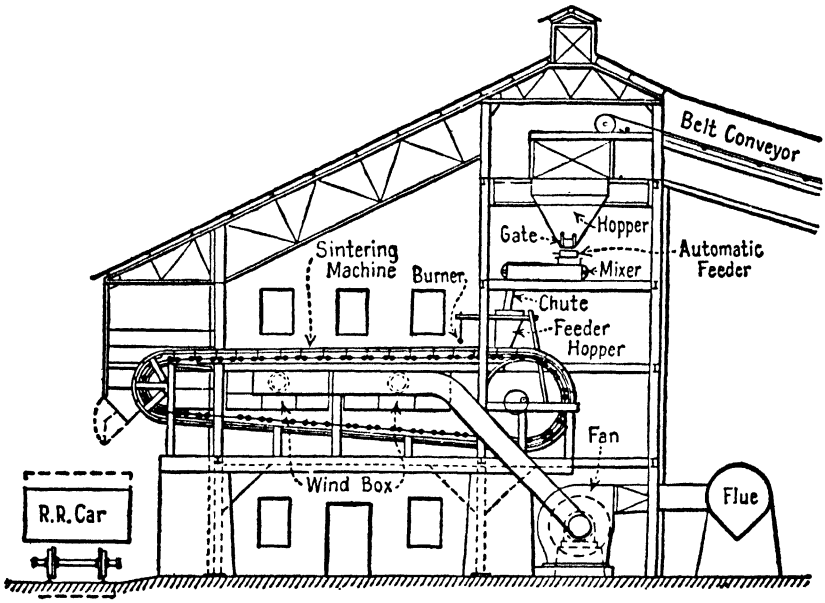


FIG. 2. Section of a Dwight-Lloyd Plant. (Austin, "Metallurgy of the Common Metals")

The mixture to be sintered is delivered to the top of the plant by an inclined conveyor. Note the method of mixing with water by a screw mixer, the arrangement of the suction system and the car for receiving the discharged sinter.

Although the principal use of sintering machines is for the treatment of sulfide-bearing materials the oxidation of which furnishes the necessary heat for producing a sintered product, it is possible to use them for oxide minerals if carbon is added to the charge.

METALLURGY OF COPPER

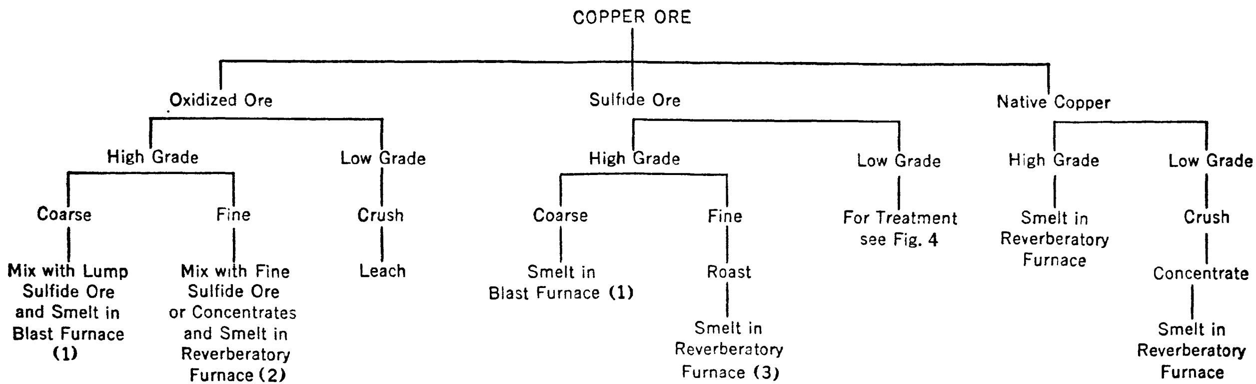
An outline of the methods by which copper is commercially extracted from ores of different types is given in Figure 3. Since the most important source of copper is sulfide ores, this is the operation which will be discussed.

The recovery of metallic copper from sulfide ores depends upon the selective oxidation of iron and sulfur in the presence of copper. The reactions which hold are:

$$2FeS + 3O_2 = 2FeO + 2SO_2\uparrow$$

$$FeO + SiO_2 = \underset{\text{(Slag)}}{FeO \cdot SiO_2}$$

$$Cu_2S + O_2 = 2Cu + SO_2\uparrow \text{ (occurs after the iron is removed)}$$



(1) This is old practice. Modern practice is to crush and treat as fine ore.
(2) In order to pre-heat it may be mixed with the fine sulfide ore before roasting or added on one of the lower roaster hearths.
(3) If preferred it may be sintered and smelted in blast furnace.

FIG. 3. Outline of Methods of Extracting Copper.

This unusual procedure of reducing an ore by bringing it in contact with oxygen is possible only because of the very low chemical affinity of oxygen for copper as compared to iron and sulfur.

The reducing agent in this case is really the sulfur. Hence an important part

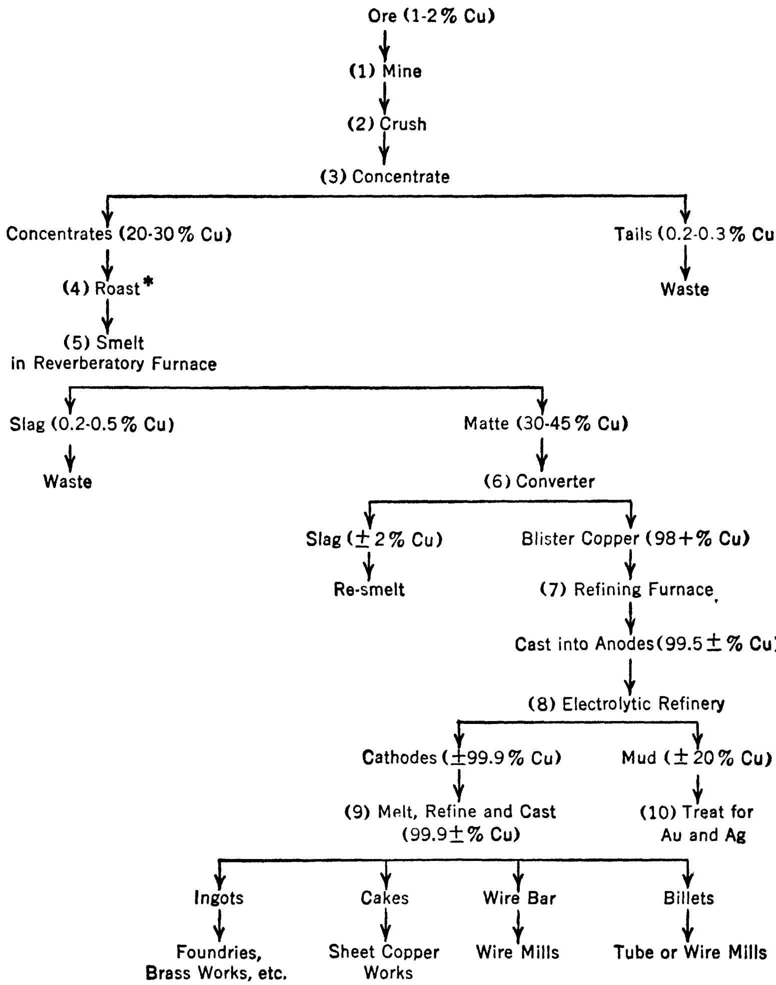


FIG. 4. Outline of the Treatment of a Low-grade Sulfide Copper Ore.

* This is omitted in some cases and the concentrates smelted raw. In other cases the concentrates are sintered and smelted in a blast furnace.

of the smelting consists in proper adjustment of the sulfur content before the final smelting operation.

The mechanical steps involved are shown in Figure 4. In this diagram the function of the reverberatory furnace is to produce a molten combination of iron-copper sulfide (the matte). The function of the converter is to oxidize the iron and sulfur and reduce the copper as indicated by the above equations.

Concentration of Ore—The ore is usually concentrated (see earlier discussion of concentration) at or near the mine to avoid shipping expense and the concentrates are shipped to the smelter, often a considerable distance from the mine but sometimes nearby. These concentrates consist, as a rule, primarily of copper and iron sulfides often contaminated by small quantities of other sulfides and silicate minerals which were not removed by the concentrating operation. There are also, frequently, small amounts of precious metals present.

Roasting Copper Concentrates[3]—The purpose of this operation is to adjust the ratio of copper to sulfur so that, when the product is fused, a matte (copper-iron sulfide) will be produced with a copper content which is most desirable. The optimum matte grade varies with the composition of the concentrate and the equipment available for treating it.

In some concentrates the copper-sulfur ratio is satisfactory without roasting and a few plants charge this material directly to the reverberatory smelting furnace without roasting. In a majority of plants the concentrates are put through a multiple hearth roasting furnace (see earlier discussion) but the amount of sulfur removed in the roasting varies widely depending on the final copper-sulfur ratio desired.

Where roasting is practiced the product, commonly called calcines, is charged, while still red hot, to the reverberatory furnace.

Smelting in the Reverberatory Furnace—In the reverberatory furnace the copper present in the charge first forms Cu_2S, then the remaining sulfur which is not volatilized forms FeS and these two sulfides unite to form matte which takes up most of the precious metals, some Fe_3O_4 and small amounts of other impurities.

TABLE 5—COMPOSITIONS OF VARIOUS MATTES

Per Cent Cu	*Per Cent Fe*	*Per Cent S*	*Ratio Cu:S*
10	57.325	27.625	0.36
15	53.000	27.000	0.55
20	48.625	26.375	0.76
25	44.250	25.750	0.97
30	39.875	25.125	1.19
35	35.500	24.500	1.43
40	31.125	23.875	1.67
45	26.750	23.250	1.93
50	22.375	22.625	2.21
55	18.000	22.000	2.50
60	13.625	21.575	2.95

Table 5 gives the percentages of copper, iron and sulfur in various mattes, assuming that the sum of these three constituents is 95 per cent. The table also gives the ratios of copper to sulfur. By adjusting this ratio in the feed to the reverberatory smelting furnace, with an allowance for sulfur which may be driven off during fusion, a matte of the desired composition will be obtained.

A line drawing of a reverberatory matting furnace is shown in Figure 5. They vary somewhat in size but the average furnace is about 110 feet long by 24 feet wide and 10 feet high inside. The usual capacities vary from 800 to

[3] For a description of the apparatus used for roasting see Chapter 7.

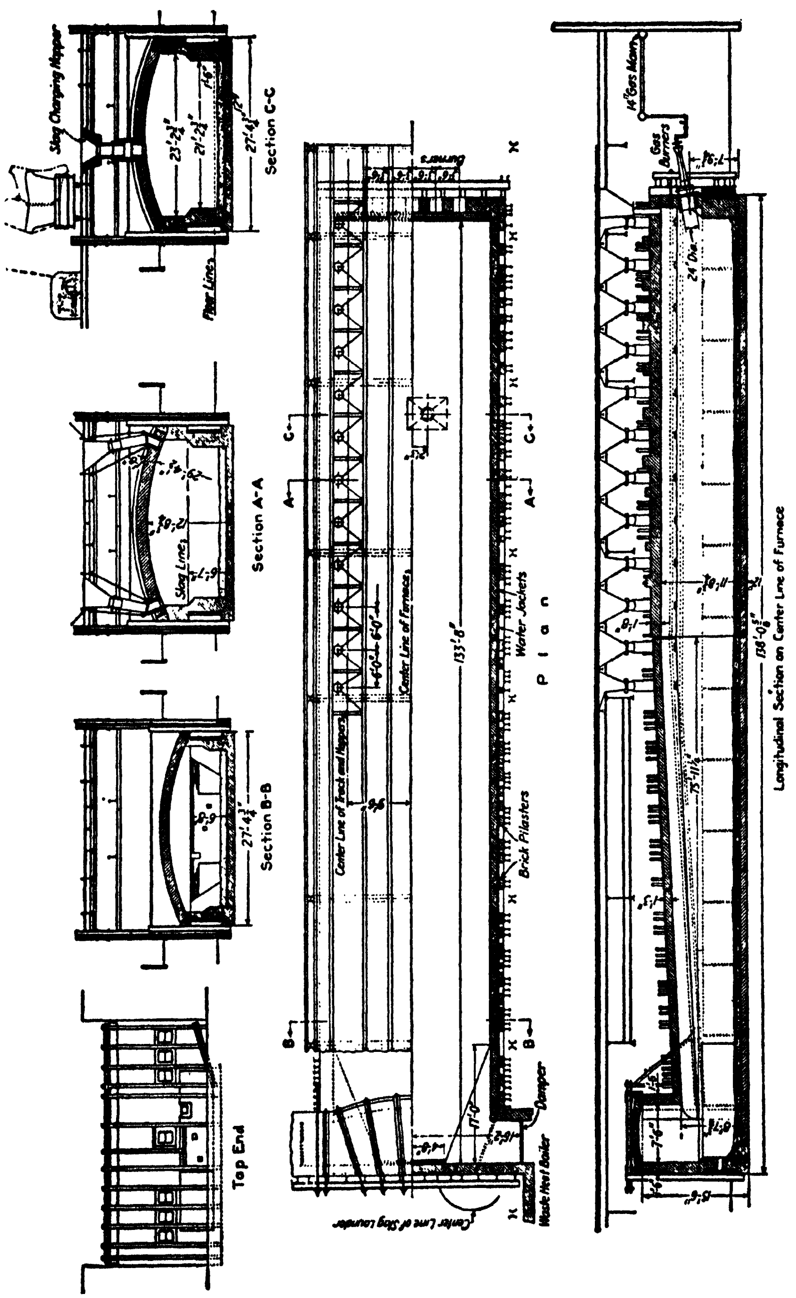


FIG. 5. Reverberatory Smelting Furnace at Anaconda.

Note brickwork with buck-stays and tie-rods for holding the furnace together. Note the water cooling of the hearth, the gas burners, the matte and slag tap holes, the charge hoppers for ore and molten slag, etc.

1000 tons of solid charge per day but some have smaller and some larger capacities. The largest capacity recorded is over 1500 tons per day.

The roof is usually of silica brick, the sides of firebrick, often with magnesite brick at the slag line, and the bottom is of fritted silica or sometimes of poured slag. Water-cooling at the slag line is favored at some plants and at least one plant favors suspended roofs of magnesite.

The fuel is either pulverized coal, fuel oil or natural gas depending on which is most economical. The burners are always at one end and the flue at the other. In most cases the gases pass through waste heat boilers before entering the stack and about 40 per cent of the calorific value of the fuel is recovered as steam.

The charge is brought to the top of the furnace in dumping cars or conveyors and fed by gravity either through drop holes near the center of the roof at the firing end or along the side walls. The latter method is more generally used and is always necessary if moist charges of unroasted concentrates are fed. The charges are introduced at short intervals which gives the general effect of continuous feeding.

Part of the charge consists of molten iron-silicate slag, containing some copper, which is formed in the converter, to be described later.

Whenever slag is poured from a converter, it is transferred in a ladle to the reverberatory furnace and charged by pouring through a spout inserted in the side wall near the firing end. Occasionally, if the concentrates are unusually low in lime a little limestone is added to the charge to make a suitable slag, but normally the charge consists only of concentrates and converter slag.

The compounds existing in the solid charge may be Cu_2S, $CuFeS_2$, $CuSO_4$, CuO, FeS, $FeSO_4$, Fe_2O_3, Fe_3O_4, SiO_2, CuO, various silicates, arsenic and antimony compounds, precious metals. There may be also small amounts of lead, zinc, nickel and other elements in the form of various compounds. As a result of a large number of reactions during the fusing of the charge three products are made. The first, called matte, consists principally of copper and iron sulfides with smaller amounts of nickel, lead and zinc sulfides if present, precious metals and traces of selenium, tellurium, etc. The matte settles to the bottom of the furnace.

On the matte floats a slag consisting primarily of silicates of iron, lime and alumina with small amounts of other silicates.

The molten matte and slag have a certain amount of mutual solubility depending on temperature and composition of each, but fortunately, under normal smelting conditions, this solubility is measured only in fractions of a per cent.

The third product of reactions during smelting is a mixture of SO_2 and SO_3 resulting from the action of oxides on sulfides and the decomposition of sulfates by heat. These join the combustion gases.

The matte is withdrawn at about 1150° C. as needed for the converters through tap holes at any convenient point below the slag line along the sides or flue end of the furnace. The slag is tapped at frequent intervals above the matte either at the flue end of the furnace or on one side near the flue end.

The slag may be received in slag cars and taken molten to the dump or granulated and removed in railroad cars. A normal slag is SiO_2 37-39 per cent, FeO 43-45, CaO 3-6, Al_2O_3 5-7, other oxides ± 10. About 3 million B.t.u. are required to smelt one ton of hot roasted concentrates.

Before the general adoption of concentration to raise the grade of furnace charges, most copper ores were smelted in lump form in shaft furnaces. At present with the modern fine concentrates this procedure is practically obsolete.

Production of Matte in Electric Furnace—The electric smelting of copper ores for the production of a copper matte is now practiced both in Norway and in Finland. The furnace charge consists of a mixture of raw and roasted concentrates, fluxes and converter slags. The furnace burden is calculated just as for the fuel-fired matting furnace, the fluxes being limestone or quartz as suits the gangue of the ore. Converter slags are worked up for recovery of their copper content by charging into this same furnace along with the ore. The copper matte produced is no different from that of the older fuel-fired copper furnace. The power consumption amounts to about 450 K.W. hours per ton of solid charge. The latest furnace is a three-phase furnace of 9,000 K.V.A. operating at 110 volts and treating 250 tons of charge per day.

Recovery of Arsenic—Roasting and smelting operations produce considerable dust which settles in flue systems or is caught by electrostatic or other means. With this dust such volatile constituents as As_2O_3 is condensed. Normally this dust is smelted with the regular charge but in a few instances it is first treated to revolatilize the arsenic which is caught in special condensers and recovered for market.

Converting Copper Matte—The final step in production of crude copper metal takes place in the converter, where air is blown through molten matte.

The most common type of copper converter is shown in Figure 6. It is a horizontal steel cylinder lined with magnesite brick and supported on rollers which permit it to be rotated completely around. Along one side is a row of blowpipes or tuyeres and nearly opposite, at the center, is an opening for receiving the charge.

The usual procedure in converting copper matte is to turn down the converter so the tuyeres will be above the charge line and the opening slightly above a horizontal plane passing through the axis. A charge of liquid matte is added which will nearly half fill the converter, followed by some siliceous flux. The air is turned on, the converter turned so the charge opening is at the top and blowing continued until most of the FeS is oxidized to FeO and SO_2. The FeO combines with SiO_2 to form slag which is then poured off and taken to the reverberatory smelting furnace, for the removal of the copper which it contains. More matte and flux are then added and the operation repeated.

After several repetitions the converter will be nearly half full of Cu_2S which is then blown without flux to form Cu and SO_2.[4]

Although the iron is separated from the copper by the formation of iron silicate slag in the converter, it is removed from the system only after it has been passed back through the reverberatory furnace.

If a refinery is nearby, the copper is charged molten to a refining furnace, otherwise it is cast into cakes for shipment to a refinery.

The product from the converter is known as blister copper and usually contains more than 98.5 per cent copper. The remaining 1.5 per cent or less may be made up of nickel, iron, selenium, tellurium, lead, arsenic, antimony, bismuth, sulfur, precious metals, combined oxygen, etc.

[4] See equations, p. 921.

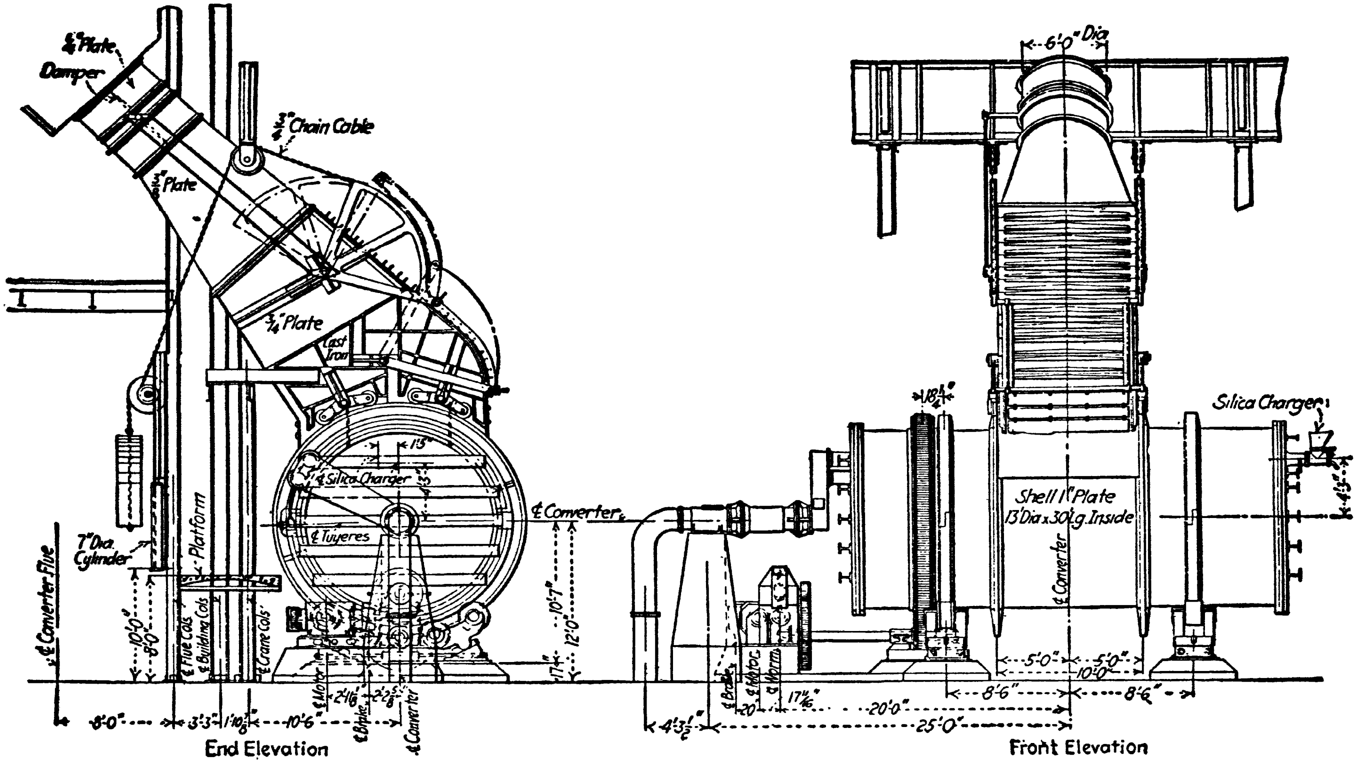


FIG. 6. Elevation of a Peirce-Smith Converter. (Hofman-Hayward, "Metallurgy of Copper")

Note the "Tacoma Hood" which is supported by rollers on the converter shell. This gives a fairly tight joint and prevents dilution of the sulfurous gases, thus allowing their utilization for liquid SO_2. Note the system for opening the trap door in the hood to allow the introduction of charge to the converter. Note the method of supporting and turning the converter and the method of air connection.

In rare instances the converter gases are used for the production of sulfuric acid or liquid SO_2.

Electrolytic Refining of Blister Copper—The blister copper which comes from the converter contains a number of impurities which must be removed before it is ready for use. This is commonly accomplished by electrolytic refining by a process wherein the impure copper on an anode is transferred through a bath of copper sulfate to a cathode where it is deposited as pure copper. The details of this as well as the production of copper from acid solutions are given in the section on ELECTROMETALLURGY OF NONFERROUS METALS in the latter part of this chapter. (Page 949.)

The blister copper is full of gases and may contain sulfur, iron and copper oxide. It is not satisfactory for casting directly into anodes and so is first subjected to a pyrometallurgical refining process.

Preparation of Copper Anodes. The furnaces used for the preparation of anodes from blister copper are of the reverberatory type but are much shorter than the furnace used for smelting. They usually treat a charge of 200 to 400 tons of copper which means that the hearth has a capacity of 740 to 1480 cubic feet. They are fired with pulverized coal, oil or natural gas and are nearly always equipped with waste heat boilers.

If solid copper is used, it is introduced into the furnace through side doors by means of an electric charging machine resembling those used for open hearth steel furnaces. Several hours are required to melt the charge.

If molten copper is charged, it is brought to the furnace in a ladle and poured into a spout inserted through one of the doors. The steps in the treatment of the molten copper are as follows:

(1) Oxidize by means of air blown through steel pipes inserted through a door and extending below the surface of the copper. This operation continues until the bath is converted into the eutectic of copper and cuprous oxide which is at 3.45 per cent Cu_2O. It usually requires 1½ to 2½ hours.
(2) Carefully remove the slag containing the oxidized impurities, principally FeO which has combined with SiO_2.
(3) Cover the bath with coke.
(4) Introduce the unseasoned trunk of a moderately large tree through a door into the furnace and submerge the end in the molten copper. This causes violent ebullition of the copper and through contact with the coke and reducing agents in the pole the Cu_2O is gradually reduced. The operation is continued until the bath contains 0.3 to 0.4 per cent Cu_2O, which requires about 2 hours.

It has been found that when the usual casting methods are used, copper with this amount of oxide will cast into anodes having a flat surface which is desirable if uniform corrosion in the electrolytic bath is to take place.

When the above condition of the copper is obtained, it is cast continuously into anodes weighing 450 to 600 pounds each. Heavy copper molds are used, arranged on a revolving wheel. The solid anodes are removed when the wheel has made about half a revolution after which the molds are sprayed with an emulsion of bone ash or other wash before receiving a new charge.

Preparation of Finished Shapes from Cathodes. The copper which is electrolytically deposited from solution onto the cathode is usually about 99.97 per cent pure. This is sufficient for most commercial uses but the physical structure is such that it cannot be fabricated directly into wire, sheets or other commercial forms. It is common practice for manufacturers of brass and other alloys to make their copper additions in the form of cathode copper cut to suitable sizes, but for all other purposes the cathodes are melted and cast into shapes suitable for further fabrication.

The furnaces used are of the same sizes and constructions as those used for preparing anodes and the operations are also the same.

The principal impurity removed in the oxidizing step is sulfur occluded as electrolyte or absorbed from furnace gases during melting.

The amount of Cu_2O left in the finished copper is carefully regulated to produce a satisfactory set and meet trade specifications.

Oxygen-free Copper—To meet a growing demand from consumers for a copper free from oxygen, three types of such material are now being commercially produced. One type is made by adding phosphorus in sufficient quantity to remove the last traces of oxygen and act as protection against reoxidation during casting. A second type removes the last of the oxygen by bringing the copper into intimate contact with charcoal and reducing gases in a closed pour-hearth and casting in a reducing atmosphere. A third type produces the cathodes in a brittle form and breaks them into granules which are washed, briquetted, heated in a reducing atmosphere and extruded into bars or rods. The pressure during extrusion causes the copper to coalesce.

All three of the above forms have excellent physical properties but the phosphorized copper is lower in electrical conductivity due to residual phosphorus.

Uses of Copper—The largest use of copper is as wire, followed by its use in alloys, principally brass. Because of its resistance to corrosion, it has a wide use in the form of sheet copper for protection of surfaces exposed to the atmosphere. Its use as tubing is also important.

The uses of copper in the United States between 1930 and 1939 are summarized in Table 6.

METALLURGY OF LEAD

The common procedure for the extraction of lead is based on the fact that unlike copper, lead does not readily combine with or dissolve iron. Since lead oxide is easily reduced to metallic lead, it is possible to produce a relatively pure product by direct fusion with coke in a shaft furnace, leaving the iron present to be slagged.

An outline of the usual practice in lead smelting is given in Figure 7.

The production of a rich concentrate from lead sulfide ores may be carried out by gravity methods if the lead sulfide is fairly coarse and not associated with other sulfides. If the lead mineral is finely divided or if other sulfides are present, differential flotation is commonly used.

The sulfide concentrate cannot be converted to lead by economical methods and must therefore be oxidized to remove the sulfur and form lead oxide preparatory to reduction.

TABLE 6—CONSUMPTION OF COPPER *

Purpose	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939
Electrical manufactures (a)	221,000	162,000	90,000	90,000	101,000	128,000	164,000	212,000	150,000	185,000
Telephones and telegraphs	122,000	70,000	27,000	18,000	18,000	18,000	26,000	40,000	30,000	39,000
Light and power lines (b)	130,000	85,000	49,000	31,000	36,000	55,500	72,000	83,000	62,000	67,000
Wire cloth	9,200	4,900	4,200	5,000	4,600	5,600	6,500	6,800	6,000	8,000
Other rod and wire	93,700	55,000	30,000	48,000	40,000	48,000	90,000	102,000	60,000	95,000
Ammunition	5,100	5,000	3,900	10,500	13,500	13,700	11,900	14,100	12,500	14,500
Automobiles (c)	87,000	61,600	32,300	49,000	63,000	95,000	108,000	112,000	55,000	85,000
Buildings (e)	50,000	45,000	29,000	36,000	36,000	49,000	71,000	70,500	67,500	89,000
Castings, n.e.s. (d)	55,400	36,000	27,000	36,000	36,000	36,000	39,000	40,000	31,000	33,000
Clocks and watches	2,600	2,000	1,500	2,800	2,200	2,400	3,400	4,000	3,000	3,600
Coinage	850	100	100	100	900	1,500	2,000	100	....	....
Copper-bearing steel	1,900	1,200	800	1,500	2,100	2,300	3,900	4,600	2,600	4,200
Fire-fighting apparatus	1,700	1,300	1,000	1,100	1,000	1,200	1,300	1,500	....	....
Radiators, heating	3,000	1,700	1,000	2,400	1,000	1,100	2,000	2,100	2,000	3,600
Radio receiving sets	13,000	10,000	7,000	11,500	12,500	16,000	24,000	23,100	21,000	27,000
Railway equipment (f)	8,600	1,800	700	800	2,100	1,800	4,000	7,100	1,700	2,700
Refrigerators (h)	15,000	13,000	9,000	11,400	15,700	15,400	15,000	13,500	6,700	10,000
Shipbuilding (h)	5,000	3,200	2,100	1,800	3,200	1,100	5,000	6,400	6,000	8,500
Washing machines	1,200	1,600	1,500	1,000	1,400	1,300	1,500	1,500	....	....
Water heaters, household	1,800	1,400	1,000	1,500	1,500	1,500	1,500	1,500	....	....
Air conditioning (g) (h)	....	....	....	....	3,800	4,600	6,400	7,200	6,000	6,000
Other uses	57,000	40,000	27,300	40,000	42,000	46,000	59,000	62,000	46,200	68,000
Manufactures for export	71,100	48,200	22,600	15,600	25,500	29,500	31,600	45,000	38,800	51,900
Totals	956,150	650,000	368,000	415,000	463,000	574,700	749,000	860,000	608,000	801,000
Use in pounds per person	15.52	10.43	5.77	6.60	7.31	9.01	11.66	13.31	9.34	12.21
Shipments by refineries (i)	808,784	600,754	335,965	381,729	417,110	578,239	808,953	878,186	521,675	845,230

* American Bureau of Metal Statistics, as reported in The Mineral Industry, Vol. 48, p. 163.

(a) Generators, motors, electric locomotives, switchboards, light bulbs, etc. (b) Transmission and distribution wire and bus bars. (c) Does not include starter, generator, and ignition equipment. (d) Bearings, bushings, lubricators, valves and fittings. (e) Excludes electrical work. (f) Includes air conditioning beginning with 1933. (g) Other than railway. (h) Exclusive of electrical equipment. (i) From primary refineries only.

Sintering Lead Concentrates—Unfortunately, lead oxide, particularly when contaminated with antimony or other oxides, has a low melting point and roasting lead sulfide by ordinary methods must be carried out below 750° C. if sticky charges are to be avoided. At these temperatures, much of the lead is converted

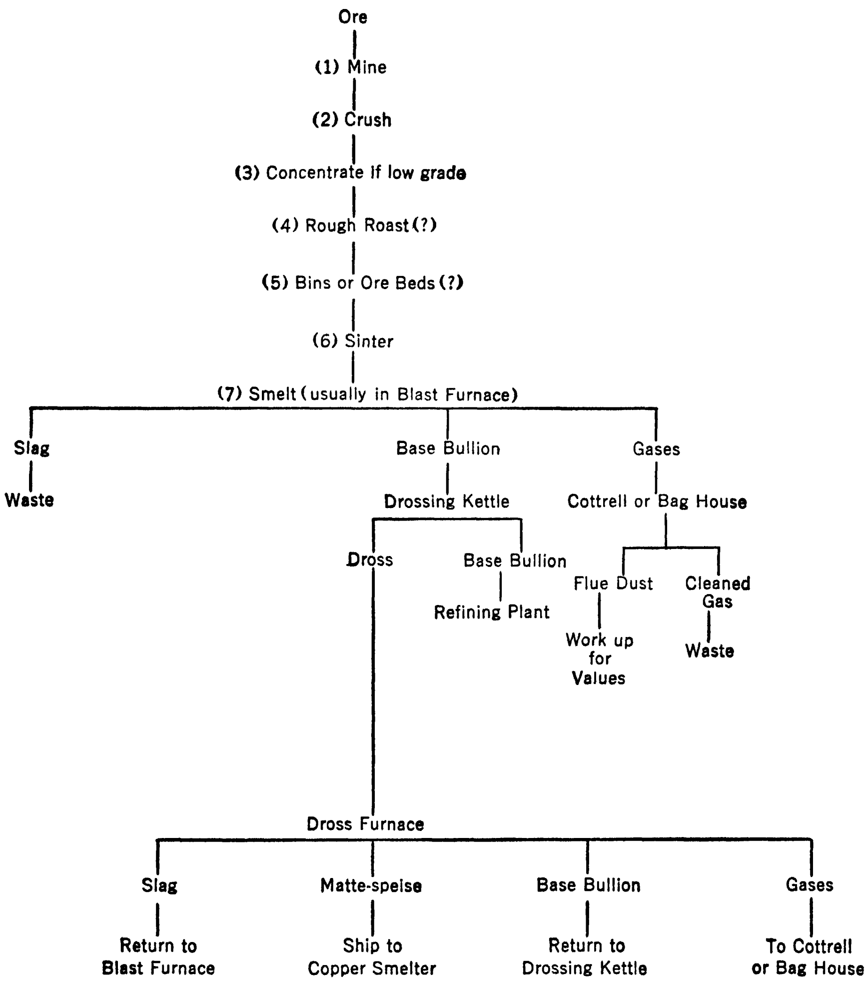


FIG. 7. Usual Treatment of a Sulfide Lead Ore.

Lead ores are mined on a less extensive scale than copper ores and almost entirely by underground methods.

to sulfate instead of oxide and these sulfates would be reconverted to sulfide during reduction. As a result, the standard practice for desulfurizing lead concentrates is to treat them on a sintering machine (see Figure 2). This treatment minimizes sulfate formation because of the high temperature reached and the fact that sulfurous gases are removed by the suction fan as fast as formed.

It has been found that the most satisfactory desulfurization is obtained by two passages over the machine, the products from the first passage being crushed and sometimes mixed with a small amount of raw concentrates before the second passage.

Smelting Sintered Concentrates and Oxidized Lead Ores—The usual equipment for smelting sintered lead concentrates and rich oxidized ores in the blast furnace is illustrated in Figure 8.

At the bottom of the furnace is a well insulated hearth or crucible which, during operation, is kept nearly full of molten lead on which floats the slag. Above the crucible is a row of steel water jackets, pierced just above the hearth by a row of tuyeres. Above the first tier of jackets may be a second tier similar to the first, or, if preferred, a belt of firebrick extending to the feed floor.

The furnace is usually oblong in horizontal cross-section. The width at the tuyeres varies from 42 to 60 inches and the length from 15 to 20 feet or more. The height from tuyeres to feed floor is 18 to 25 feet. There is no brick lining inside the water jackets. The capacity of the furnaces varies from 300 to 600 tons of charge per day.

The lead ore and sinter mixed with such fluxes as are necessary to produce a free-running slag low in lead (approximately 1 per cent) is charged near the top of the furnace with sufficient coke to fuse the charge and reduce the lead compounds (usually 12 to 15 per cent of the weight of the ore and flux). A proper slag will have the composition: SiO_2 22-28 per cent, FeO 33-38, CaO + MgO 17-22, ZnO 10-20, S 1-2, Pb 1-0. The fluxing materials such as lime and silica are added in quantities sufficient to produce such a slag.

Cold air at moderate pressure is introduced through the tuyeres piercing the water jacket just above the crucible. The fused charge trickles to the crucible where the lead separates from the slag. The hot molten metal dissolves a considerable amount of copper, iron and lead sulfides as well as arsenic and antimony compounds. It is withdrawn continuously through a channel or "siphon tap" which extends from the inside of the crucible near the bottom to a shallow basin or "lead well" situated on the outside of the crucible just below the tuyeres. An examination of the figure will show that the crucible always remains full of lead with a shallow bath of slag on its surface. The height of metal in the lead well depends on the pressure within the furnace so that with constant conditions, as fast as it is reduced from the charge it will flow from the crucible through the siphon tap to the lead well and thence to a receiving ladle.

The slag is tapped at short intervals through a tap hole just above the metal level in the crucible. After flowing through two outside settlers to allow any occluded metal to fall out, it is received in a slag pot and removed to the dump.

Preliminary Refining—*Drossing the Lead.* The metal from the lead well is collected in a large steel or cast iron kettle and allowed to cool to just above 327° C., the solidification point. During cooling it may be agitated by poling, or with steam, or by mechanical stirrers. This operation allows sulfides, oxides and certain other dissolved impurities to come out of solution and be collected, together with mechanically entrained materials, as a dross which is skimmed from the surface of the metal. Sulfur is then often stirred in to unite with any alloyed copper, which then floats to the surface as sulfide, which is skimmed and added to the primary dross. The drossed lead is cast and shipped to the refinery.

Treatment of Lead Dross. This material, amounting to 10 to 25 per cent of the metal from the lead well, is smelted with fluxes in a small reverberatory

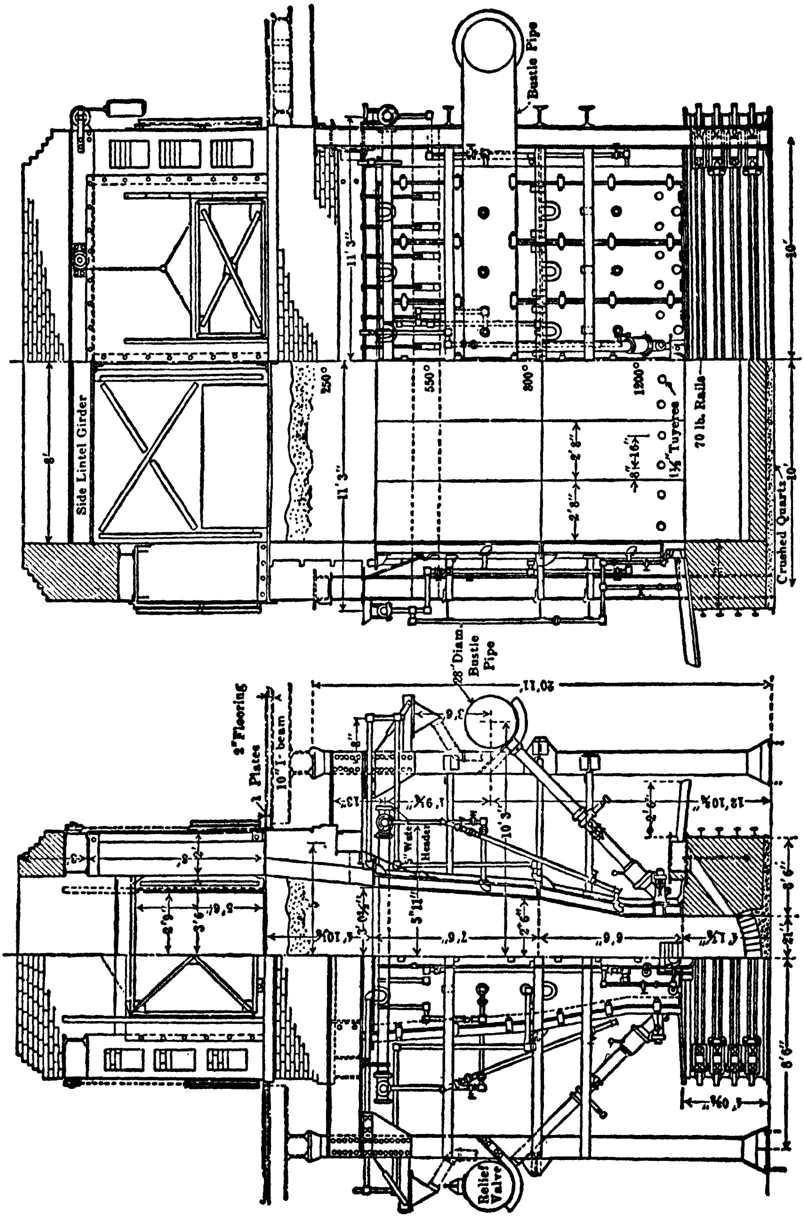


FIG. 8. Closed-top Lead Blast Furnace. (Austin, "Metallurgy of the Common Metals")
Note the dimensions and other features of the drawing.

furnace. There are three products from this operation: an impure metal which is added to the blast furnace metal in the drossing kettle, a slag sufficiently high in lead to justify its addition to the blast furnace charge and a matte containing iron, copper and lead sulfides with some precious metals, arsenic and antimony compounds, etc., which is sold to a copper smelter where it is usually added to the converter charge. This separation is based on the equilibrium of three liquid phases, a condition which is so unusual as to be almost unique.

Refining Lead—The first step in refining lead is to remove the arsenic, antimony, tin and bismuth which are usually present to a greater or less degree in drossed lead. Since these elements are alloyed with the lead and tend to make it hard, their removal is commonly called "softening" the lead.

The second step in refining lead is to remove and recover the precious metals which are usually present to some extent. Since silver commonly predominates, the operation is spoken of as "desilverizing."

"Softening" Lead—Arsenic, antimony and tin are readily removed by selective oxidation. It may be carried out in a small reverberatory furnace holding 100 to 300 tons where, by subjecting the bath to an oxidizing furnace atmosphere for 12 to 24 hours, at a bright red heat, the above impurities are oxidized and combine with lead oxide to form lead arsenate, antimonate and stannate which float to the surface and are removed. Addition of litharge (PbO) to the furnace or agitation with air will speed up the softening operation. The skimmings from the softening furnace are worked up for antimonial lead.

Softening processes have been patented [5] in which the arsenic, antimony and tin are oxidized in the presence of soda salts to form sodium compounds rather than lead compounds. These processes have some theoretical advantages but have been used commercially to only a minor extent.

Bismuth is less easily oxidized than lead and therefore cannot be removed by selective oxidation. Until recently, bismuth-bearing leads have been treated by the Betts electrolytic process [6] in which the lead is deposited on the cathode and the common impurities including bismuth and the precious metals remain as a slime. (See section at end of chapter.) The Betts process gives excellent technical results but its high cost prevents its general use.

A process for bismuth removal known as the "Betterton process" [7] has recently been adopted in some refineries. It is based on the fact that a calcium-magnesium alloy stirred into the molten lead will unite with the bismuth and form a dross which can be skimmed from the surface and worked up for bismuth.

Desilverizing Lead—The usual procedure for removing the precious metals from lead is known as the "Parkes process" and is based on the fact that if zinc is stirred into lead carrying precious metals, it unites with them to form compounds such as Ag_2Zn_3. When the lead is cooled nearly to the solidifying temperature, these compounds float to the surface and may be removed.

The steps in the process are as follows:

(1) Heat the softened lead in cast iron or steel kettles holding 60 to 200 tons.
(2) Skim off the dross.
(3) Add sufficient zinc to saturate the lead (0.6 per cent by weight) and enough in addition to form compounds with the precious metals. Much of this zinc may be in the form of second skimmings from the previous bath (see step 9 below).

[5] U. S. Pat. 1,804,054.
[6] McIntyre, P. F., Trans. A. I. M. E., *121*, 271 (1936).
[7] Betterton, J. O. and Lebedeff, Y. E., Trans. A. I. M. E., *121*, 205 (1936).

(4) Raise the temperature nearly to red heat and stir thoroughly with a motor-driven stirrer.
(5) Cool until a crust begins to form around the edge of the kettle.
(6) Skim the alloy which has risen to the surface, put it in a cast iron cylindrical press having a perforated bottom and squeeze out as much of the occluded lead as possible by a hydraulic or steam-driven plunger. The cakes consisting of the compounds of precious metals and zinc contaminated with considerable lead are subsequently worked up.
(7) Add more zinc, heat and stir.
(8) Cool until a considerable solid ring of metal adheres to the edge of the kettle.
(9) Skim thoroughly without pressing, depositing the skimmings in containers beside the kettles. The skimmings contain considerable excess zinc and much occluded lead. They are to be added to the next lot of lead, so the principal object is to remove as much of the precious metals as possible rather than keep the weight of skimmings down.

Removal of Residual Zinc from Desilverized Lead—The lead, after desilverization by the above process, contains about 0.6 per cent zinc. This may be

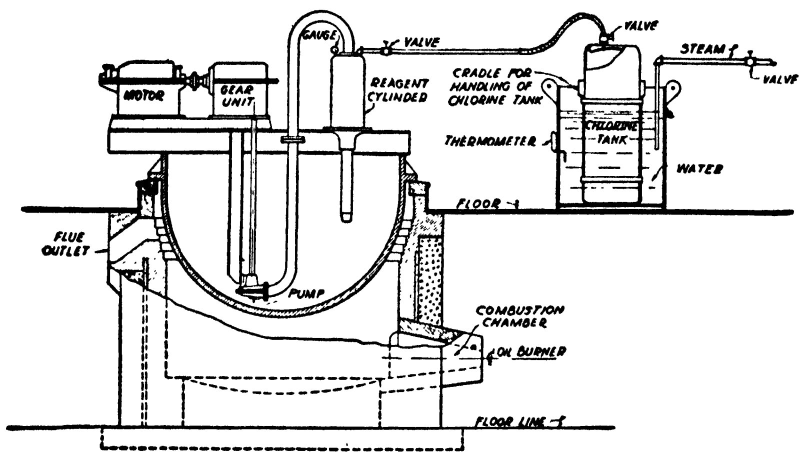


FIG. 9. Betterton Dezincking Machine.

Note the kettle arrangement, the centrifugal pump for circulating the lead, the chlorine tank and the reaction chamber.

removed by selective oxidation in a reverberatory furnace but the method being increasingly used is to treat the molten metal in a kettle with chlorine gas. The zinc will be completely converted to chloride and float on the surface before the chlorine begins to form any appreciable amount of lead chloride. The apparatus for this operation is shown in Figure 9.

The lead, after thoroughly cleaning the surface with caustic soda, is cast into bars for market.

Treatment of Zinc Skimmings—The pressed skimmings from the desilverizing kettle are heated in a graphite retort to a temperature above 937° C., the boiling point of zinc. The zinc distils off and is condensed for re-use, leaving the precious metals and lead as a rich bullion.

The lead is removed from the precious metals by a selective oxidation process known as "cupellation." The bullion is heated to a bright red heat in a small reverberatory type furnace with a removable hearth lined with a mixture of limestone and fire clay and, sometimes, Portland cement. A blast of air is played on the surface, oxidizing the lead to PbO which floats as a liquid on the surface, which is drained off as fast as it forms. The lead oxide may be returned to the blast furnace or used as an oxidizing agent in the softening furnace.

When all the lead is removed, the precious metals are cast into anodes for electrolytic parting.

The workability of this process is obviously dependent on the relative rates of the different reactions involved. The individual reactions are not subject to control, but the rates fortunately balance out so that a considerable proportion of the lead can be recovered as metal. The function of the coal is apparently merely that of maintaining the necessary temperature.

Treatment of Lead Concentrates in Ore Hearths—In the St. Louis district a considerable quantity of low-silica lead concentrates, practically free from silver, is treated in equipment called "ore hearths." The operation is simple and relatively crude but 60 to 80 per cent of the lead content of the concentrates is recovered quickly and cheaply.

The apparatus consists of a shallow hearth filled with molten lead with a hood above it for carrying off the considerable amount of fume formed, for later recovery.

A charge of rich lead sulfide concentrate mixed with coal is fed intermittently to the back of the hearth and a light blast of air forced through it. The following reactions take place:

$$\begin{aligned} 2PbS + 3O_2 &= 2PbO + 2SO_2 \\ 2PbO + 2SO_2 + O_2 &= 2PbSO_4 \\ PbS + 2PbO &= 3Pb + SO_2 \\ PbS + PbSO_4 &= 2Pb + 2SO_2 \\ PbS + 3PbSO_4 &= 4PbO + 4SO_2 \end{aligned}$$

The lead is ladled out as fast as it forms. The gangue material forms a sticky slag with some of the PbO and is raked off the surface for subsequent reduction in a blast furnace.

The fume is collected in bag houses and returned to the hearth, making an appreciable circulating load.

Uses of Lead—The principal uses of metallic lead are for grid plates in wet storage batteries, cable covering, solder, type metal, ammunition and sheet lead. The distribution of the uses in the years 1933 to 1939 is shown in Table 7.

In the battery plates, type metal, ammunition and much of the sheet lead, antimony is added as a hardener and to promote resistance to corrosion. In solder the lead is alloyed with various amounts of tin.

One of the principal uses of lead is as oxide or basic carbonate for pigments.[8]

[8] See Chapter 26, White Lead.

TABLE 7—LEAD CONSUMPTION IN THE UNITED STATES *

(In tons of 2000 lb.)

Purpose	*1933*	*1934*	*1935*	*1936*	*1937*	*1938*	*1939*
White lead..........	59,100	64,500	80,000	85,500	86,000	71,000	75,000
Red lead and litharge †	38,000	42,000	47,500	54,000	57,000	43,000	57,200
Storage-batteries....	147,000	163,000	175,000	191,000	192,000	167,000	198,000
Cable covering......	31,400	35,200	38,900	61,400	90,000	60,000	74,700
Building............	26,000	30,000	32,000	40,000	45,000	36,000	50,000
Automobiles........	5,000	7,300	10,000	11,100	12,000	6,000	8,900
Railway equipment..	200	1,100	500	2,400	3,800	1,200	......
Shipbuilding........	100	200	200	200	300	300	......
Ammunition........	32,300	34,800	29,200	32,500	39,500	31,200	42,300
Terne plate.........	2,500	2,600	4,700	6,200	6,400	4,300	5,400
Foil................	22,500	16,200	15,900	28,500	21,700	22,000	21,800
Bearing metal.......	11,400	12,100	13,000	16,500	15,000	9,000	12,800
Solder..............	16,000	16,000	20,000	22,000	22,000	15,000	20,000
Type-metal.........	11,000	13,000	15,000	17,000	17,000	12,000	14,000
Calking............	12,000	10,000	12,000	13,500	15,000	12,000	16,000
Castings............	5,000	5,000	5,000	5,750	6,000	6,000	7,500
Other uses ‡........	30,000	35,000	40,000	46,000	50,000	50,000	63,700
Totals..........	449,700	488,000	538,900	633,550	678,700	546,000	667,000

* Amer. Bur. of Metal Statistics. The Mineral Industry, Vol. 48, p. 353. These estimates are for the total consumption of lead irrespective of whether its origin be primary or secondary. Antimonial lead is included and the manufacture of lead for export under drawback provisions is included.

† Not including oxides for storage batteries.

‡ Conjectural. Under "other uses" the largest item in recent years has been the manufacture of lead tetraethyl for tempering gasoline, which has been increasing rapidly. Also included are lead for brass-making, collapsible tubes, lead-lined pipe, lead-headed nails, and many miscellaneous uses.

METALLURGY OF ZINC

Zinc, like copper and lead, occurs in nature principally as sulfide. Carbonate occurs in the upper layers of sulfide deposits and occasional deposits consist of oxide and silicate, but these are rare. A large, unique deposit of zinc minerals consisting of the minerals willemite (Zn_2SiO_4), zincite (ZnO) and franklinite $(Fe, Mn, Zn) O \cdot (FeMn)_2O_3$ occurs near Ogdensburg, New Jersey.

Methods for the extraction of zinc by fire methods must have been developed around the fact that under normal conditions of reduction by carbon or carbonaceous gases, the reducing temperature of zinc oxide lies above 937° C., the boiling point of the metal. A further limitation is the fact that zinc vapor is readily oxidized by CO_2. This means that reverberatory or blast furnaces are not suitable for the treatment of zinc ores. The equipment universally used is some type of reduction retort attached to a condenser for collecting the zinc vapor.

An outline of the procedure for recovering zinc from sulfide ore is given in Figure 10.

Successful operation of the retort requires a high grade concentrate, usually running about 60 per cent zinc.

Any zinc entering the retort charge as sulfide or sulfate remains unvolatilized so it is essential that the desulfurizing operation be as complete as possible. It is usual practice to produce a roasted product with about 1 per cent sulfur.

Because of the difficulty in preventing considerable sulfate formation in roasting zinc sulfide concentrates in hearth roasters and the high temperatures required to decompose $ZnSO_4$, it has become common practice to give the concentrate a partial roast in a multiple hearth roaster followed by sintering to complete the desulfurization. The sinter is then crushed to a size suitable for the subsequent reduction in the retort.

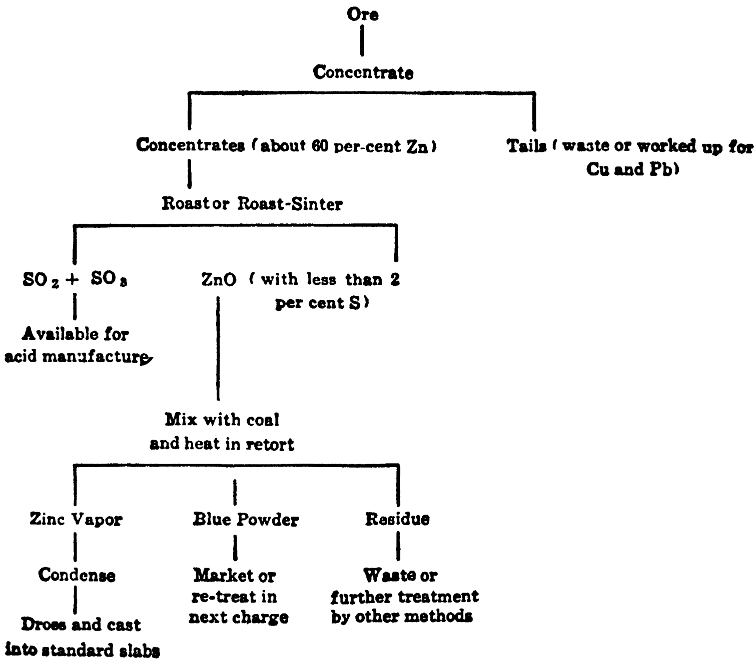


FIG. 10. Outline of Zinc Production from Sulfide Ore.

Reduction of Desulfurized Zinc Concentrates—A Belgian type zinc retort furnace which represents the most common practice is shown in Figure 11. The retorts are cylinders about 5 feet long by 9 inches diameter inside and are made of fire clay or a mixture of fire clay and silicon carbide. The back end is closed and the front end open. The condensers are of clay shaped like a frustum of a cone. They are open at both ends with the large end inserted in the open end of the retort. They are cooled wholly by radiation.

The furnace chamber has a longitudinal vertical partition extending nearly to the top, dividing the chamber into two parts each containing 100 to 200 retorts in 4 or 5 vertical tiers. The back ends of the retorts are supported by projections from the central wall and the front end rests in an aperture in the front wall.

The furnace is gas fired and is equipped with regenerators for preheating the air and also the gas, if the latter is free from hydrocarbons.[9]

[9] For the operation of regenerators, see Chapter 23.

A furnace campaign covering charging, distilling and discharging usually takes 24 hours and has the following steps:

(1) Charge the hot, empty retorts with roasted ore mixed with about 35 per cent non-coking coal.
(2) Put the clay condensers in place and lute the joint between condensers and retorts with clay.
(3) Continue heating until the charge has been raised to above 1150° C. causing the reaction $ZnO + C$ (in excess) $= Zn + CO$. The zinc is in the form of vapor and passes with the CO gas into the condensers where the zinc deposits as liquid and the CO passes on to be burned at the mouth of the condensers.
(4) Collect the zinc by scraping it from the condensers into a collecting kettle supported on a movable crane. This is done three times during a campaign.
(5) Remove the condensers, clean out the residue from the retorts and start a new campaign.

The life of a clay retort is between 30 and 40 days and, of the more expensive silicon carbide retorts, several months.

The zinc recovery is over 90 per cent, with the metal contaminated by lead and cadmium, if these occur in the charge.

Continuous Retorts—Although most of the zinc recovered by fire methods is produced in small retorts, operated intermittently, a continuous retort developed by the New Jersey Zinc Company is now in use in a few plants.[10] It consists of a vertical, rectangular, silicon carbide retort about 6 feet by 1 foot in cross-section and 30 feet high. It is heated by gas burned in chambers adjoining the side walls.

The desulfurized concentrates are mixed with reducing carbon and are briquetted, using a tar-pitch binder. The briquettes are then heated to red heat to distil off hydrocarbons and are charged hot at the top of the retort, using a trapped feeding device. The briquettes pass by gravity through the retort and are heated to above 1150° C. The products of reaction pass out through a large condenser made of refractory material attached to the retort at the top of the heating chamber. The spent briquettes are discharged at the bottom of the retort over a rotating cylinder to a water bosh from which they are withdrawn by a screw discharge.

These retorts have many theoretical advantages but thus far the older units have been successful in competing with them.

Electric Furnace Production of Zinc—In the electrothermic method, roasted zinc ores or oxidized ores are smelted with suitable fluxes in a closed-type electric furnace. Charcoal or coke is the reducing agent most commonly used. At the temperature at which the furnace operates the reduced zinc is in the form of vapor and leaves the furnace mixed with the gases produced in the reduction, almost entirely carbon monoxide. The gangue of the ore is fluxed with limestone or silica or both to produce a slag, fluid at the temperature of the furnace operation and basic enough to prevent solution of too much zinc.

The furnace gases carrying the zinc vapor are sent to condensers where by

[10] Bunce, E. H. and Handwerk, E. C., Trans. A. I. M. E., *121,* 427 (1936).

quick cooling, zinc can be dropped in the form of a powder. Or by more elaborate condensing apparatus a portion can be dropped as molten zinc and

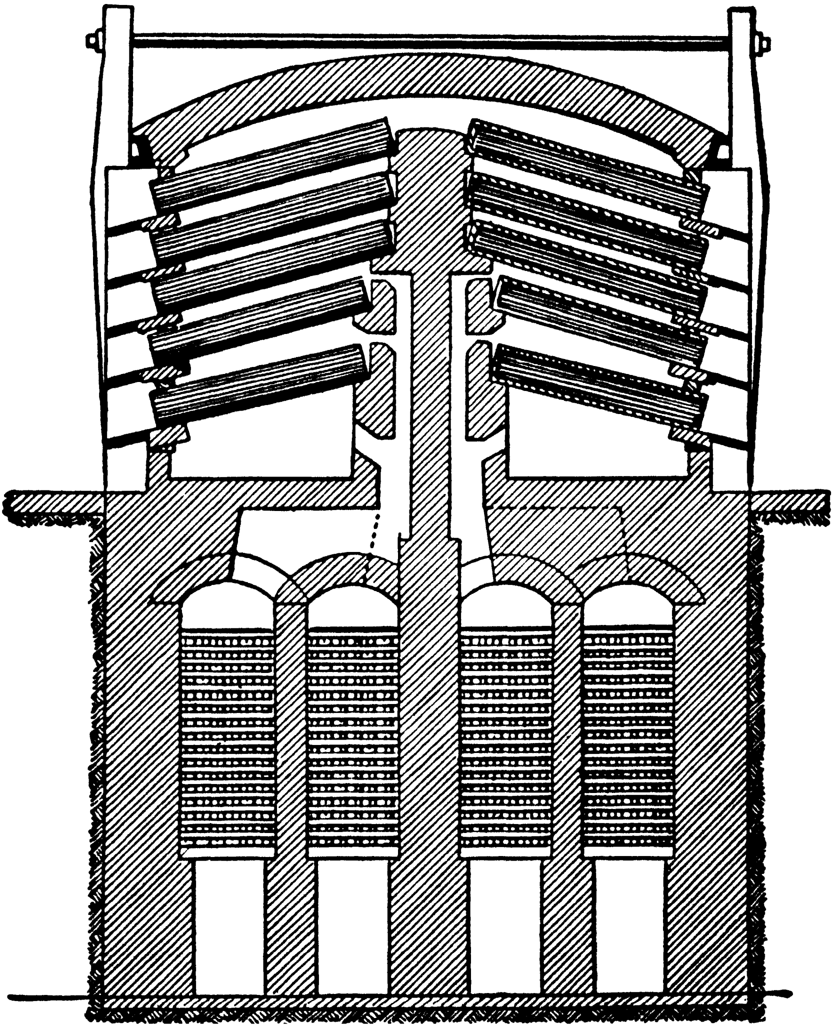


FIG. 11. BELGIAN RETORT FURNACE.

Note the regenerative chambers for gas firing and the method of introducing the gas-air mixture. Note also the method of supporting the retorts and their angle of inclination. The working floor is indicated above the regenerative chambers.

the remainder as powder. Though this electrothermic process has no important place in the industry today, it is used for the redistillation of zinc waste to produce blue powder.

Purification by Distillation—Zinc may be refined in batch lots by redistillation. The more volatile cadmium (b.p. 778° C.) is recovered as a first condensate and the less volatile constituents remain in the residue.

A continuous redistillation process developed by the New Jersey Zinc Company, is now in use consisting of two connecting rectifying columns.[11] The molten impure zinc is fed to the first column which is maintained at a temperature just above 937° C., the boiling point of zinc. The non-volatile constituents trickle to the bottom while the zinc and cadmium pass to the second column, which is maintained at a temperature just above 778° C., the boiling point of cadmium. Here the zinc condenses and trickles to the bottom while the cadmium passes to a condenser attached to the top of the second column.[12]

The invention of this distillation purification was an important advance. It effected the removal of cadmium much more completely than any other available process. This led to a great improvement of zinc die-castings, which previously had been of indifferent quality.

Electrolytic Zinc—See the section on Electrometallurgy at the end of this chapter for a discussion of the production of electrolytic zinc.

Production of Zinc Oxide—Zinc oxide is commonly produced by two methods usually called the "French process" and the "American process."

In the French process metallic zinc is heated in a retort to the boiling point; the resulting vapor is mixed with air and burned to finely divided oxide which is recovered by filtering through cloth bags. If the original zinc is pure, the product is correspondingly pure and may be used for pharmaceutical purposes.

In the American process low grade oxide ores are mixed with coal, placed on a grate and subjected to a gentle blast of air from below. Sufficient excess coal is used to maintain reducing conditions together with a temperature which will reduce and volatilize zinc. The vapor is reoxidized in the upper part of the furnace or in the flue system and the finely divided oxide is collected by filtering through cotton bags. The purity of the product depends on the character of the charge. If the charge contains lead or cadmium, these elements are found in the product.

Most of the oxide produced by the American process is used in paint, rubber or enamel manufacture.[13]

Originally the production of oxide by this process was all carried out in batch operations on fixed grates. Recently a method has been developed by the New Jersey Zinc Company, whereby moving grates are used with suitable other equipment to make the process continuous.[14]

Manufacture of Zinc Dust—Finely divided metallic zinc known as zinc dust may be produced by pouring a thin stream of molten zinc in front of a jet of high pressure air. The molten zinc is disintegrated into fine particles and solidified so rapidly that only an extremely small amount of surface oxidation takes place on the particles.

Uses of Zinc—Zinc in sheet form, plane or corrugated, is used for many purposes but the principal use is as a coating for iron and steel commonly called

[11] Peirce, W. M. and Waring, R. K., Trans. A. I. M. E., *121*, 445 (1936).
[12] See Chapter 2 for a discussion of distillation.
[13] See Chapters 25 and 39.
[14] Bunce, E. H. and Haslam, H. M., Trans. A. I. M. E., *121*, 678 (1936).

galvanized iron. The second largest use is in brass and similar alloys. The data on distribution of uses, 1932 to 1939, are given in Table 8.

TABLE 8—ESTIMATED CONSUMPTION OF ZINC IN THE UNITED STATES *

(In short tons)

Use	*1932*	*1933*	*1934*	*1935*	*1936*	*1937*	*1938*	*1939*
Galvanizing:								
Sheets	52,500	74,400	83,300	110,000	132,000	135,000	108,500	147,500
Tubes	16,000	22,600	22,000	25,000	36,000	37,000	29,300	43,000
Wire	12,100	21,700	20,000	25,000	30,000	33,000	23,600	30,900
Wire cloth	4,400	4,800	4,000	5,000	6,000	7,000	5,600	7,000
Shapes †	24,000	24,500	22,700	30,000	38,000	40,000	31,000	46,600
Total	109,000	148,000	152,000	195,000	242,000	252,000	198,000	275,000
Brass making	66,000	94,000	98,000	112,000	168,000	169,000	102,000	175,000
Sheet zinc	40,000	41,300	40,900	56,500	55,000	58,000	46,000	62,000
Die castings	17,000	26,000	32,000	55,500	72,000	88,000	48,000	84,000
Other purposes ‡	27,000	41,000	37,000	42,000	48,000	39,000	27,000	30,000
Totals	259,000	350,300	359,900	461,000	585,000	606,000	421,000	626,000

* Am. Bur. Metal Statistics, The Mineral Industry, Vol. 48, 604.

† Includes hardware, chains, and all other articles not elsewhere mentioned. The estimates for the use of zinc under this head, and also for wire cloth, are probably incomplete; the enumeration for 1934 includes figures from consumers not previously accounted for.

‡ Includes slab zinc used for the manufacture of French oxide, lithopone, atomized zinc dust, wire, slush castings, and for desilverization of lead.

METALLURGY OF NICKEL

Although some nickel is produced from the mineral garnierite, a hydrosilicate of nickel and magnesium, found on the island of New Caledonia in the South Pacific Ocean, the principal part of the world's supply comes from sulfide deposits situated near Sudbury, Ontario. The nickel occurs here associated with copper and its extraction is closely associated with the extraction of copper.

Extraction of Nickel from Copper-Nickel Sulfide Ores—The ore is mined and concentrated by methods exactly the same as those used for copper ores. The concentration is by differential flotation. Two concentrates are obtained, one sufficiently high in copper and low in nickel to be worked up directly for copper, and another carrying most of the nickel but also a considerable amount of copper. The latter is smelted in a reverberatory furnace to produce a copper-nickel-iron matte which is blown in converters to the point where the iron sulfide has been eliminated, leaving a matte with about 75 per cent Cu + Ni. It is at this point that the real metallurgy of nickel begins.

Two commercial methods are used for the extraction of nickel from copper-nickel matte. These are the Orford or "Top and Bottom" process and the Mond process.

Orford Process. This process depends on the fact that if copper-nickel matte is fused with sodium sulfide and the mixture allowed to cool slowly, it will separate into two layers, the upper being a mixture of copper and sodium sulfides, containing only small amounts of nickel sulfide, while the bottom layer is nickel sulfide containing only small amounts of copper sulfide.

An outline of the process is given in Figure 12.

The fusion is carried out in a small blast furnace using coke as fuel. The sodium sulfide required for the operation is obtained by adding sodium sulfate to the charge. The sulfate is reduced to sulfide by the coke. The fused mixed sulfides are run from the furnace into large conical pots where they are allowed to cool and separate after which the pots are dumped and the "tops" separated from the "bottoms."

The first bottoms are re-treated to effect a more complete removal of the copper.

The second bottoms carry most of the nickel and only small amounts of cop-

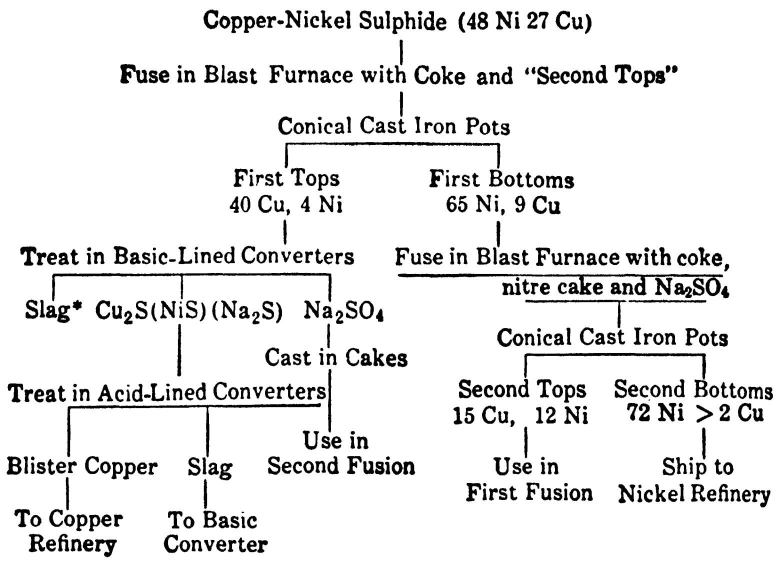


FIG. 12. Outline of Orford Process.

* This slag accumulates in a sticky condition in the converter. About every four hours the temperature is raised, the slag poured out and sent to the reverberatory smelting furnace.

per. They also carry metals of the platinum group in sufficient quantity to make this district one of the world's most important platinum producers.

The final extraction of nickel from this material is outlined in Figure 13. First the sulfur is removed by roasting the crushed sulfide, then the resulting oxide is reduced by mixing with carbon and fusing in a reverberatory furnace. The resulting metal is cast into anodes and electrolyzed to eliminate the remaining copper and other impurities and recover the nickel as cathodes and the platinum as anode slimes.

Mond Process. The basis of this process is the fact that finely divided nickel heated to 80-90° C. in an atmosphere of CO gas will form the volatile compound nickel carbonyl ($Ni(CO)_4$) which on heating to a higher temperature decomposes into Ni and CO.

The process is simple in principle but the reactions involved require careful control and considerable retreatment of materials is required to obtain the high extractions necessary. For these reasons the amount of matte treated by this process is much less than that treated by the Orford process. Some prefer Mond process nickel because it is free from cobalt whereas cobalt follows the nickel in the Orford process.

Originally the raw material for this process was the copper-nickel matte from the converters. At present it is common practice to start with nickel bottoms from the Orford process.

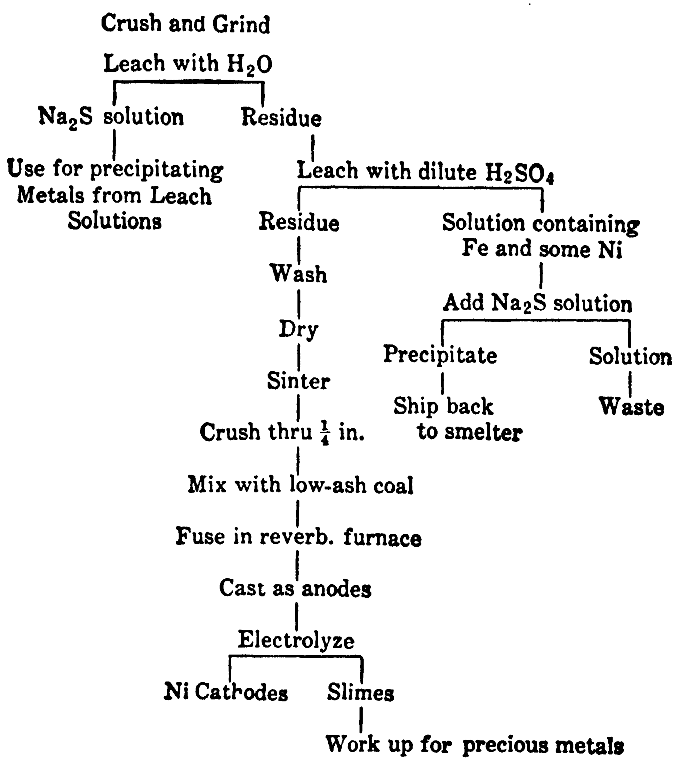


FIG. 13. Flow Sheet Showing Production of Pure Nickel from Orford Bottoms.

Omitting the various retreatments, the steps in the process may be stated as follows:

(1) Crush and roast the nickel sulfide "bottoms" to produce oxide.
(2) Reduce the nickel oxide to finely divided nickel. This is done in a multiple hearth furnace made of cast iron with hollow hearths in which gas is burned to raise the temperature in the furnace to 350° C. At this temperature the oxide is reduced to metal by passing water gas ($H_2 + CO$) through the furnace, countercurrent to the nickel oxide.
(3) Pass the nickel powder through a furnace similar to the one used for reducing the oxide. The temperature of the furnace is kept between 75° and 90° C. and CO gas is passed over the metal to form volatile nickel carbonyl. The residue is worked up for copper, cobalt and platinum.

(4) The volatilized carbonyl is passed over nickel shot, heated to about 150° C., which causes it to decompose, depositing the nickel on the surface of the shot and freeing the CO for reuse.

Uses of Nickel—The principal use of nickel is as an alloying constituent in steel, but such alloys as monel metal (67 per cent Ni and 28 per cent Cu) and nickel silver (50-60 per cent Cu, 25-20 per cent Ni and 25-20 per cent Zn) are important. The use of nickel as a plating on brass and other alloys to protect them from corrosion, although accounting for little tonnage, is also important.[15]

MISCELLANEOUS RECOVERY OPERATIONS

Because of space limitations it is impossible to give complete descriptions of the procedures used to extract all the non-ferrous metals from their ores. Most of the principles of smelting, leaching and refining have already been discussed but several others may well be mentioned.

(1) The fact that the trioxides of arsenic and antimony are volatile at low temperatures makes it possible to roast low grade ores containing these elements and, by collecting the fumes, obtain a concentrated product to be used as such or subsequently reduced.
(2) Antimony sulfide is easily fused, making it possible to remove it from rich ores at a relatively low temperature. The resulting sulfide may be reduced to antimony by heating with iron.
(3) Gold is frequently recovered from its ores by means of mercury which dissolves the gold, forming an amalgam. The mercury is then distilled and recovered for reuse leaving the gold as residue. Most of the gold is obtained by leaching the finely ground ore with solutions containing small fractions of a per cent of NaCN. The reaction is

$$2Au + 4NaCN + \tfrac{1}{2}O_2 + H_2O = 2AuNa(CN)_2 + NaOH$$

The gold cyanide is soluble and is removed from the sludge by filtration. The metal is recovered by the reaction of the cyanide with zinc.

$$2NaAu(CN)_2 + 2Zn + 2H_2O = 2Zn(CN)_2 + 2Au + H_2 + 2NaOH$$

(4) A great deal of silver is recovered as one of the by-products in lead and in copper smelting, but some is extracted from ores by leaching with sodium cyanide solutions.
(5) Metallic chromium and tungsten are produced by sintering the ores with sodium carbonate to form sodium chromate or tungstate which are leached from the contaminating materials and by a series of chemical operations precipitated from solution and converted to the pure oxides. These are subsequently reduced to metal.
(6) Mercury is obtained by direct roasting of the sulfide ore at just below red heat. Since this is above the boiling point of mercury (357° C.) and since mercury is not oxidized at this temperature, it passes off as a metallic vapor which is readily condensed to liquid mercury.

$$HgS + O_2 = Hg + SO_2$$

[15] For a discussion of the use of nickel in alloys, see Chapter 23.

The recoveries of aluminum, magnesium, calcium and beryllium are discussed in a later section of this chapter.

Such metals as silver, tin, vanadium, molybdenum, manganese, tantalum, etc., are for many purposes highly important, but since their extraction uses the fundamental procedures discussed in connection with other metals, they will not be considered here, but references to their metallurgy will be found in the Reading List at the end of this chapter.

NONFERROUS ALLOYS

Because of the fact that many metals are made harder and stronger and more resistant to corrosion by the addition of one or more other elements, the use of alloys is very extensive and the development of new useful alloys is continually the subject of extensive research. When the large number of metals is considered together with additional nonmetallic elements available for alloying, it is evident that the field is practically unlimited.[16]

Microscopic and X-ray studies of alloys supplemented by spectroscopic analysis have pointed the way to systematic development of useful alloys, particularly those whose properties are subject to change by heat treatment. The subject is so large and the number of alloys so great that even the citing of examples will not be attempted here.

Alloying technique is also being improved. In cases where there is a wide difference in melting point between the elements to be used or where one may be easily oxidized or volatilized, it is common practice to make up master alloys containing a known excess of the minor constituent and add this alloy in calculated amounts. For example, if a copper alloy were desired containing a small amount of silicon, the latter element would be added in the form of a rich silicon-copper alloy previously prepared.

In preparing alloys it is important to prevent or at least minimize oxidation during melting and also to prevent overheating which tends to promote gas absorption. In the brass and bronze industry it has become standard practice to use electric induction furnaces for melting because of the possibility of accurate control of furnace conditions.

In casting alloys it is important to have suitable molds. If the molds are made of metal, the surface should be coated with a mold wash which will not give off gases, will prevent the casting from sticking to the mold surface and give a smooth finish to the casting.

Care should be taken to pour the metal at a suitable temperature, usually less than 100° C. above the melting point of the alloy. Also care should be taken to minimize oxidation during pouring.

Powder Metallurgy—The term "powder metallurgy" is used to describe a procedure of growing importance whereby metals are produced in finely divided form and either in a pure state or mixed with other elements are pressed into finished shapes or into forms which may be subsequently fabricated into finished shapes. Annealing, or "sintering" as the operation is frequently called, usually follows the pressing operation and sometimes precedes it.

[16] See Chapter 23, The Metallurgy of Iron and Steel, for a discussion of the alloy steels.

One of the earliest applications of powder metallurgy was in the production of tungsten wire for lamp filaments or other purposes. This was patented in 1909 by W. D. Coolidge of the General Electric Co. The tungsten oxide powder was reduced by hydrogen at temperatures much lower than the melting point of the metal. The resulting metal powder was pressed, swaged at red heat and drawn into wire. It was later found that a small amount of thoria mixed with the tungsten powder before pressing inhibited grain growth during subsequent annealing and made the final lamp filament less liable to failure during vibration.

One interesting and valuable attribute of powder metallurgy is that it opens the way to the production of materials which cannot be successfully produced by fusion. For example, graphite may be mixed with metallic powders and the mixture pressed and heated to form a bearing which requires no lubrication. It is also possible to mix a highly abrasive, very hard material having a high melting point such as tungsten carbide with a metallic powder and by pressing and sintering, form it into a valuable cutting tool.

Numerous other applications of powder metallurgy are being continually developed and, although it may never become a serious competitor of casting or forging, it will make possible the development of valuable unique products which will be of great service to industry.

Metal powders may be made by reducing finely divided oxides as in the case of tungsten, but some powders are more conveniently made by electro-deposition in cells where conditions are controlled to give pulverulent rather than coherent electrodeposits.

A third method for making powder is to disintegrate solid metals by some convenient method.

Where finely divided oxides are used, these may be prepared by grinding natural oxide minerals or artificial oxides. For example, iron powder is made by reducing high grade natural minerals such as hematite or magnetite or by reducing the oxide scale formed by heating iron or steel.

The reduction of oxides may be accomplished by heating in contact with hydrogen or other reducing gases. For complete reduction, precautions must be taken to maintain a temperature sufficiently high and to remove the gaseous products of reduction so that the reaction may go to completion.

Oxides of chromium, titanium and similar oxides difficult to reduce are being successfully treated with hydrogen added in the form of calcium hydride. The hydride mixed with the oxide gives off, on heating, large volumes of hydrogen gas which, being released at the surface of the oxide to be reduced, at once combines with the oxygen and the resultant water vapor is promptly swept out by the excess of released hydrogen.

A variety of procedures are used for compressing the metallic powders and further treating the product. These procedures vary in part because of the ultimate use for which the finished product is designed and in part to the opinions of the producer. For example, it is sometimes desired to produce a relatively porous bearing through which oil may be drawn by capillary attraction. In other cases a dense product with relatively high tensile strength may be the objective. Each of these requires a special technique.

PART TWO

W. S. Landis
Vice President, The American Cyanamid Company

ELECTROMETALLURGY OF NONFERROUS METALS

Aluminum—It has not proved commercially possible to reduce the oxide of aluminum, Al_2O_3, by heating with carbon for by such a process, aluminum carbide instead of the metal is formed. Electrolysis of the oxide dissolved in a melted bath of the double fluoride of aluminum and sodium, to which some calcium fluoride is added, is used universally in the extraction of this metal. Aluminum as demanded by the trade must be of a high degree of purity, and as the usual impurities, silicon, titanium, and iron, are less readily oxidizable than the aluminum itself, the usual furnace methods of purification by oxidation are not applicable in the case of this metal. Instead, the bath and everything entering into it must be most carefully freed of all foreign elements, so that the metal as extracted will meet the exacting demands of the trade.

The chief source of alumina is bauxite, analyzing:

	France	*Arkansas*	*South America*
Al_2O_3	75.0%	57-60%	58-61%
SiO_2	1.0	4-7	2-4
Fe_2O_3	12.0	2-7	2-4
H_2O	12.0	28-30	28-31

Preparation of Pure Al_2O_3—Three processes may be used for the extraction of the pure alumina from this raw material.

(*1*) *Fusion Process.* Bauxite is fused in a reverberatory furnace with sodium carbonate forming sodium aluminate. The fused mass is leached with hot water, filtered, the alumina precipitated from the filtrate by carbon dioxide and dried for use in the electrolytic pots.

(*2*) *Bayer Process.* Bauxite relatively low in silica is finely ground and calcined below a red heat. The temperature of calcination is important, but is very much dependent upon the particular bauxite under treatment. This finely ground bauxite is charged into pressure vessels or autoclaves containing a solution of caustic soda of about 45 per cent strength. The autoclaves are heated by the direct introduction of steam and are actively agitated; the pressure usually carried is about 100 pounds per square inch. With a properly calcined material the alumina passes into solution as sodium aluminate while most of the impurities remain insoluble.

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$

When solution is complete, a matter of some hours, pressure is released from the autoclave and the contents are discharged into a receiving vessel. The solution is then diluted, by the addition of approximately an equal volume of water, and filtered. The rotary vacuum type of filter following a series of thickeners is now universally used.[17] The impurities, consisting of a finely divided slime containing silica, titanium, iron oxide and insoluble double aluminates and silicates, are separated. Because of the high iron content, these find some application

[17] See Chapter 2.

as the purification mass in the removal of sulfur from illuminating gas. The filtered solution is then sent to large open tanks provided with agitators, and a small quantity of aluminum hydrate is added to seed the batch. Agitation is carried on from 36 to 48 hours, and aluminum hydrate, $Al(OH)_3$, crystallizes out of the sodium aluminate solution leaving a diluted caustic mother liquor. The aluminum hydrate is settled and filtered from the dilute solution of caustic, washed, and sent to rotary dryers where it is calcined at red heat to free it from water. This calcined alumina of very high purity is then ready for charging into the electrolytic pots.

The dilute caustic liquor returns to a vacuum evaporator and is concentrated up to the original 45 to 50 per cent strength and used for the treatment of a new batch of calcined bauxite. Losses of caustic in the operation are made up by adding fresh caustic or causticized soda solutions.

(3) *Hall Process for Purification of Bauxite.* Bauxite is fused in an electric furnace with just sufficient carbon to take care of the reduction of the impurities, silica, titanic acid and ferric oxide. These impurities reduce to an alloy which can be separated readily from the fused mass of alumina. This process as originally developed did not produce an alumina of the desired purity for the highest grade metal. In more recent years it has been revived on a large scale. The most important improvement consisted in adding scrap iron to the furnace charge thus producing a heavier alloy which would separate better from the fused alumina, and of finely dividing the fused oxide as tapped from the furnace by mechanical means. However, even at its best the purity of the alumina so produced is not up to the standards of that from the Bayer process.

Production of Metal—This is an electrolytic process involving the use of direct current for plating the metal out of a fused bath. It is not possible to plate aluminum from a bath containing water, one obtaining only the oxide or hydroxide. The bath, therefore, must be anhydrous and at the same time a conductor of electricity. The actual bath used consists of a mixture of sodium fluoride and aluminum fluoride modified by the addition of other salts which reduce the melting point and lower the specific gravity of the fused bath. A typical bath has the approximate chemical formula:

$$2AlF_3 \cdot 6NaF \cdot 3CaF_2$$

There are some variations in this composition between the different operating companies.

This bath, when fused at about 950° C., can dissolve about 20 per cent of its weight of calcined Al_2O_3, which can be plated out by the passage of direct current through it. Molten aluminum appears at the cathode which is at the bottom of the bath. Oxygen appears at the carbon anode and, at the temperature of operation, combines with the carbon to produce carbon monoxide and carbon dioxide. The electrolytic cells, or as they are commonly called the "pots," are rectangular iron boxes 8 feet or more long, about 4 feet wide and about 2 feet deep. They are made of heavy sheet steel, heavily reinforced with structural shapes. Inside, this box is filled with a mixture of tar and carbon tamped in and of such shape as to leave a basin or cavity in the center. This same carbon material also forms the side linings up to and even with the top of the steel box. Above this pot and insulated therefrom are the heavy conductors from which are suspended carbon electrodes, using adjustable clamps permitting the raising and lowering of the individual carbon. These electrodes vary in size from 3 inches in diameter up to a foot square, the practice in the different countries varying somewhat as to the arrangement and size of the individual carbon blocks. The cells are connected in series, that is the pot of one to the electrode assembly of the next.

The prepared bath is charged into the pot and melted down by nearly short-circuiting the electrodes. When the pot is filled with its molten bath, calcined alumina is thrown on top and the electrodes raised to the operating position,

FIG. 14. Pot Room—Aluminum Plant. (Courtesy Aluminum Co. of America)

which normally shows a drop in potential of from 6½ to 7 volts. From time to time the alumina floating on top of the molten bath is stirred in by the attendant, since a crust forms just underneath it and solution would be relatively slow without this periodic breaking of the crust and stirring in of the alumina. The energy consumed in overcoming the resistance of the bath in the cells is sufficient to keep the bath molten, hence no external heating is required.

Molten metal, melting point 658° C., plates out on the bottom of the box for the bath is so formulated that in its fused condition it is lighter in weight than the molten metal. Periodically a tap hole is opened and the metal run into ladles for casting into ingots.

The electrodes are made of an ash free carbon, since any impurities they contain will get into the bath and ultimately into the metal. The consumption is high due to oxidation, amounting to nearly one pound per pound of metal produced. Normally a modern cell of the larger size takes a current of about 20,000 amperes and the over-all energy consumption amounts to about 4 hp. years per short ton, or 13 kw. hr. per pound, of metal.

Refining Aluminum—An electrolytic process for refining aluminum has been developed by Hoopes. The equipment is a vertical cell in which the bottom layer consisting of molten aluminum-copper alloy resting on a carbon plate serves as anode. Above this is an electrolyte consisting of a mixture of fused fluorides and Al_2O_3 lighter than the copper-aluminum alloy and heavier than pure aluminum. At the top is a layer of pure aluminum. The anode becomes depleted in aluminum by the electrolytic action leaving the impurities behind. Pure aluminum is tapped from the top. From time to time the aluminum to be refined is alloyed with the copper remaining in the anode. This cycle is continued until the anode copper becomes too impure to use, when it is replaced by new copper.

Uses of Aluminum—The outstanding property of aluminum as compared with most other metals is lightness. It is this property which accounts for rapidly increasing use for various purposes such as aircraft construction and other means of transportation.

The development of strong alloys containing principally aluminum, some of them amenable to heat treatment, has contributed to such uses. One of the most important of these is known as duralumin, an alloy containing 2-4 per cent Cu and fractions of a per cent of Si and Mg with, occasionally, other elements.

MAGNESIUM [18]

The first metallic magnesium was produced by the electrolysis of a fused bath of magnesium chloride a century ago. In recent years this industry has become extremely important, for the metal is about one-third lighter than aluminum, with many of the desirable properties of the latter. It is becoming useful in the form of alloys, the most important of which carries about 95 per cent magnesium and 5 per cent of other constituents: aluminum, chromium, manganese and antimony. These alloys are particularly strong and rigid either in cast, rolled or extruded form and are finding increasing use in the manufacture of aircraft and other light structural products, though there are still difficulties in imparting corrosion resistance.

Electrolytic Production—The older process, and the one in most general use, consists in electrolyzing a bath of fused magnesium chloride. Usually, small amounts of sodium chloride are added to the bath to reduce the melting point, but such additions must be very carefully controlled, otherwise there is possibility of simultaneously plating out this addition agent and the presence of metallic sodium is of great disadvantage in metallic magnesium, for most applications of the latter.

The equipment used is very much the same as that in the aluminum industry. Pots are of the same construction, though generally somewhat smaller. The voltage across the cell is approximately the same, approximately 7 volts. The power consumption about 4 hp. years per ton, or again almost the same as for aluminum.

The process, however, differs from that of aluminum in that the fused bath itself is electrolytically decomposed, plating out magnesium at the cathode and setting free chlorine at the anode. Although attempts have been made to produce

[18] Also see Chapter 9.

magnesium by way of the oxide dissolved in a fused bath, this process has not been commercially successful.

Production of Magnesium Chloride—The production of fused magnesium chloride is a complex operation, since the natural sources involve first a recrystallization of a hydrated product. It is not possible to dry such product to the extent of complete elimination of moisture by heating without serious decomposition of the magnesium chloride and the production of an oxy-chloride. This oxy-chloride cannot be used for a magnesium bath. In order, therefore, to obtain the necessary high purity of magnesium chloride in completely anhydrous form,

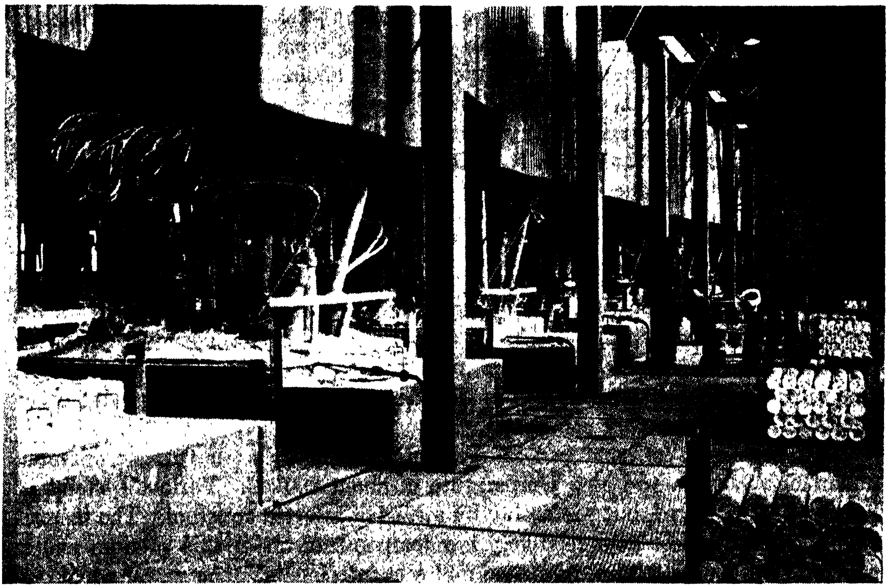


FIG. 15. Cell Room—Magnesium Plant. (Courtesy Dow Chemical Co.)

it is necessary to remove the last traces of water by heating in an atmosphere of either hydrochloric acid, or preferably, and most widely used, of ammonium chloride. Only by such indirect method can the last traces of the water be removed and the material made suitable for the magnesium bath.

Most of the magnesium in the United States is produced by the Dow Chemical Company, who obtain the magnesium chloride from the brine wells in the vicinity of Midland, Michigan. Early in 1941 the Dow Company put a new plant in operation at Freeport, Texas, to extract the magnesium chloride from 100 million pounds of sea water, per day.

Carbon Reduction—A recent development in the production of magnesium now practiced in several countries is the direct reduction of magnesium oxide by carbon. Magnesium oxide is easily obtained by calcination of magnesite $MgCO_3$. For this particular purpose the purity need not necessarily be high, an ordinary grade running from 90 to 95 per cent has been satisfactorily used. The calcination should be complete to the "dead burned" state such as is common in the refractory industry.

The reducing agent employed is most commonly low-ash carbon. This may be coke of good quality, charcoal or petroleum coke. The purity affects the process only that the less contamination the lower will be the power consumption of the process. Ordinarily it will not affect the quality of the product. Other reducing agents such as calcium carbide and ferro-silicon have been suggested and tried out on a small scale. Even burned dolomite, along with such reducing agents, has shown possibility of producing an acceptable magnesium in the small scale operations, but the power consumption is much greater than when the high grade burned magnesite and the carbonaceous reducing agents are employed.

The raw materials are briquetted with an oil or pitch binder and are charged into a closed electric furnace, preferably dropping them into a multi-phase arc. The magnesium is reduced at a temperature of about 2,000° C., but since its boiling point is 1120° C., the reduced metal first appears in the form of a vapor, diluted by carbon monoxide. Any impurities in the charge are usually reduced and vaporized at the same time so that the furnace need have no tapping hole.

The reaction of reduction

$$MgO + C = Mg + CO$$

is a reversible one and if the gases are not quickly cooled to condense the magnesium it will again re-oxidize. It, therefore, is necessary to dilute these gases for cooling and condensation, and this is accomplished by an ingenious system of injecting large volumes of hydrogen into the gases as they leave the furnace. The magnesium itself is recovered in the form of a powder, together with other volatilized impurities that condense.

This powder is collected and charged into a second electric furnace operated under high vacuum and at a temperature of about 900° C. Various systems of heating are employed, but preferably by means of inserted resistors. The magnesium again volatilizes at a relatively low temperature under this vacuum and is condensed to metallic form, re-melted and cast into ingots. The power consumption of this process overall, including that utilized for the production of hydrogen to make up for losses, is slightly under 3 hp. years per ton of metal or 10 kw. hr. per pound. The metal after this double distillation is of exceptional purity.

MISCELLANEOUS METALS

Calcium—Calcium is produced in relatively small quantity because of limited demand, by the electrolysis of a fused calcium chloride bath to which is added chlorides of the alkali metals in relatively small quantity to reduce the melting point. The metal plates out on a suspended cathode which is withdrawn slowly from the molten bath. Since the melting point of calcium is well above that of the fused bath, the metal is separated in the form of a rod.

Beryllium—For the sake of completeness and because it has found a real place in the alloy field, beryllium is merely mentioned here briefly. It is produced similarly to magnesium by electrolysis of a fused bath of beryllium chloride. Attempts have been made to produce it by a process similar to that of aluminum by dissolving beryllium oxide in a fused bath but the details of the procedure are not available.

Sodium and Potassium—The uses of these two metals put them in the class of chemical reagents rather than metals. Their production is discussed in Chapter 12, Electrochemical Industries.

ELECTROLYTIC PRODUCTION OF COPPER

In certain parts of the world there are great deposits of oxidized copper ores. These are leached with sulfuric acid, yielding a solution of copper sulfate containing more or less impurity, all dissolved in an excess of sulfuric acid. This solution is then treated in the electrolytic cell using an insoluble anode, and the copper is plated out at the cathode and at the same time sulfuric acid solution is regenerated. The solution leaving the cell, still containing much of its copper but enriched in acid is reused on a fresh batch of ore.

Such electrolytic recovery of the copper is not unlike the operation described under copper refining below. The electrolytic equipment is essentially the same except that the anode of the cell is made of lead, ferrosilicon, magnetite or other conducting material which is insoluble in the solution. Since copper is extracted from an oxidized salt, the energy requirements of the extraction cell are many times greater than those in the refining cell. The voltage between the adjacent plates runs from 2 to 2½ volts, and the power requirements from 2,000 to 2,500 kw. hr. per ton of copper. This operation is carried out on a large scale in several important copper producing centers of the world, notably at Chuquicamata, Chile; Inspiration, Arizona; and Katanga, Belgian Congo.

Leaching is usually by percolation of solution through ore in large rectangular tanks often holding 5,000 to 10,000 tons each. When the ore cannot be satisfactorily treated in this way the solution unit usually consists of heavy agitators followed by separation equipment which may consist of classifiers, sedimentation tanks and filters, as best fits the individual problem. All this equipment must be acid proof for it is customary to carry a considerable strength of acid through the solution units and into the precipitation cells. It is extremely important that high clarity be maintained in the solution going to the precipitation cells for suspended particles of solid matter become enmeshed in the copper plate and disturb the electrolytic operation, and influence the purity of the recovered copper. Slime particles in the cells tend to produce rough cathodes and this in turn leads to possible short-circuiting through abnormal growth of the deposit at a localized point.

In the cell room the operation is so conducted as to plate out the maximum of copper and the minimum of impurities by adjustment of solution strength, free acid and current density. It is necessary, from time to time, to purify this solution by bleeding of a portion of the solution to the purification units. Here, through additions, temperature control and various other specialized methods the impurities are precipitated and removed from the system.

While it is theoretically possible to produce copper in a single operation of equal quality to that of the best electrolytically refined grade, in general the product of this type of process is rarely of such high grade. However, there are installations producing the equivalent of electrolytic grade due to their careful clarification of solutions and the holding of the impurities at a low level.

ZINC

In the electrolytic process for the production of zinc, oxidized ores or roasted sulfide ores are leached with sulfuric acid. This yields a solution of zinc sulfate carrying the soluble impurities in the ores. The solution undergoes an intensive purification, cadmium being precipitated by zinc dust. Iron is oxidized to the ferric state and with aluminum arsenic and antimony is precipitated as a basic compound by careful control of acidity. Nickel and cobalt are removed by further treatment with organic reagents, so that finally a relatively pure zinc sulfate solution is obtained carrying more or less free sulfuric acid. This is sent to the electrolytic cells and the zinc plated out at the cathode, using insoluble anodes. The manganese in solution comes out as oxide on the anodes. The zinc produced by this process is of a very high degree of purity (over 99.9 per cent).

By careful control of the roasting operation a very considerable proportion of the zinc sulfide in the ore can be converted to zinc sulfate which is converted to an equivalent of sulfuric acid in the electrolytic cell. In practice the roasting is regulated to prevent excessive sulfate formation. On the other hand the zinc sulfide sometimes occurs in a calcite matrix ($CaCO_3$) and unless the ore is rich in zinc, there will be a material increase in consumption of acid due to the presence of the calcitic gangue. In such cases it is necessary to supply sulfuric acid as such and an acid plant is frequently a part of the electrolytic zinc process.

As carried out, there are two general modifications of this electrolytic process. In the earlier developments the ore was roasted at a low temperature and the zinc oxide dissolved in a relatively weak acid. After purification the solutions went to the precipitating cells, containing 10 to 12 per cent of zinc. Because of the weak acid used in dissolving, impurities are relatively low, and consequently purification is easy. Copper, cadmium and the other heavy metals are precipitated by treatment with zinc dust. The metals of the third group are usually not very troublesome in this process, and by practically complete neutralization of the acid they can be dropped out as basic salts. In general the current density is held down to about 35 amperes per square foot of cathode surface.

In the so-called high current density process, much stronger acid is used for leaching and there is a greater tendency to dissolve impurities. In consequence more careful purification is required to produce a solution which will operate satisfactorily in the cells which carry a current density of approximately 100 amperes per square foot of cathode. The chief advantage of the high density process lies in the fact that the solution reactions are more energetic and, therefore, the equipment is smaller, and the cell room requires only about half the cathode area of the low density process. This means a very material reduction in capital cost and most of the recently installed plants operate on the high density principle. The purity of the metal is approximately the same for either process.

The power requirement for the production of electrolytic zinc is about 3,000 kw. hr. per ton of metal.

ELECTROLYTIC REFINING OF IMPURE METALS

Copper—The purpose of the electrolytic refining of copper is to remove the impurities, such as Cu_2S, Cu_2O, Au, Ag, Pt, Fe, Ni, Co, As, As_2O_3, Sb, Sb_2O_3, Bi, Bi_2O_3, Se and Te which occur in the material produced by the converter. The blister copper is first given a preliminary refining and then cast into plate form for use as anodes. (See p. 929.)

These plates are suspended in a bath of copper sulfate and sulfuric acid and a direct current passed from the crude metal plates to the cathodes, where the copper is deposited, minus the impurities. At the anode, Cu_2S and Cu_2O drop to the bottom as the copper is dissolved out around them, and slowly pass into solution. As and As_2O_3 partly dissolve through the action of the current and partly drop to the bottom, slowly passing into solution. Sb and Sb_2O_3 partly pass into solution and partly into insoluble basic salts. Bi and Bi_2O_3 pass into solution and are precipitated out as basic salts. Au, Ag, Pt, Se, Te are not dissolved by the current and drop to the bottom of the tanks as a mud or slime. Fe, Ni and Co pass into solution and are not plated out so long as copper is present in the solution. Arsenic is not plated out if the solution contains sufficient free sulfuric acid. In this way, practically speaking, only copper is plated out on the cathode, and the impurities either collect in the slime at the bottom of the tank or accumulate in the solution. It is thus necessary to remove and purify the electrolyte at proper intervals.

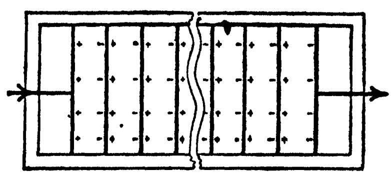


FIG. 16. Arrangement of Series Electrodes.

In practice, the electrolytes used contain from 10-15 per cent copper sulfate and 5-15 per cent sulfuric acid. Since one ampere of current flowing from an anode to a cathode only plates out one ounce of copper in a day and it is not possible with the above electrolytes to use a current density of over 15-20 amperes per square foot of cathode surface without danger of forming rough plating and consequent danger of short-circuits, it can be seen that a refinery of any large output must use enormous surfaces. This has led to the development of two systems of connecting the plates in the electrolytic tanks, the series and the multiple.

In the series system (Figure 16) a number of copper anodes are suspended in the bath about ½ to ¾ in. apart, only the two end ones being connected with the source of current as shown. The current dissolves copper from the first plate and deposits it on the near side of the next plate; the other side of the second plate is dissolved and plated out on the near side of the third plate and so on through the tank. When the anode is nearly consumed it is mechanically separated from the deposit of pure copper on its back. This system is not in most general use, although the largest refinery in the world has a section equipped with it. Its advantages lie in having less copper under treatment at any one time, and less copper tied up in conductors.

In the multiple system the anodes and cathodes are arranged alternately, all the anodes being connected to the positive source of current and the cathodes to the negative. The cathodes are thin sheets of electrically precipitated copper made in special tanks by plating copper on greased copper plates from which it is stripped by hand. Figure 17 shows a modern tank house.

The solutions in copper refining accumulate impurities and become foul so that the purity of the copper plated out decreases unless means are taken to remove these foreign elements. These solutions also accumulate copper. It, therefore, is necessary to set apart a certain number of cells in the copper refinery

FIG. 17. Tank House—Electrolytic Copper Refinery. (Courtesy Rhokana Corp.)

and equip these with insoluble anodes, usually of lead. The electrolyte, after flowing through the regular refinery circuit which is always arranged to permit gravity flow from one end of the house to the other, then passes to these special units where copper is plated out somewhat in the character described under electrolytic copper recovery.

Arsenic and antimony are precipitated by chemical means and accumulated iron and similar compounds by regulation of acidity so as to produce basic salts that can be dropped out and filtered from the solution.

From time to time it is necessary to remove a refinery tank from the circuit. All the electrodes are taken out, the tank drained and the mud which has accumulated in the bottom is very carefully collected for it frequently contains very high values in silver and gold. The tanks are so arranged in the house that a "jumper" is easily affixed to lead the current by any tank out of service and a rubber hose enables one to by-pass such tank with the circulating solutions.

The refinery mud is boiled up with sulfuric acid to eliminate as much of the base metal content as possible, and is then smelted down and cast into anodes which are treated further electrolytically for the recovery of the silver and gold content.

The energy requirements in copper refining are relatively small. Since copper is dissolved at the anode and plated out at the cathode the principal consumption of energy is that of overcoming the resistance of the electrolyte and this is made as low as possible through the adjustment of the dissolved copper sulfate and its free sulfuric acid content. Thus the drop in voltage between adjacent plates averages around three-tenths of a volt. The energy requirements in the multiple system are about 200 kw. hr. per short ton of copper, and in the series system, slightly less.

Lead—Lead is refined by suspending the impure lead as anode in a bath consisting of 18-20 per cent lead fluosilicate and 8 per cent fluosilicic acid to which a little gelatine or glue has been added. Lead, zinc, nickel, and iron go into solution and lead and tin only plate out if the solution is kept relatively pure. The impurities for the most part remain as a sponge sticking to the anode.

Silver—For alloys containing above 90 per cent silver with small amounts of copper and gold, the electrolyte used is a solution of 2-4 per cent copper nitrate in 1 per cent nitric acid. Silver and copper pass into solution under the influence of the electric current and silver alone is deposited with the low current density of 18 amperes per square foot. The gold settles out as a mud in the bottom of the tanks. Because of the precipitation of the silver on the cathode as loose crystals, mechanical means must be taken to prevent crystal-growths from short-circuiting the cell.

Gold—For alloys very high in gold and containing but small amounts of silver and platinum the electrolyte used is a solution of auric chloride in hydrochloric acid. Gold dissolves and is plated out on the cathode, while the silver remains behind in the slimes and platinum goes into the solution from which it is subsequently recovered.

READING LIST

BENEFICIATION OF ORES

Lindgren, W., "Mineral Deposits," McGraw-Hill Book Co., New York (1933).

Richards, R. H., Locke, C. E., Schuhmann, R., "Text Book of Ore Dressing," McGraw-Hill Book Co., New York (1940).

Gaudin, A. M., "Principles of Mineral Dressing," McGraw-Hill Book Co., New York (1939).

Dewitt, C. C., "Froth Flotation Concentration," Ind. Eng. Chem. *32*, 652 (1940).

GENERAL

Hayward, C. R., "Outline of Metallurgical Practice," D. Van Nostrand, New York (1940).

Austin, L. S., "Metallurgy of the Common Metals," John Wiley & Sons, New York (1926).

Liddell, D. M., "Handbook of Non-Ferrous Metallurgy," McGraw-Hill Book Co., New York (1926).

Mathewson, C. H., "Modern Uses of Non-Ferrous Metals," A. I. M. E., New York (1935).

STATISTICS

"The Mineral Industry" (Annual Reviews), McGraw-Hill Book Co., New York.

ALUMINUM

Edwards, J. D., Frary, F. C., Jeffries, Z., "The Aluminum Industry," McGraw-Hill Book Co. (1930).

Anderson, R. J., "Metallurgy of Aluminum and Aluminum Alloys," Henry C. Baird & Co., New York (1924).

COPPER

Addicks, L., "Copper Refining," McGraw-Hill Book Co., New York (1921).

Hofman, H. O., Hayward, C. R., "Metallurgy of Copper," McGraw-Hill Book Co., New York (1924).

"Copper Metallurgy," Trans. A. I. M. E., Vol. 106 (1933).

Mantell, C. L., "Industrial Electrochemistry," pp. 288 et seq., McGraw-Hill Book Co., New York (1940).

OTHER METALS

Hofman, H. O., "Metallurgy of Lead," McGraw-Hill Book Co., New York (1918).

"Lead and Zinc Metallurgy," Trans. A. I. M. E., Vol. 121 (1936).

Hofman, H. O., "Metallurgy of Zinc and Cadmium," McGraw-Hill Book Co., New York.

"The Nickel Industry," Canadian Mining Journal (November, 1937).

Mantell, C. L., "Tin," Chemical Catalog Co. (1929).

Mantell, C. L., Hardy, C., "Calcium—Its Metallurgy and Technology," Trans. Electrochemical Soc. *66*, 63 (1934).

Section VI

SURFACE COATINGS

"Save the surface and you save all" is the slogan of the paint and varnish industry. The preparation of pigments, film-forming materials and vehicles involves materials and processes encountered in several other sections of the chemical industry, but the special methods of preparation and application justify the consideration of surface coatings in a separate category of their own.

CHAPTER 25

SURFACE COATINGS *

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INTRODUCTION

Functions of Protective Coatings—All living matter, vegetable or animal, is provided by nature with a protective skin. The bark of the tree, the scales of a fish, and the hide of the animal serve to protect from mechanical injury. These outer layers give not only mechanical protection but also in many cases, on account of their color and design, give optical protection. As the tree, fish or animal grows, additional bark, scales or skin is manufactured. If damaged by external agencies, repairs are made from within.

But such fortunate conditions do not surround many inanimate objects, and artificial protection afforded by paint is required. For example, unless protected by paint, ordinary iron and steel corrode, lumber warps, splits and rots, and some types of masonry disintegrate when exposed to the sun, rain and other forces of nature.

Protection, however, is not the only objective of painting. A very large proportion, perhaps the greater part, is done for decoration. Among other uses of paint are: identification, sanitation, as adhesives, and aid to illumination.

To state with certainty the original purposes of the use of paint is difficult. Both decoration and preservation were achieved by the coatings on mummy cases in Egypt and by the lacquering on tables and smaller articles in the Orient. Medieval painting was mostly for decorative purposes, but finishes on violins, for example, were certainly for protection.

It is the decorative feature of paint that accounts for the stability of the paint industry in the midst of competitive products, such as stainless steel, ceramics, new masonry and cement products, glass and plastics. To satisfy human desire for changes in color, or to decorate after structural repairs or alterations have been made, to improve color harmony with surroundings, paint is often applied to the above-named materials.

Definitions of Paint—The term "paint" is used in a generic as well as in a specific sense. In the former, it includes various kinds of liquid compositions which, in the form of thin films, are converted into solids. That is, they dry by the influence of air, light, or heat, or deposit a solid film by evaporation of a volatile solvent. In this sense of the word, the various products of the paint in-

* The author has drawn freely upon the material written by H. A. Gardner, George B. Heckel, Gustave W. Thompson and Maximilian Toch in the Fifth Edition of this book.

dustry include house paint, refrigerator enamels, sign paints, varnish, cellulose nitrate lacquer, putty and many other compositions.

Paint in the specific sense is a mixture of a powder, called the pigment, and a liquid, called the vehicle. It dries to a relatively opaque film. For many decades, the principal vehicle has been a mixture of linseed oil and turpentine or petroleum spirits. The oil serves to bind the pigment particles into a uniform mass; the turpentine or petroleum spirits is added to reduce the consistency of the oil-pigment mixture to a convenient degree.

Varnish contains no pigment, and the dry film is usually glossy, although sometimes ingredients are added to produce a film without gloss. Such a varnish is called a flat varnish. Varnishes are usually classed as spirit or oleoresinous. A spirit varnish is a solution or dispersion of a resin in a volatile liquid. It dries by evaporation of the volatile solvent. Examples of spirit varnish are cellulose nitrate lacquer and shellac varnish. An oleoresinous varnish is a solution of a mixture (usually cooked) of a drying oil and resin, in a volatile liquid. It dries by evaporation of the volatile portion, followed by oxidation and polymerization of the residue. Examples of oleoresinous varnish are spar varnish and floor varnish. A third type of composition, namely, thickened oil, is also called varnish, specifically, bodied oil varnish. The oleoresinous type is thus a hybrid. Examples of straight oil varnish are patent leather [1] and lithographic varnishes.

A paint made with varnish instead of oil as the vehicle is characterized by a harder and smoother film. The brush marks prominent in a paint made with raw or boiled oil are absent. From its similarity in appearance to a ceramic enamel, such a paint was first called an enamel paint, but usually the shorter term "enamel" is now used.

MATERIALS OF PAINT

Pigments, drying oils, resins, volatile solvents and driers comprise the principal raw materials of paints. Many of them are important articles of foreign as well as of domestic commerce.

Pigments—Pigments may be classed according to their sources, or to the properties they impart to paint. They thus may be natural or synthetic, that is, mineral or chemical; organic or inorganic; white or colored; opaque or transparent. They may impart rust inhibitive properties and they may be reactive or inert towards the vehicle.

Natural or Mineral Pigments. Among naturally occurring materials used as pigments are iron ores, clays, chalk, barytes, talc, mica and diatomaceous earth. In some cases, their production is a simple matter. Ochre, sienna and chalk normally require only ordinary milling and elutriation, but air flotation may also be used. Others, however, are more difficult to prepare. Considerable amounts of mica are put through an expensive wet milling process. The so-called micronizing process is also used to prepare minerals for use in paint.[2]

Synthetic or Chemical Pigments. The synthetic, or chemical, pigments exceed, by far, the natural pigments in tonnage and value, including as they do,

[1] See Chapter 45.
[2] For further discussion of these operations and their equipment see Chapter 2

the lead, zinc and titanium white pigments, the large number of inorganic and the equally large number of organic colors. Production of these pigments usually involves problems of careful control of physical and chemical reactions. Fuming, precipitating and calcining processes are used in the preparation of the inorganic pigments. The organic pigment colors are salts or lakes of dyestuffs or are pure insoluble dyes.

Reactive Pigments. By reason of their chemical nature, some pigments react with the drying oils or their fatty acids. The usual reaction is that of a base with an acid, for example, zinc oxide or red lead with fatty acid to form metallic soaps. Other pigments, e.g., titanium dioxide, are chemically inert. Incidental ingredients may be present in, or may be added to, pigments normally inert, whereby such pigments become reactive. The addition often takes the form of a coating on the pigment particle. Similarly, reactivity of pigments may be reduced by coating the particles with a protective layer of inert material.

Opacity[3]—The opacity of a white paint is created by the difference in the refractive indexes of the pigment and vehicle. It is also influenced by the size of the pigment particle and by the proportions of pigment and vehicle. The refractive indexes and average particle size of the important white pigments are given in Table 1.

TABLE 1—REFRACTIVE INDEX AND PARTICLE SIZE OF SOME PIGMENTS

	Refractive Index	*Mean Particle Diameter (Microns)*
Basic carbonate white lead	2.00	0.7 to 1.20
Basic sulfate white lead	1.93	0.6 to 0.7
Zinc oxide	2.02	0.2 to 0.6
Zinc sulfide	2.37	
Titanium dioxide	2.5 (2.7)	0.3 to 0.6
Lithopone	1.8	0.4
Lead titanate	2.7	0.3
Barytes	1.64	
Calcium sulfate	1.59	
Silica, quartz	1.55	
Silica, diatomaceous	1.45	
Zirconium oxide	2.40	
Antimony oxide	2.2	
Average paint vehicle	1.5	

It will be noted that the pigments may be divided into two groups, those having an index above 1.8 and those having an index of approximately 1.5. The former group comprises the opaque or prime pigments, the latter the non-opaque or extender pigments.

Extenders.[4] If the extending pigments impart no hiding power to paint, it may be asked: Why are they used? There are several reasons. Certain pigments, notably zinc sulfide and titanium dioxide, impart an excess of hiding power to many paints. Replacement of a portion of the prime pigment with

[3] Hanstock, R. F., J. Oil and Colour Chem. Assoc., *20*, 5 (1937).
Judd, D. B., National Bureau of Standards J. of Research, *19*, 287 (1937).
[4] Fuller, W. R., A. S. T. M. Bulletin, Aug., 1940, pp. 35-38.
Nelson, H. A., Paint and Varnish Production Clubs, Official Digest, *142*, Jan., 1935.

an extending pigment legitimately lowers the cost of the paint. In other cases, the particle shape of certain extending pigments improves the properties of both the liquid paint and the dry film. Judicious amounts of needle-shaped or flake-shaped pigments impart less objectionable settling of the pigment in the liquid paint. These pigments also tend to reduce cracking of dry paints. Another use of importance is as substrates for organic pigment colors.

THE INDIVIDUAL PIGMENTS [5]

The number of pigments is so large that a comprehensive description of their manufacture and use cannot be made in this chapter. Brief descriptions of the commonly used pigments will be followed by detailed descriptions of the more important ones.

White lead	: See Chapter 26.
Zinc oxide	: See Page 973.
Leaded zinc oxide	: See Page 980.
Lithopone	: See Page 981.
Zinc sulfide	: See Page 980.
Titanium dioxide	: See Page 982.

Fibrous Talc—This pigment is used in house paints to impart "tooth" to the film. The coarser grades are used in zone-marking (traffic) paints to impart a rough light-diffusing surface. It is mainly natural magnesium silicate and the only important deposits are in the Governeur district of New York State and in California.

China Clay—Numerous types of clay are mined, washed by elutriation, and used as extending pigments and as substrates for color lakes. Its use seems to be declining. Georgia and South Carolina are the principal sources.

Silica—Silica exists in a number of types ranging from anhydrous quartz to highly hydrated types. The anhydrous types are hard and cause excessive wear on paint-grinding mills. These types also settle rapidly in most paints, but nevertheless substantial amounts are used in paints and wood fillers to give "tooth."

Diatomaceous Earth[6]—This is a soft variety of silica. It tends to reduce settling in paints. It reduces gloss and for this reason is used in flat varnishes, and in flat wall and traffic paints. The principal deposits of diatomaceous earth are in California, Oregon and Florida.

Barium Sulfate—The natural product, barytes, is not very widely used in paints, but the precipitated form, blanc fixe, is an important ingredient. Large amounts of the latter are used with zinc sulfide and titanium dioxide to form lithopone and titanium-barium. It is also used as a substrate for reduced colors. Missouri and Georgia account for approximately half of the barytes produced in this country.

Calcium Carbonate—In the forms of chalk, limestone, sugar calcite and the precipitated compound, calcium carbonate is widely used in putty and calk-

[5] This section was largely adapted from the material of Maximilian Toch, Fifth Edition, this Manual, Chapter 17.

[6] Hall, H. W., Paint, Oil and Chem. Review, April 14, 1938.

ing compounds, calcimine, casein and flat wall paints.[7] Until recently, the natural product with the highest light reflectance was obtained from the chalk cliffs of England, but comparable products are now being produced from deposits in Kansas. The precipitated form has a higher light reflectance than the natural variety. Products, the particles of which have been coated with resins, resin- or fatty-acids, metallic soaps or other coating agents, are regularly available.

Calcium Sulfate—This is not a widely used extender, except in combination with zinc sulfide and titanium dioxide. The precipitated variety is used for these products. Calcium sulfate is an important ingredient in paints for masonry surfaces, where it imparts alkali resistance.

Mica—The use of this pigment grew rapidly during the 1930's. On account of its flake form it tends to reduce cracking of paint films.[8] It is marketed straight and also in combination with magnesium silicate in zinc sulfide-magnesium and titanium-magnesium. The best type of pigment mica is muscovite and most of it is found in South Carolina. Wet milling yields a product with thinner flakes than does dry milling.

Iron Oxide—Various iron oxide ores such as limonite, siderite and hematite, and clays stained with iron oxide are perhaps the oldest of pigments. On account of their relatively low cost, they will no doubt continue to be used for a long time to come, although they are deficient in tinting strength and brilliance.[9]

The preparation of the ores for pigment purposes is a matter of milling and subsequent separation of coarse particles by elutriation. Ochres require very little preparation but some of the red oxides require considerable milling. Having a hardness approximating that of quartz, they must be finely ground or they will cause excessive wear on paint-grinding mills.

Red iron oxide pigments are widely used in primers for structural steel, automobile bodies and ship bottoms and in freight car and barn paints. The principal use of ochre, sienna and umber is as tinting colors. Large amounts of selected iron ores have always been imported and refined for pigment uses. World War 2 curtailed this trade enormously and the end of the war may find the market completely dominated by domestic ores or synthetic products.

Ochre—This is a clay stained yellow with hydrated iron oxide. The best grades are found in France, South Africa and India, but considerable domestic ochre is used, especially since World War 2. Ochre contains from 15 to 20 per cent of iron oxide (Fe_2O_3).

Sienna—This is a brownish-yellow pigment containing upwards of 60 per cent of iron oxide. It is named for the town of Siena, Italy, where large deposits are located. Sienna is marketed in the raw and burnt (calcined) states. The color of the latter is brownish red.

[7] Wilson, H., and Skinner, K. G., Bulletin 395 Bureau of Mines, U. S. Department of Agriculture, 1937.

[8] Atwood, F. C., American Paint J., *19,* No. 39, July 8, 1935.

[9] Ayers, J. W., Paint and Varnish Production Clubs, Official Digest, *130,* 298-307, Nov., 1933.

Santmyers, R. M., U. S. Bureau of Mines. Information Circ. 6504, Sept., 1931. *Ibid.,* Circ. 6627, May, 1932.

Umber—A greenish-brown ore containing some 45 per cent of iron oxide and 15 per cent of manganese dioxide, umber is named for a department of central Italy, where it was first found. Better grades are located on the island of Cyprus and are called Turkey umber. The color becomes dark brown when burnt.

Red and Brown Oxides—Numerous deposits of these exist in various parts of the world. The brightest red oxides are found along the Persian Gulf and in Spain. A brown oxide found in the United States, principally Pennsylvania, is known as metallic brown.

Black Iron Oxide—This is the magnetic oxide, Fe_3O_4. It is found mixed with slate when it is known as mineral black, and is also manufactured. It finds some use in metal protective paints.

Synthetic Iron Oxides—These have several advantages over the natural products. They are softer, more finely divided, have higher strength and opacity and are available in many varieties of yellow, brown, red and black colors. They are made by calcination or precipitation processes. A long standing example of the former is Venetian red, prepared by calcining a mixture of calcium oxide and ferrous sulfate. The result is a product containing from 10 to 40 per cent of ferric oxide mixed with calcium sulfate. The color of precipitated pigments varies with the conditions of precipitation and to the degree the product is subsequently oxidized, or calcined.

Red Lead—The classical rust inhibitive paint consists of red lead and linseed oil. Red lead is made by roasting litharge, PbO, in air and may be represented by the formula Pb_3O_4. The conversion of litharge to red lead is rarely complete, a core of unchanged litharge remaining in the larger particles. The pigment is graded according to the percentage of true red lead in it, the principal grades being 85, 95 and 97. When made into paint, the unchanged litharge, especially in the 85 per cent grade, reacts with the oil and fatty acids to make a thick and unusable product. Hence, only the quantities needed for immediate use are mixed. The percentage of litharge in the higher grades is sufficiently low so that ready-mixed paints are practical. Exposed to the weather, films of red lead paint bleach markedly due to the formation of lead carbonate, lead sulfate and other products.

At one time, a special grade of red lead called orange mineral was made by calcining basic carbonate white lead, but today the orange mineral grade is made from litharge in the same way as the other grades. Orange mineral is not an important pigment. Its principal use is for its color in printing inks or in enamels.

Toluidine Red—The most light-fast red organic pigment is toluidine red which is made by coupling metanitro-para-toluidine [10] with beta naphthol.[11] It is made in two colors, regular and extra deep. It has good brightness, stands up well under heat, and is relatively non-bleeding. However, it is rather expensive.

Para Red—A much cheaper pigment than toluidine red, para red is made by coupling para nitraniline [12] with beta naphthol. It is sufficiently light-fast

[10] See Compound 288, Chapter 27.
[11] See Compound 368, Chapter 27.
[12] See Compound 271, Chapter 27.

for many uses, but has a greater tendency to bleed and does not stand heat so well as the former.

Lithol Red—This is another azo color, a coupling of 2-naphthyl-amine-1 sulfonic acid [13] with beta naphthol. It is used principally in the form of its calcium and barium salts. Lithol red is non-bleeding and stands heat well but ranks considerably below toluidine red in light fastness.

Chrome Yellow—Lead chromate is the basis of a group of pigments important not only for the wide range of color but also for their relatively low cost. They are prepared by reacting lead acetate or lead nitrate with sodium dichromate. Lead acetate produces a somewhat greener undertone than does the nitrate. The hue depends upon the basicity of the product and the presence of other insoluble compounds of lead. Normal lead chromate is yellow. The basic chromate $PbO \cdot PbCrO_4$ is reddish orange and is usually called chrome orange. A very pale yellow, known as primrose, is obtained by the co-precipitation of lead sulfate with the chromate.

If 10 to 12 per cent of lead molybdate, or tungstate, be precipitated along with the chromate, the product is brighter and has more tinting strength. Also the color range is extended further into reds and scarlets.[14]

When exposed to light and weather, all lead chromate pigments tend to darken, but this tendency is much less in the case of the chrome oranges than in the cases of the light chrome yellows and the molybdates. Lead chromates are sensitive to alkali. The orange types are used in anticorrosive paints.

Zinc Yellow—An excellent rust-inhibitive pigment whose use is rapidly growing, zinc yellow is prepared by reacting zinc oxide with potassium dichromate. The product is a complex salt, the approximate composition of which may be represented by $K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$.[15] Some recent types are essentially a basic zinc chromate, containing no potassium. Its color is greenish yellow and its tinting strength is rather low. The rust-inhibitive properties are ascribed to the slight solubility of the pigment in water.

Cadmium Pigments—Two cadmium compounds are used as pigments, the sulfide and the selenide, known as cadmium yellow and cadmium red, respectively. Various mixtures of the two, with or without blanc fixe, giving a variety of hues, are produced. Cadmopone is analogous to lithopone, and is a mixture of cadmium sulfide with blanc fixe. Cadmium pigments are relatively stable towards light and heat, but in exterior paints the sulfide tends to be oxidized to the white sulfate.

Hansa Yellow—This is an organic pigment of the azo [16] class, one widely used member being a coupling of meta-nitroparatoluidine with acetoacetanilide.[17] Hansa yellow has good brightness, tinting strength, light fastness and alkali fastness. It is non-toxic.

Yellow Lakes[16]—A few transparent yellow lakes are employed in decorative finishes.

[13] See Compound 398, Chapter 27.
[14] Linz, A., Ind. and Eng. Chem., *31*, 298 (1939).
[15] Brizzolara, A. A., Denslow, R. R., and Rumbel, S. W., Ind. and Eng. Chem., *29*, 656 (1937).
[16] For an explanation of the classes of dyes, see Chapter 28.
[17] See Compound 143, Chapter 27.

Iron Blue—Otherwise known as Prussian blue, this is one of the oldest chemical pigments. Its light fastness is excellent and its tinting strength is high, but is extremely sensitive to alkali. Two well-known types of iron blue are known as Milori and Chinese blues. The distinction is slight, but Milori types tend to be redder than the Chinese types. Iron blue is made by an indirect process by which ferroferrocyanide is first prepared by reacting ferrous sulfate and sodium ferrocyanide in the presence of some ammonium salts. The white product is then oxidized to blue ferriferrocyanide. It retains considerable sodium and ammonium compounds. The product has been considered to be a chemical compound or a co-ordination complex, but there is evidence that the alkali ferrocyanide is merely physically adsorbed.[18]

An interesting phenomenon concerning iron blue is its reduction by drying oils to the white ferro-compound. Kept in a closed container, blue paints bleach and green paints turn yellow. However, when applied on a surface, the original color is quickly restored by oxidation in the air.

Ultramarine Blue—One of the oldest artist's pigments is the expensive mineral, lapis lazuli. The offer of a prize for a synthetic substitute stimulated research in Europe and resulted in the discovery in 1828 of the process by which ultramarine blue is still made. Various mixtures of china clay, sodium carbonate, silica, carbon and sulfur are calcined. Ultramarine blue is rather transparent, is light-fast, and alkali-fast, but is destroyed by acids.

Phthalocyanine Blue—One of the most important developments in the field of pigments was the appearance of phthalocyanine blue on the market in 1935. It is usually a copper compound of phthalocyanine, but types containing no metal are also known. Its hue is a very desirable one, but its special claim to recognition is its fastness not only to light, but also to acids, alkali and heat. However, the relatively high cost operates against its use wherever its special properties are not needed.[19]

Blue Toners—Included in the list of blue organic pigments are a few toners made by precipitating dyestuffs, such as Victoria blue and methyl violet, with tungstic or molybdic acids.

Blue Lead—This pigment is also known by the longer term, basic sulfate blue lead. Its composition[20] is usually within the following ranges:

	Per Cent
Lead sulfate, min.	45
Lead oxide, min.	30
Lead sulfide, max.	12
Lead sulfite, max.	5
Zinc oxide, max.	5
Carbon and undetermined matter, max.	5

Many tests have indicated that it has excellent rust-inhibitive properties despite its carbon content. It is rarely used for its color, which is a rather weak bluish gray.

Originally a by-product obtained during the smelting of certain lead ores,

[18] Ihne, E. R., and Kanning, E. W., Ind. and Eng. Chem., *31*, 88-91 (1939).
[19] Dahlen, M. A., Ind. and Eng. Chem., *31*, 839-847 (1939).
[20] A. S. T. M. Specification D 405-41.

blue lead is now made under strict control in furnaces built especially for the purpose.

Chrome Green—This is a mixture of chrome yellow and iron blue. Because of its brightness, opacity, light-fastness, high tinting strength and relatively low cost, chrome green is the most widely used green pigment. Its principal defect is its sensitivity to alkali.

Chromium Oxide Green—This is by far the most permanent of the green pigments, being very resistant to light, heat, acids, and alkalis. It has, however, rather low tinting strength. It is made by calcining a mixture of sodium bichromate and reducing agent such as sulfur and carbohydrates.

Guignet's Green—This is the hydrated chromium oxide prepared by calcining a mixture of sodium chromate and boric acid. The resulting chromium borate is then decomposed with water. Like chromium oxide, it is fast to light, heat, acids and alkalis. It is brighter and cleaner than chromium oxide, but on the other hand, it has less tinting strength and opacity.

Phospho-tungstic Green—Certain basic dyestuffs precipitated by phosphotungstic acid, or less commonly, phospho-molybdic acids, comprise an interesting group of green pigments. These pigments are rather transparent, and are sensitive to alkalis, but are fairly light-fast.

Phthalocyanine Green—Introduction of chlorine into phthalocyanine changes the blue color to green. Like its blue relative, phthalocyanine green is fast to acids, alkalis, light and heat.

Carbon Black[21]—Tremendous amounts of natural gas are burned with a smoky flame to make carbon black, or gas black, as it is also called. The mass tone is black but tints have a reddish or brownish hue.[22]

Lampblack—Solid and liquid hydrocarbons are burned to make this black pigment. The gray colors made with lampblack have a bluish tone as contrasted with the reddish tone of carbon black.[21]

Bone Black—This pigment is made by calcining bones in the absence of air. It is approximately 15 per cent carbon and 85 per cent calcium phosphate, and consequently it does not have the enormous tinting strength of carbon and lampblack. On the other hand, its mass tone is very intense and grays made with it are neutral.

Graphite—Both the natural[23] and the artificial[24] forms are used to some extent principally in paints for metal.

Bronze Powders[25]—Various metals, stamped into thin flakes, have been used as pigments for many decades. The first was probably waste gold leaf. But gold was expensive and processes for obtaining other metals, particularly bronzes, in flake form were developed about the middle of the nineteenth century. Aluminum eventually became the substitute for silver powder. Still more recently, lead has been added to the list of metal flakes.

[21] Snyder, J. W., Paint and Varnish Production Clubs, Official Digest, *130*, 285-292 (1933).
Venuto, L. J., *ibid.*, *194*, 159-173 (1940).

[22] For a discussion of the making of carbon black and lampblack see Chapter 18.

[23] See Chapter 18.

[24] See Chapter 12.

[25] Edwards, J. D., "Aluminum Powder and Paint," 2nd Ed., Reinhold Publishing Corp. (1936).

The older method of making thin flakes of metal is to stamp small pieces of sheet or foil under heavy hammers until the particles are thin enough. A lubricant, such as a metallic soap, is added to prevent the particles from adhering to each other. After the stamping operation, most grades of powders are polished under revolving brushes bearing on the interior wall of a cylindrical drum.

During the 1930's paste bronze powders made their appearance. They are made in a ball mill [26] charged with the metal, a lubricant, petroleum spirits and steel balls. Smaller and thinner flakes are produced. Another important feature is the convenience of handling a paste instead of a dusty powder.

Metal powders, especially aluminum, are made in a wide range of particle sizes. The coarser sizes are called varnish powders and the finer ones, lining powders. Both types are used in paints, but only the lining powders are used in printing inks. Very coarse powders, called glitter and metallic, are used for some purely decorative effects.

The characteristic properties of bronze powders in paint are opacity and resistance to the passage of moisture. These properties are the result of the overlapping arrangement of the flakes similar to that assumed by leaves that have fallen from trees, wherefore, the phenomenon is called "leafing." This property is due to the coating of lubricant and to the polishing which the flakes receive.

Zinc Dust—This material was originally the "blue dust" by-product in the production of spelter, but today it is made in furnaces specially designed and operated for its manufacture. It is not in the form of flakes as are the metals described above. It is a valuable pigment for rust-inhibitive paints and is a component of special paints for galvanized iron.[27]

Flushed Colors—This term is applied to color pigments that have been transferred directly from the water wet press cake to oil or other paint vehicle without passing through the dry state. Practically all pastes of basic carbonate white lead in linseed oil have been made in this way for many years, as described in Chapter 26 on white lead. About 1930 the method was successfully extended to include many pigment colors.

To flush a pigment the damp press cake is mixed in a heavy-duty mixer with the vehicle, a small percentage of a flushing aid sometimes being added. The vehicle displaces the water, most of which rises to the top and is poured off. The residual water is removed under vacuum. Colors may be flushed in a wide variety of vehicles.

In general, it may be said that flushed colors have higher tinting strength than dry colors; they settle less, and impart better gloss. On the other hand, the same pigment, flushed, must be stocked in several vehicles against one item for the dry color. The extra cost of the flushed color must be credited with the cost of grinding the dry color.

[26] Hall, E. J., U. S. Patents 1,569,484, January 12, 1926; 2,002,891, May 28, 1935.
[27] "Metallic Zinc Powder in Industrial Paint," The New Jersey Zinc Co., 160 Front Street, New York (1934).

WHITE ZINC PIGMENTS[28]

Zinc Oxide—Though this material was known as a laboratory product in the eighteenth century and was, from time to time, mentioned and offered as a possible substitute for white lead, it was not until towards the middle of the nineteenth century that it became commercially available as a painting material. Its production on a practical scale was due to the labors of LeClaire, a contracting painter and philanthropist of Paris, and his friend, Sorel, an industrial chemist, to whom also is due the invention of "galvanized" iron. LeClaire's motives were philanthropic. His desire was to produce a satisfactory white pigment to replace white lead and thus eliminate the danger of lead poisoning.

LeClaire, being what we should today style a "socialist," was especially concerned with the situation as he found it among his own employees. To him is generally accorded the honor of introducing zinc oxide as a pigment, though his larger fame comes from his repute as "the Father of Profit-Sharing," which system he established not only in his own shops, but also in the Compagnie de la Vielle Montagne, to which he transferred his process for the manufacture of zinc oxide.

His establishment obtained a number of painting contracts from the Government. These he executed with zinc oxide, acknowledging the fact after attention had been called to them by their durability and permanence of color.

The ultimate result of the controversy then started was a series of Government restrictions prescribing the substitution of the new pigment for white lead in various departments. These restrictions lapsed and were revived from time to time, but finally in 1915 a law went into effect prohibiting the manufacture or use of white lead in France.

In the LeClaire-Sorel process metallic zinc or spelter is the raw material used. Because it was invented in France, it is commonly called the *French Process* and the product *French zinc* or *French zinc oxide;* and because the zinc ores pass through two manufacturing stages, the process is frequently called the *Indirect Process.*

Another process invented shortly after, in America, by Jones and somewhat modified by Wetherill, produces the oxide directly from zinc ores.[29] From the country of its origin, it is known as the *American Process* and from its character, as the *Direct Process.* The details of the process as well as the character of the ore that is used determines the nature of the product.

Raw Materials—Any ore of zinc can be used as a raw material. In decreasing order of their economic importance, they are:

Sphalerite, or "zinc blende," zinc sulfide, ZnS, sometimes found practically pure, but generally associated with sulfides of other metals.

Smithsonite, zinc carbonate, $ZnCO_3$.

Calamine, hydrous zinc silicate, $2ZnO \cdot SiO_2 \cdot H_2O$.

Willemite, the orthosilicate, Zn_2SiO_4.

Zincite, zinc oxide, ZnO.

[28] The author has drawn freely upon the material written by George B. Heckel for previous editions of this book.
[29] Ingalls, W. R., "Metallurgy of Zinc and Cadmium," McGraw-Hill (1906).

Franklinite, a combination of manganous, ferrous, manganic and ferric oxides with zinc oxide, $(Fe, Mn, Zn)O \cdot (Fe, Mn)_2O_3$, in which the metallic elements are present in variable proportions. The ore from Franklin, New Jersey, averages approximately: iron, 42 per cent; manganese, 14 per cent; zinc, 16 per cent.

There are various other zinc minerals usually found associated with those above enumerated and utilized with them, but they are, by themselves, of little economic importance.

Preliminary Treatment—The treatment of the ore depends upon its character and its associations. These operations, however, usually involve sorting, crushing, sizing and mechanical separation.[30]

For many years, especially for the direct process, the most important ores were those mined at Franklin, New Jersey. This deposit consists mainly of willemite, franklinite, and zincite in a gangue of calcite; though associated with these are found many other zinc-bearing minerals. The ore is delivered on a picking table, where the larger pieces of waste are removed by hand. The residual ore is reduced by rock breakers and crushers to buckwheat size. Franklinite contains iron oxides and is strongly magnetic. This property is utilized in its separation. The crushed ore is delivered on a belt, by which it is carried beneath the poles of powerful electro-magnets, across which a second belt moves at right angles to the belt carrying the ore. Coming beneath the magnets the franklinite is lifted to the under side of the transverse belt and carried by it to one side, while the remaining material passes forward to receiving bins. The franklinite, being carried by the upper belt out of the magnetic field, falls into a separate bin.[31]

Improved metallurgical practices have reduced the former advantage of franklinite for the production of direct process zinc oxide to a level where many producers are successful with zinc sulfide ores. Usually the ore is concentrated by jigging and flotation processes. By a preliminary roasting[32] the concentrate is converted to a material that analyzes approximately 90 per cent zinc oxide. In some cases, it is desirable to use fire methods for concentrating the ores. These methods resemble the preliminary roasting described above, or are essentially the production of crude zinc oxide fume which must be re-processed.

French Process Zinc Oxide—In this process, metallic zinc (spelter) of the desired purity is volatilized from metal pots or retorts. Air is admitted to the vapors which ignite and burn to zinc oxide, according to the equation, $Zn + O = ZnO$. The oxide is conducted from the furnace by the suction of a fan and thence to a settling chamber or to large vertical cloth collecting bags in a bag room. (See Figure 1.) In passing through the collecting system, the finely divided pigment forms large flocs which are retained by the bags, the air and other gases accompanying the pigment readily escaping. About one-half pound of oxide per square foot of bag surface is collected per day. From time to time, the pigment is removed from the bags, tested, graded and packed in barrels or in paper bags.

[30] See Chapter 2.

[31] Richards and Locke, "Textbook of Ore Dressing," 3rd Ed., p. 294, McGraw-Hill (1940).

[32] See Chapter 24.

Electrothermic Process—A variation of the French process is known as the Electrothermic Process, in which molten zinc is volatilized by passing electric current through it between carbon electrodes.[83] (See Figure 2.) The zinc fume is oxidized under controlled conditions as it leaves the furnace. In one such installation, a particle with an average diameter of 0.15 micron is obtained.

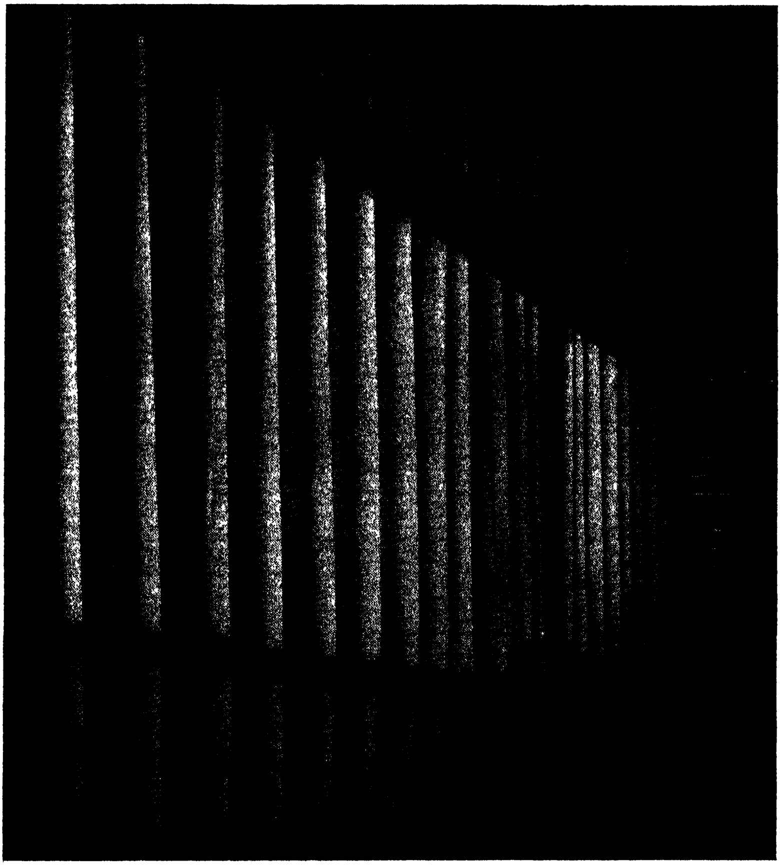

FIG. 1. Zinc Oxide Bag Room. (Courtesy St. Joseph Lead Co.)

Metallic zinc for French process oxide is usually prepared by heating an intimate mixture of ore and anthracite in a retort to a temperature well above the boiling point of zinc. As rapidly as the metal is formed, it is therefore distilled and condensed in fire clay condensers.[84] Metallic zinc is also prepared electrolytically.[84]

Grades of Oxide—French process oxide was formerly sold in three grades designated respectively as *White Seal, Green Seal* and *Red Seal.* However,

[83] Anon., Chem. and Met., *48,* No. 2, 142-145 (1941).
[84] See Chapter 24.

other grades of French process oxides which do not correspond to any of these seals are now made.

White Seal. This grade is characterized by brilliant whiteness, high apparent volume and extreme fineness. It is packed 150 pounds to the barrel, as compared with 300 pounds of other oxides.

Green Seal. Equal in whiteness to "White Seal" but less voluminous.

Red Seal. The cheapest of the three grades, and neither so white nor so smooth in texture as the others.

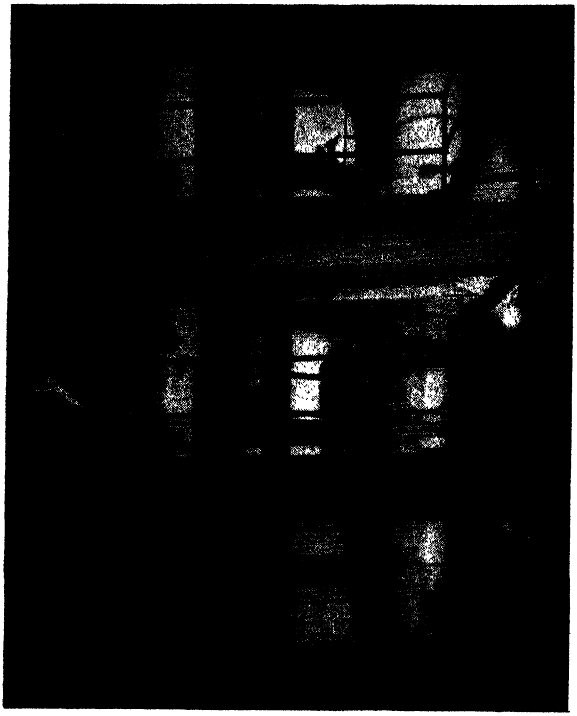

FIG. 2. Electrothermic Process Furnace for Zinc Oxide. (Courtesy St. Joseph Lead Co.)

American Process Zinc Oxide—In this process, as already stated, the raw materials are the oxidized ores of zinc, usually concentrated to contain from 20 to 90 per cent of zinc oxide. In the older type of furnace, the crushed ore, intimately mixed with anthracite, is put upon perforated grate bars. The furnace is built upon the plan of a fire box and is provided with an under grate blast. It is opened only for charging and for removal of the clinker after a charge is burned out. In one of the newer types of furnace, the charge of ore and anthracite in the form of briquets is contained on a moving grate.[85] (See Figure 3.) In still another type, the charge is passed through a preheater to a furnace where the required final heat is supplied by a current of electricity between two carbon

[85] Breyer, F. G., American Paint J., July 20, 1936.

electrodes. A feature of this furnace is the careful control which allows the zinc to be volatilized without being accompanied by undesirable gases such as sulfur dioxide.

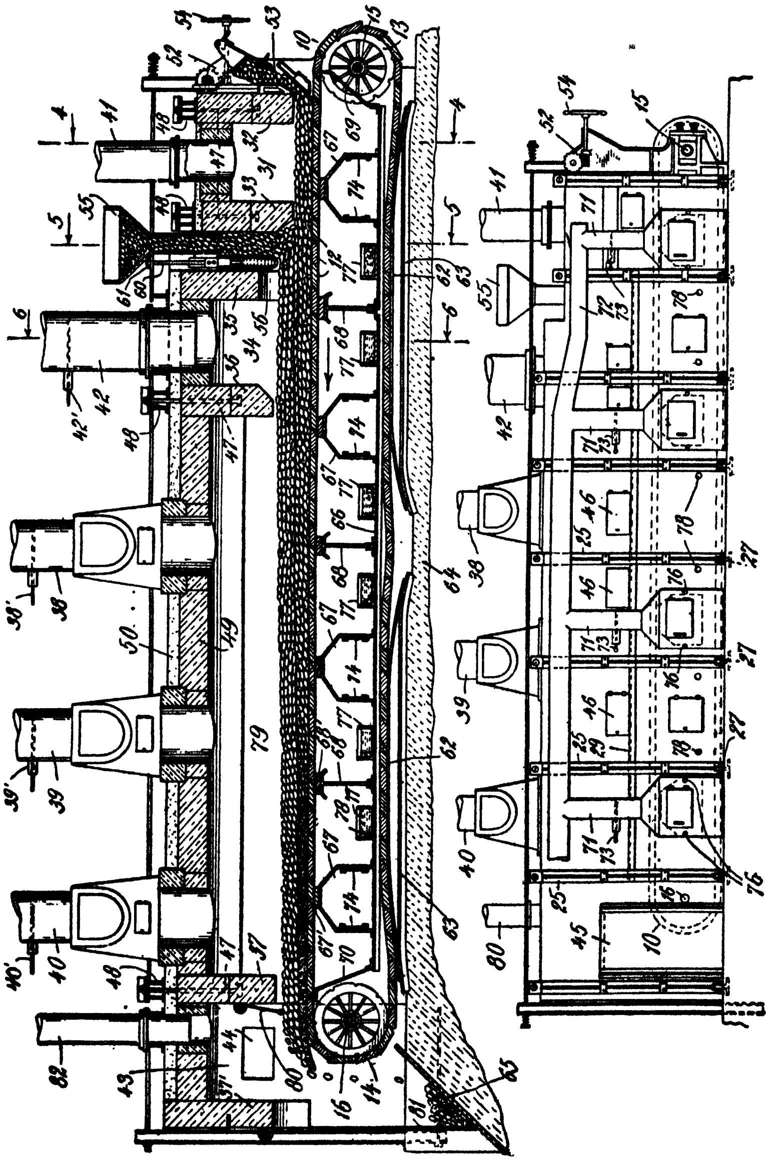

FIG. 3. Mechanical Zinc Oxide Furnace.

The chemistry of the American process is a combination of the retort method of preparing metallic zinc with the French process of preparing the oxide. The zinc compounds in the ore are reduced to metal at temperatures considerably above the boiling point of the metal. From this stage, the metallic vapors are converted to oxides as in the French process.

When the ore is a "blende" (zinc sulfide), the products of the preliminary roasting are sulfur dioxide, SO_2, and zinc oxide ZnO, according to the formula, $ZnS + 3O = ZnO + SO_2$. In some cases the sulfur dioxide is allowed to escape into the air; in others it is further oxidized to SO_3, the production of sulfuric acid [36] thus becoming a subsidiary branch of the industry. With this ore, then, the process of manufacturing the oxide really starts with zinc oxide as the raw material. It will be seen, in considering the remaining ores, that this is always the case.

When carbonate ores (*smithsonite*) are utilized, carbon dioxide is driven off and goes forward with the furnace gases, leaving zinc oxide as a residue, according to the simple equation $ZnCO_3 = ZnO + CO_2$. Here again, we have zinc oxide as the real raw material in the oxide furnace.

In the case of the silicates, the silica takes no part in the reaction, and remains behind as a furnace residue. Since the formula for *willemite* is $2ZnO \cdot SiO_2$ and that for *calamine*, $2ZnO \cdot SiO_2 \cdot H_2O$, and since, in the latter, the water and the silica are excluded from the reaction, here once more we have zinc oxide as the raw material of the process. With zincite, which is itself zinc oxide, and with franklinite, in which the zinc is present as oxide, the same situation obtains. It will be seen, therefore, that the production of zinc oxide always involves first the reduction of the oxide, ZnO, to metallic zinc, and secondly, the re-oxidation of this product to ZnO.

The residue, after the removal of the zinc from franklinite, contains iron and manganese. This residue is further treated in blast furnaces to produce spielgeleisen. This product runs from 19 to 21 per cent manganese, from 1 to 2 per cent silicon and under .08 per cent phosphorus, the balance being iron. In the Bessemer [37] process it is used as a recarburizer and as a source of manganese, as well as for special purposes in the open hearth process and in foundry practice.

Physical Chemistry of Zinc Oxide Manufacture—Although the chemical reactions involved in the production of zinc oxide from its ores are simple and few, the physical chemistry of the oxide furnace is, on the other hand, a somewhat complex problem, and a correct understanding of it has a considerable bearing on the successful conduct of the process.

Depending upon the conditions of manufacture, the particles of zinc oxide vary in shape and size. The fine particle French process oxides are sometimes considered to be amorphous, although X-ray examination shows them to be crystalline. The American process oxides are usually decidedly crystalline and much larger. The crystalline forms may be placed in two classes, "rounds," of no definite shape, and acicular, that is, prismatic or needle-like.[38] Under usual conditions, the American process oxides are more or less acicular, whereas the French process oxides are not. It is possible, however, to prepare the acicular type by the French process and the so-called amorphous type by the American process. The shape of the particle seems to be influenced primarily

[36] See Chapter 7.
[37] See Chapter 23.
[38] Depew, H. A., Ind. and Eng. Chem., *27*, 905 (1935).
Kekwick, L. O., J. Oil and Colour Chem. Assoc., *21*, 118-133 (1938).
Werthan, S., Paint and Varnish Production Clubs, Official Digest, *206*, 267-279, May, 1941.

by the method of oxidizing the zinc fumes; the size seems to be controlled by the rate of cooling.

An extremely fine particle size is made for use in rubber.[39] Types of intermediate average particle size are prepared for use in paints, inks, and paper coatings. A grade composed of relatively large average particle size is made for ceramics.

Wet Process Zinc Oxide—Zinc oxide prepared by precipitation methods has not been very successful. In this process, the zinc is precipitated as the hydroxide or the basic carbonate, which is dried and calcined. In general, zinc oxide prepared in this way has very little hiding power, but is claimed to be more reactive with drying oil fatty acids. It is therefore suggested as a modifier of vehicles, or of other pigments.

Zinc Oxide in Paint—As a pigment for paint, zinc oxide is readily wetted by oils. It reacts to some extent with fatty acids to form soaps that tend to thicken paint so that settling of the pigment portion is retarded. The zinc soaps also tend to make the dried film harder, so that it chalks less and retains tints well. The tendency to dry hard is so pronounced that, in many climates, an exterior paint film containing only zinc oxide and linseed oil cracks excessively and may peel off in large sheets. Where the humidity is sufficiently high, as in the tropics or near the sea, the cracking is repressed and such paints may eventually perish by chalking. Zinc oxide is an efficient absorber of ultraviolet light and is said to reduce the destruction of paint vehicles by this agent. As a white base for tinted paints, zinc oxide ranks high because of the degree to which the original color is retained in such paints.

Zinc oxide possesses other properties that make it valuable in paint. In contact with hydrogen sulfide fumes, it does not change color, as any zinc sulfide that may be formed is also white. It resists the growth of mildew, partly because of the hardness which it imparts to films, but probably more because it poisons the mildew.

For exterior paints, the best zinc oxide pigments are those in which extremely fine particles are absent. The usual grade of zinc oxide for exterior use contains a variety of particle sizes and shapes; such as round and acicular. At the present time, the economic factors are such that this kind of pigment is made by the Direct process.

For interior decorative paints, zinc oxide—usually the French process—is generally used in much higher percentages than in exterior paints. In wall paints it is combined with various other pigments, because it produces films that withstand washing more effectively and because it decreases any tendency of the paint film to discolor or *after yellow* in service.

In the manufacture of enamels, the *French process* oxides play an important part, especially "White Seal" and "Green Seal," or grades corresponding thereto. They are preferred because their use yields a film of excellent color and luster.

Other important uses of zinc oxide are in the compounding of rubber,[40] paper coatings,[41] inks, plastics[42] and ceramics.[43] These uses are discussed in other chapters of this book.

[39] See Chapter 39.
[40] See Chapter 39.
[41] See Chapter 37.
[42] See Chapter 31.
[43] See Chapter 21.

Leaded Zinc Oxides—Since most ores of zinc contain more or less lead in the form of galena, the direct process zinc oxide procured from it contains more or less lead in the form of the basic lead sulfate, the basicity being up to 25 per cent, expressed as PbO. A zinc oxide pigment is termed a "lead-free" product when it contains, at most, only a few hundredths of a per cent of lead. According to the Federal specification and the American Society for Testing Materials specification, a lead-free oxide, American process, must contain at least 98 per cent ZnO; French process, 99 per cent. The most common grades of leaded zinc oxide are the 5 per cent and the 35 per cent, but other percentages are available.

At one time it was considered that the excellent results obtained with leaded zincs of the 35 per cent grade were due to the zinc oxide and the basic sulfate of lead existing in solid solution. Equally good results were not obtained with mechanical mixtures of basic lead sulfate and some zinc oxide pigments. More recently however, it is considered by many that the poor results heretofore obtained with blended products were due to the presence of large quantities of extremely fine particle size zinc oxide or to the form of the particles. Hence, today a large proportion of the high-leaded zinc oxide is a mechanically prepared mixture. Manufacturers, however, furnish the co-fumed products to consumers who specify it. The ideal conditions for the formation of zinc oxide and basic lead sulfate are not identical. Each of the pigments is whiter and brighter when made separately, and the desire for a whiter product is partly responsible for the increasing use of the blended product.

In the manufacture of paints, leaded zinc oxide is used for the same purpose as mixtures of zinc oxide and basic sulfate of lead.

Zinc Sulfide Pigments—Chemically precipitated zinc sulfide pigments are made in three groups: (1) zinc sulfide, (2) composite zinc sulfide pigments, and (3) lithopone. The minimum zinc sulfide contents established by the American Society for Testing Materials for these groups are 97, 45, and 26 per cent, respectively, but they are often referred to as straight zinc sulfide, 50 per cent zinc sulfide, and 30 per cent zinc sulfide. Each pigment is especially adapted for use in particular fields which often overlap.

Zinc Sulfide. Two methods account for practically all of the zinc sulfide produced today. In the older process, hydrogen sulfide is passed into a solution of zinc sulfate.

Freshly precipitated and dried zinc sulfide made according to this method has very poor hiding power and other pigmentary properties. These properties are improved by calcining the washed and dried material at temperatures ranging from 600° to 900° C.[44] At the proper time the material is quenched in water to prevent the oxidation of zinc sulfide to zinc sulfate. This quenching is supposed to change the structure and certainly contributes materially to the quality of the pigment. Very careful wet milling follows, then drying and finally dry milling and bolting.

In the other process, zinc sulfate is reacted with a thiosulfate according to the equation

$$ZnSO_4 + Na_2S_2O_3 + H_2O \qquad ZnS + Na_2SO_4 + H_2SO_4$$

[44] Work, L. T., and Odell, I. H., Ind. and Eng. Chem., *25*, 411, 543 (1933).

Since sulfuric acid reacts with thiosulfate to form free sulfur, a base, such as sodium carbonate, is added to neutralize the acid as rapidly as it is formed.

The particle size of zinc sulfide made by this process is such that calcination is not needed to develop good hiding power and other properties. On the other hand, if merely dried, the pigment is light sensitive (see lithopone). However, mild calcination or roasting further improves the pigmentary properties. No quenching is required.

Composite Zinc Sulfide Pigments. Three types of composite zinc sulfide pigments are now in commercial use—a mixture of zinc sulfide with (1) barium sulfate, (2) calcium sulfate or calcium carbonate, and (3) magnesium silicate. For convenience, these pigments are called Zinc Sulfide-Barium, Zinc Sulfide-Calcium, and Zinc Sulfide-Magnesium, respectively. They are also known as high strength lithopones.

Zinc Sulfide-Barium may be made by a method analogous to that of making lithopone, except that part of the zinc sulfate is replaced by zinc chloride, the amount of barium sulfate formed being proportionately reduced. However, most of this pigment is probably made by mixing uncalcined normal lithopone and straight zinc sulfide in the proper proportions and then calcining, quenching, drying, and grinding the mixture. Zinc Sulfide-Calcium is made with calcium instead of barium sulfide. Zinc Sulfide-Magnesium is made by mixing zinc sulfide and magnesium silicate, a portion of which is often of the micaceous type.

Lithopone. This pigment, the product of the double precipitation of barium sulfate and zinc sulfide, was the first of the group of zinc sulfide pigments to be produced. It is generally considered to have been patented in England, by J. B. Orr, about 1874, and first produced under the name "Charlton White." It later became more familiar to the consuming trade as "Orr's Enamel." Investigation, however, shows that a Frenchman, G. F. De Douhet, discovered it some twenty-five years earlier.[45] About twenty years after Orr, the manufacture of lithopone received great impetus in Germany, some six or more important plants being established there. Its production in the United States followed shortly thereafter.

Its importance as a paint pigment, however, was not realized until it began to be utilized for the manufacture of flat interior wall paints, since which time the growth of the industry has been phenomenal. In 1935 the production in the United States alone was over 300,000 tons. Approximately, 80 per cent of the total production is consumed in the manufacture of paints.

The manufacturing process consists essentially of the simultaneous precipitation of barium sulfate and zinc sulfide from aliquot solutions of barium sulfide and zinc sulfate, the reaction being as follows:

$$BaS + ZnSO_4 = BaSO_4 + ZnS.$$

The barium sulfide for the operation is obtained by furnacing carefully purified and finely ground barytes with coal, the reaction being represented by the equation:

$$BaSO_4 + 4C = BaS + 4CO.$$

[45] British Patent 13,092 in 1850 and U. S. Patent 8356 in 1851.

After precipitation, the pigment is washed, calcined, and quenched, as was described under zinc sulfide.

The furnacing, however carefully conducted, always produces some zinc oxide which appears in the finished product. The average composition of an acceptable product is from 71.5 to 72.5 per cent of barium sulfate and from 27.5 to 28.4 per cent of zinc sulfide, with the zinc oxide content under 1 per cent. Most of the present production contains less than 0.5 per cent.

Until about 1920, the outstanding objection to lithopone as a paint pigment was its sensitiveness to light. Up to that time, much of the lithopone became gray on exposure to sunlight but recovered its original whiteness in the dark. Many theories have been advanced to account for this peculiarity, but the one commonly accepted is that metallic zinc is formed photochemically by ultraviolet light. Contributing causes for this action are the presence of impurities, notably chlorides, hence great attention is paid to the purification of raw materials.

Among other methods for rendering lithopone light-proof is the addition of small amounts of salts of vanadium, chromium and tungsten, phosphoric acid, and substances that readily yield sulfur, such as mixtures of thiosulfate, sulfites and polythionates with ammonium salts. As a result of one method or another, light-sensitive lithopone is now a rarity.

Titanated Lithopone. This term is applied to a composite pigment containing approximately 85 per cent of lithopone and 15 per cent of titanium oxide. By some manufacturers it is prepared by mixing the pigments before calcination; by others, after calcination.

Zinc Sulfide Pigments in Paint—Zinc sulfide pigments are white and dense. The unreduced pigment has hiding power and tinting strength values from two to three times those of lithopone, yet lithopone ranks high in these respects and, commercially, is the most important pigment in the group. If any differentiation is to be made, it might be said that straight zinc sulfide finds application in specialties where high hiding with a minimum of pigment is desired, such as enamels, printing inks and nitrocellulose lacquers; lithopone is the chief pigment in flat wall paints and enamel undercoaters. These pigments are also used in linoleum, oilcloth, automobile tires, floor tiling, and hospital and druggists' sundries.

Lithopone—and to a somewhat lesser degree the high zinc sulfide composite pigments and titanated lithopone—is made in many modifications to suit the requirements for different types of vehicles and uses. These modifications are brought about by regulating the proportion of zinc oxide in the composition, by addition of various compounds before calcination, by the manner of milling the calcined pigment, and by addition of metallic soaps or other compounds. In general, the modifications include pigments described as "general purpose," "coarse texture," "fine texture," "reactive," "non-reactive," "thixotropic," "water dispersion," "low consistency," and "high consistency."

TITANIUM PIGMENTS

Although titanium is one of the most abundant elements in the earth's crust, being ninth in the list, its successful use in pigments is a twentieth century development. Ground rutile and ilmenite are reported to have been used in paint in England and America as early as 1869, but probably the first study of white titanium dioxide pigments was begun about 1908 by Rossi and Barton at Niagara Falls, N. Y. The First World War held up the commercial development but at its end manufacture of a paint pigment was under way simultaneously in Norway and the United States. In the United States, in 1921, the first pigment appeared, a composite one consisting of titanium dioxide 25 parts and blanc fixe 75 parts. In 1925, titanium-calcium and straight titanium dioxide appeared. The list of titanium pigments now includes:

Straight titanium dioxide (95 per cent or higher TiO_2)
Titanium-barium, consisting of titanium dioxide and barium sulfate (blanc fixe)
Titanium-calcium, consisting of titanium dioxide and calcium sulfate
Titanium-magnesium, consisting of titanum dioxide and magnesium silicate
Lead titanate

Most of these are made in several types, characterized by crystal form, particle size and method of milling.

Titanium Dioxide—*Sulfuric Acid Process.* There are several titanium-bearing minerals, of which ilmenite is the most abundant. Largely on account of availability and cost, ilmenite beach sand imported from India is the principal ore used today in the United States.[46] After being ground, the ore is digested with concentrated sulfuric acid to convert the titanium and iron to soluble sulfates. To start the reaction, the batch is gently warmed by the addition of a small amount of water. In a short time the reaction becomes violent. Scrap iron is added to reduce the ferric sulfate to the ferrous state. Ferrous salts are more readily washed out of the hydrous titanium oxide pulp formed later on. The solution is clarified and the concentrations of the sulfuric acid, the titanium, and the iron are adjusted for the next step.

The titanium sulfate is then hydrolyzed by boiling, the iron remaining dissolved in the sulfuric acid. The insoluble hydrous titanium oxide is washed and filtered off, then fed into a rotary kiln, where it is dried and finally calcined at a temperature of approximately 800° to 850° C. The end product of the calcination is titanium dioxide, which is milled either wet or dry to a suitable fineness. The conditions of calcination are important, as it is at this stage that the high hiding power of titanium dioxide is developed. The milling operation is also important, and widely different properties may be developed by different milling procedures.[47]

The composite pigments, titanium-barium and titanium-calcium, are made in two ways, co-precipitation or dry blending. If made by co-precipitation, the requisite amount of blanc fixe or calcium sulfate in pulp form is dispersed in the hydrolyzing vessel, after which the process is essentially the same as described above.

To make the composite pigments by dry blending, the desired proportions

[46] Dislocation of transocean shipping due to the Second World War will probably change this status.

[47] Work, L. T., Tuwiner, S. B. and Gloster, A. J., Ind. and Eng. Chem., *26,* 1263 (1934).
Work, L. T., and Tuwiner, S. B., *ibid.*, *26*, 1266 (1934)

of titanium dioxide and extender—blanc fixe, calcium sulfate, or magnesium silicate—are merely thoroughly mixed in large vessels. There appears to be no essential difference in the composite pigments, traceable to the method of manufacture.

Fluoride Process. This process was proposed by S. S. Svendsen and is based on the insolubility of ammonium iron fluoride and the solubility of the corresponding titanium salt, ammonium titanium fluoride.[48]

Ilmenite is digested with ammonium fluoride at an elevated temperature. The insoluble iron salt is removed and the solution is further purified by the removal of the heavy metals. Ammonia is then added to the solution under rigidly controlled conditions to precipitate the titanium as hydrous titanium oxide. This hydrous titanium oxide is termed gamma titanic acid and gives a characteristic X-ray pattern. The ammonium fluoride solution is separated from the precipitate and is ready to be used again. The precipitate is calcined and milled in the usual manner. The rutile type of crystal is obtained in this process.

The ammonium fluoride of the iron system is also recovered and returned to the system. The process is therefore cyclic and only a small amount of ammonium fluoride needs to be added to replace that lost in the process.

Other Titanium Pigments—Lead titanate ($PbTiO_3$) is made by calcining a mixture of litharge and titanium dioxide. Although largely titanate of lead, the commercial pigment contains approximately 7 per cent or less of lead sulfate due to the method of manufacture. It is ivory in color. The cause of the color is more or less obscure, but is believed to reside in the lead titanate itself. It is not entirely due to the litharge. The pigment is remarkable for its resistance to chalking.

Other titanates have been proposed as pigments and have actually been prepared, but none as yet has shown much promise as a pigment.

When tinted paints chalk, they undergo more or less fading due to a relatively greater change in the opacity of the white pigment than of the tinting pigment when the vehicle disintegrates. To reduce this effect in the case of titanium pigments, compounds of certain metals such as chromium and vanadium have been introduced during the manufacture. Gray, buff and ivory-colored titanium pigments have been prepared by this means.

Properties of Titanium Dioxide—The wide acceptance of titanium dioxide as a pigment is primarily due to its high hiding power, as indicated by its high refractive index. The early types and most of the present ones have the crystalline form of anatase with a refractive index of approximately 2.55, but some types are now made, which have the crystalline structure of rutile, with a higher refractive index of 2.7.

Titanium dioxide is chemically inert, and exterior paints made with the older types chalk freely, that is, the binder perishes, leaving pigment powder on the surface. Varying degrees of resistance to this tendency have been achieved by precipitation or calcination in the presence of catalysts, such as antimony oxide or aluminum oxide. An important property of the pigment is its non-toxicity. Titanium pigments are used in other industries, such as rubber, paper and rayon, as well as in the paint industry.

[48] Svendsen, S. S., U. S. Pat. 1,995,334; 2,042,434; 2,042,435; 2,042,436; 2,165,315.

ANTIMONY PIGMENTS

Antimony Oxide[49]—This is a white pigment made by roasting antimony ores in much the same manner as zinc oxide is made. Paint pigment grades originated in Europe and were first successfully made in the United States about 1930. Antimony oxide is a pigment of small particle size, of soft texture and low oil absorption. It imparts high hiding power to a paint by reason of its high refractive index, 2.2 Paints made with this pigment do not chalk excessively.

Probably a wider use of antimony oxide is in ceramics, but the material for this use differs from that used in paints.

WHITE LEAD PIGMENTS

For a description of the manufacture of lead pigments, see Chapter 26.

LINSEED OIL

Linseed oil, the best-known member of the vegetable drying oil family, is obtained from the seed of the flax plant (*Linum usitatissimum*). Flax is also the source of linen. The same plant, however, cannot be used to produce both linen and oil, as that grown for fibre must be cut before the seed is ripe. The flax plant flourishes in a wide range of climates, the principal countries being the United States, Canada, Russia, India, and Argentina.

In the United States, the legal weight of a bushel of flaxseed is 56 pounds. The percentage of oil in the seed ranges from 32 to 43, the average being equivalent to somewhat less than 2½ gallons of oil per bushel of seed.

Separating the Oil—Two methods account for the entire production of the United States. These are hydraulic pressure and Anderson Expeller. The solvent extraction of linseed oil is not practiced in the United States today.

Composition and Properties—According to Jamieson, the composition of the acids of linseed oil is:

		Per Cent
Palmitic	$C_{15}H_{31}$,COOH	8 to 11
Stearic	$C_{17}H_{35}$,COOH	
Oleic	$C_{17}H_{33}$,COOH	5 to 19
Linolic	$C_{17}H_{31}$,COOH	23 to 63
Linolenic	$C_{17}H_{29}$,COOH	24 to 50

The amount of unsaponifiable matter in linseed oil is of the order of 1 to 2 per cent, and consists of compounds of phosphorus, calcium and magnesium with non-oleaginous matter, probably carbohydrates (mucilage). If allowed to age, the mucilaginous matter will separate and along with foreign matter will settle as "foots" to the bottom of the container. Heating the oil to 450° F. or higher accelerates the separation and the oil is said to "break."

The characteristic property of the "drying" oils is due to the high degree of unsaturation of their fatty acids. Oxygen from the air is absorbed at the

[49] Riker, H. S., American Paint J., *17,* No. 39, 47 (1933).

double bonds, giving rise to a sequence or concurrence of oxidation, polymerization and association reactions that finally result in the conversion to a solid or gel. The role of each of the reactions is influenced by such factors as temperature, free fatty acids, light, and the presence of certain metallic and other compounds. In fact, polymerization and association may be brought about by heating the oil in a vacuum. The solid product is called linoxyn. Among other products are carbon dioxide, water, and low molecular weight fatty acids and aldehydes. In thin films, the conversion, called drying, requires a period of 48 hours or more, depending upon temperature, relative humidity, and the amount of light. By the addition of small percentages of compounds of lead, manganese or cobalt, the drying may require as short a time as 8 hours or less.

To a certain extent, the drying property of linseed oil is indicated by its iodine value. According to the specifications of the American Society for Testing Materials for Raw Linseed Oil, this should be not less than 177. The value depends upon the type of flax and the place where it is grown. At one time the average iodine value of North American seed was much higher than that of today's wiltproof and heavier bearing flax.

The amber color of raw linseed oil varies according to its origin, degree of maturity of the seed and to the care used in separating it. Sunlight bleaches the oil, and the yellow color imparted by the oil to exterior house paints fades quickly after application of the paint. On the other hand, the color is often intensified in diffuse light and in the dark. Much of the yellowing is due to changes in the highly unsaturated acids such as linolenic. For example, soybean oil, containing less of such acids, yellows less, whereas perilla oil, containing more, yellows more. Suitable refining reduces the tendency to yellow.

Tremendous amounts of linseed oil are used in the raw unrefined state in paint and linoleum. Lesser amounts are used in such products as brake linings, gaskets, fibre board, and foundry cores. For many products, refined, boiled or thickened types are better. Among these products are certain types of paint, varnish, ink and patent leather. Because of its cost, practically none of the oil is used for food in the United States.

Refined Linseed Oil[50]—Refining methods range from simple refrigeration and filtration to effect removal of the solid fats, foots and a small portion of the break, to more rigorous methods involving treatment with acids, alkalis, and bleaching earths.

Acid Refined Oil. Lots of 500 to 1,000 gallons of oil contained in lead-lined tanks are treated with strong sulfuric acid, 60° to 65° Bé. About 1 per cent of the acid based on the weight of the oil is added in a fine stream to the oil which is vigorously agitated during the addition and for an hour or so afterward. The mucilaginous "break" and much of the coloring matter are coagulated in the form of a muddy-greenish sludge which is allowed to settle overnight. The oil is drawn off and washed with water and steam until free from sulfuric acid. The water is allowed to settle and is then drawn off. In some cases, additional bleaching and clarification may be effected by means of fuller's earth.

Acid refining causes some hydrolysis of the oil, whereby the amount of free

[50] For discussion of treatment and use of other oils, fats and waxes see Chapter 41.

fatty acids is increased. The extent of the increase is controlled by the strength of the acid and the temperature during treatment. High acid oil wets pigments readily and is much used as a grinding oil in making paint.

Alkali Refined Oil. In preparing this oil, the acid value is reduced to 0.5 or less by neutralization with aqueous 10 per cent caustic soda solution. The amount of caustic solution is estimated from the original acid value of the oil. The oil is first warmed slightly and the caustic solution is then added in fine streams to the vigorously agitated oil. After the precipitate has coagulated, it is allowed to settle. The oil is then drawn off into a tank and after being heated to drive off residual water, it is treated with bleaching clay.

Alkali refined oil is also known as varnish maker's oil.

Boiled Linseed Oil—If small percentages of oxides, acetates or certain other salts of lead, manganese or cobalt be added to hot linseed oil, they will be dissolved, with the formation of the corresponding salts of the fatty acids. Some authorities believe that a portion of the metals also combines with the glyceryl radical of the oil molecules. The metals so introduced are called driers because they accelerate the drying of the oil, and the oil so treated is known as boiled oil.

The term is a misnomer, since the oil is not heated to boiling. During the process, the oil becomes thicker, its density increases, and its color darkens. The drying time may be shortened to 8 hours or less.

Boiled oil made according to the process described above is known as kettle boiled oil. The percentages of metals introduced into the oil are approximately, lead 0.2 per cent and manganese 0.05 per cent. Cobalt is not used much for this purpose.

A large amount of boiled oil is today made by cooking large percentages of lead and manganese into a batch of oil and then adding this product, known as "crusher's drier," to raw oil. Since the bulk of this type of oil has not been heated, it is relatively pale and unthickened. Pale color is, of course, desired, but the slightly thickened kettle-bodied oil wets pigments better and gives better leveling and greater durability to paints made with it.

A third type made by adding liquid paint drier to raw oil is called "bung hole boiled oil." Containing volatile thinner, it smacks of fraud and has no standing in the industry.

Heat-Bodied Linseed Oil—When linseed oil is heated at elevated temperatures, its viscosity increases and it is said to be "bodied." Such oils are used to some extent in paints, but their principal use is in enamels and printing inks. Bodied oils for printing inks are called lithographic oils or lithographic varnishes. The thickening is mainly a result of polymerization, but if the bodying is done in open kettles some oxidation also takes place. Considerable amounts of oil are bodied in an atmosphere of inert gas or in completely filled closed kettles whereby practically all air is excluded. Heat-bodied oils are sometimes called stand oils because of the practice at one time of preparing thickened oils by allowing the raw oil to stand in the sun for a long time.

Blown Linseed Oil—Linseed oil may also be bodied by having air bubbled through it. In this case, the reaction is mainly oxidation followed by polymerization of the oxidized molecules. Blown linseed oil is used largely in interior paints and enamels. It dries to a harder film than heat-bodied oils.

In the paint industry a wide variety of treated linseed oils are used. The linseed oil in most exterior house paints is the raw form. Refined oil is, however, used to a large extent. Boiled oil and some bodied oils are used in lesser amounts. All oil for varnish making, including bodied and blown oils, is the refined grade.

The types of linseed oil regularly made and sold include the following:

Raw	Varnish maker's	Boiled
Clarified raw	Heat-bodied	Double-boiled
Refined	Blown	Ink
Bleached	Grinders	Patent leather

MISCELLANEOUS MATERIALS

Driers and Metallic Soaps—Paint driers are compounds or compositions which accelerate the chemical or physical changes leading to the solidification of paints or varnishes containing linseed or other drying oils. They are for the most part compounds (metallic soaps) of lead, manganese or cobalt with fatty, rosin, or other carboxylic acids.[51]

Metallic soaps[52] are made in two ways, namely, by precipitation and by fusion. In the first method, a salt of the metal, e.g., lead acetate, dissolved in water, is added to an aqueous solution of soap, e.g., sodium linoleate, that has been prepared by the saponification of linseed oil with sodium hydroxide. The precipitate, lead linoleate, is filtered and dried. The process requires careful attention to details such as temperature, rate of mixing, washing and so on.

In the fusion method, lead acetate, litharge, basic carbonate of lead or other decomposable lead compound, is slowly added to hot linseed oil. Fused soaps are much darker than precipitated soaps.

For use as driers, the principal acids are linseed oil fatty acids and naphthenic acid. As previously mentioned, lead, manganese and cobalt are the important metals.

In addition to their use as driers, metallic soaps are used to thicken paints and varnishes, and to reduce their gloss. These soaps are usually stearates or palmitates of aluminum, calcium or magnesium.

Copper and mercury soaps are used as preservatives for fish nets and as an ingredient of antifouling paints. Mercury in the form of a soap may be incorporated in paints as a fungicide.

Many paint and varnish manufacturers make their own driers, but a separate industry for manufacturing driers and other metallic soaps for use in paints, lubricants, rubber, and cosmetics has developed.

Thinners—Certain volatile organic liquids are used to thin surface coatings to consistencies that enable them to be applied by brushing, spraying or other methods.

Until the middle of the nineteenth century, the only solvents and thinners available were turpentine and ethyl alcohol. Today there are dozens, but the principal ones are turpentine, solvent naphtha and petroleum (mineral) spirits.

[51] Bennett, E. F., "A Review of Driers and Drying," Chemical Publishing Co., New York (1941).

[52] See also Chapter 42.

However, large amounts of alcohol are used for shellac varnishes and cellulosic lacquers. The latter coatings also require several other solvents,[53] such as butanol, butyl acetate, amyl acetate, and acetone. In special cases, chlorinated solvents[54] are useful.

The choice of solvent depends upon the nature of the product. Straight oil paints are satisfactorily thinned with the cheapest of all, ordinary petroleum spirits. Many oleoresinous varnishes require more powerful solvents, such as solvent naphtha, or specially prepared petroleum distillates containing aromatic compounds. Solvents for cellulosic lacquers and spirit varnish resins have been mentioned in the preceding paragraph. The manufacture of these is considered in other parts of this book.[53]

The important characteristics of thinners and solvents are solvency, that is ability to reduce the consistency of the coating material, and rate of evaporation from the film. Other properties considered are color, odor, and toxicity.

MANUFACTURE OF PAINT

Combining pigment and vehicle into a uniform mixture is not a grinding process in the sense that the pigment particles are broken down into still smaller particles, although this does occur to some extent in some cases. Rather is it a problem of wetting the surface of the particles with the vehicle. The ease with which a solid pigment particle is wetted by a liquid is a function of the interfacial tension between the solid and the vehicle.[55]

Wetting Agents—Pigments vary according to the ease with which they are wet by any selected vehicle, and likewise vehicles vary according to the ease with which they wet any selected pigments. Efforts have been made to find wetting agents that would shorten the grinding time of paints or would improve the dispersion, or do both. The most extensive studies have been those of the New York Paint and Varnish Production Club and the Detroit Paint and Varnish Production Club.[56] Materials studied include zinc naphthenate, oleic acid, butyl stearate, lecithin, Aerosols, Tergitols,[53] glycol esters, amides of vegetable oils, zinc rosinate, Nuade, amyl stearate, Nopco and Sharples'[54] agents. The success of the studies has been only fair, but some of the agents have found encouraging commercial uses.

Usually a wetting agent is specific in its action and therefore many agents must be kept on hand. In some cases shorter grinding time is obtained at the expense of poorer keeping properties. Many paint manufacturers have so prepared their vehicles that addition of wetting agents makes no noticeable effect.

[53] See Chapter 30.

[54] See Chapter 11.

[55] Murray, C. A., and Bartell, F. E., Scientific Section, Nat'l Paint, Varnish and Lacquer Assoc., Circ. *546*, 370-379, Nov., 1937.

——, "The Wetting of Pigments by Linseed Oil and Paint Vehicles," paper presented before Federation of Paint and Varnish Production Clubs, Chicago, Ill., Oct. 25-28, 1939. Scientific Section, Nat'l Paint, Varnish and Lacquer Assoc., Washington, D. C.

Allen, R. A., and Lanson, H. J., Paint, Oil and Chem. Review, April 11 (1940). These papers contain bibliographies for further study.

[56] New York Paint and Varnish Production Club, Scientific Section, Nat'l Paint, Varnish and Lacquer Assoc., Circ. *495*, 376-387, Nov., 1935.

Detroit Paint and Varnish Production Club, *ibid.*, Circ. *604*, 303-313, Nov., 1940

Moreover, some pigments have been surface coated with wetting agents during their manufacture. It has also been demonstrated that in most cases the stiffer and stickier the paste that is being ground, the more rapid is the grinding and the better the dispersion.

Paint Mills—These are devices by which the mixture of pigment and vehicle is rubbed between two surfaces. In most cases the paint is given a preliminary treatment in some kind of a mixer. This may be a heavy duty kneading machine, a pug mill, a chaser, or lighter duty machines. The more thoroughly the job of mixing is done the easier will be the job of grinding, but mixing alone can not do the complete job except in rare instances.

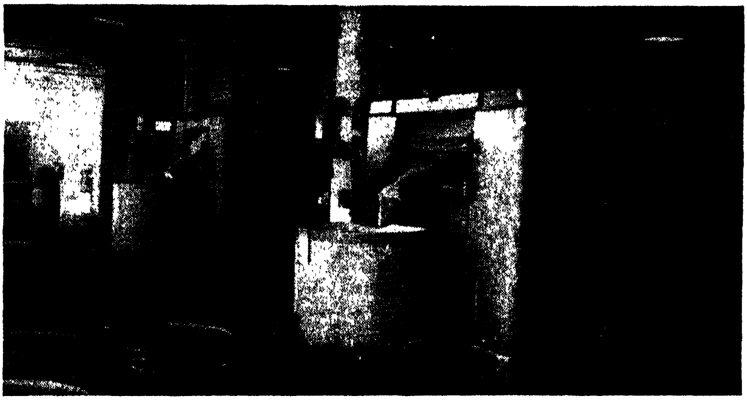

FIG. 4. Kent Roller Mill. (Courtesy Benjamin Moore and Company.)

Buhrstone Mill.[57] This is the oldest type of mill and consists essentially of two flat circular stones, between which the paint is ground. The upper stone is stationary and the lower stone revolves. The paint is fed to the mill through an eye in the upper stone and after passing through the mill is scraped from the edge of the stones. In the grinding faces of the stones is cut a system of grooves, the design of which is of utmost importance in determining the efficiency of the mill.

The buhrstone mill is gradually being displaced by other types, but it does possess some advantages. It is suitable for grinding hard pigments like silica, iron ores containing silica such as red oxide, brown oxide, sienna and umber. Some grades of these pigments cause excessive wear of any type of mill. However, it is a much simpler job to recondition a stone mill than a roller mill. The stones can be redressed in the paint factory itself, whereas the rollers must be sent out to a machine shop.

Roller Mills.[57] In this type, the paint is passed between parallel steel rollers, usually three or five to a mill. The batch of pigment and oil which has been thoroughly premixed is fed into the space formed by the first two rollers and a retaining plate between them at each end. Beginning at the loading end, each succeeding roller rotates at a higher speed, thereby rubbing and wiping off the film of paint adhering to the preceding roller. The paint on the last roller is

[57] See also Chapter 2.

scraped off by a sharp blade and directed by an apron to a receiver. In a three-roller mill, the rollers are located in a horizontal plane. In five-roller mills, the last three rollers are usually placed above the second roller. Rollers range in size from 4 inches in diameter by 8 inches long in a laboratory mill to 12 by 36 inches or larger. They are hollow so that they may be cooled by circulating water through them.

A type of roller mill with only a single roller grinds the paint between a wide beveled bar that is held against the roll under controlled hydraulic pressure.

The tendency in recent years has been to increase the speed of the rollers. High speed mills with three rollers may therefore have an output equal to that of lower speed five-roller mills.

In general, the roller mill has a greater output and disperses better than the stone mill. It is easily cleaned and hence may be used for different-colored products. On the other hand, stone mills are more difficult to clean and therefore it is often customary to have a stone mill for each different color.

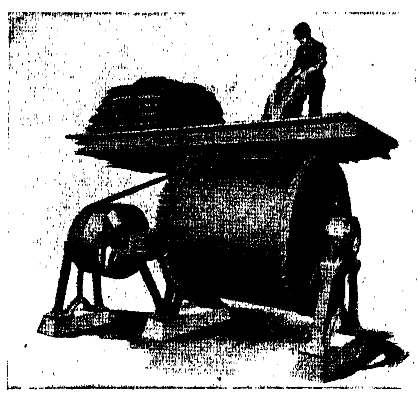

FIG. 5. Ball Mill and Loading Platform. (Courtesy Patterson Machine and Foundry Company.)

Ball Mill.[57] This is a rotating barrel or cylinder loaded with pebbles, porcelain balls or steel balls. The rotation carries the balls up the side of the cylinder from where they roll down, rubbing the paint between them at the points of contact.[58] The number of points of contact increases as the size of the balls decreases, but small balls may not fall freely enough. Two sizes of balls are often used. As the balls become smaller because of wear, replacement is made with the larger size. Porcelain balls are used where color is important. Steel balls are used where the added weight is needed to make the balls fall through products of high consistency.

To prevent contamination by metal, cylinders are often lined with stone or porcelain, or they may be made of stainless steel. They may be kept cool by jackets or by water sprays.

Ball mills have some important advantages. Separate premixing machines are not needed and products containing volatile matter can be ground without loss. They are therefore used much in the manufacture of pigmented cellulosic lacquers and the like, although grinding is not rapid. They require very little attention during operation and may be run overnight. If the production schedule is suitable, the mill need not be cleaned between batches. On the other hand, if the mill is to be used for different colors, cleaning is an important item.

[58] Promnitz, O., Farben-Ztg. *41,* 136 (1936). Paint, Oil and Chem. Review, *99,* No. 6, 23, Mar. 18, 1937.
Fischer, Earl K., Ind. and Eng. Chem., *33,* 1465 (1941).

Bramley Mill. In this mill, the grinding is done by rotating blades which wipe against the inside wall of a horizontal cylinder. The blades are fastened to radial arms and the pressure which they exert against the wall of the cylinder may be varied to suit the product. (See Figure 6.) Many of the considerations of a closed system applying to the ball mill obtain for the Bramley mill, but the output of the latter is much greater.

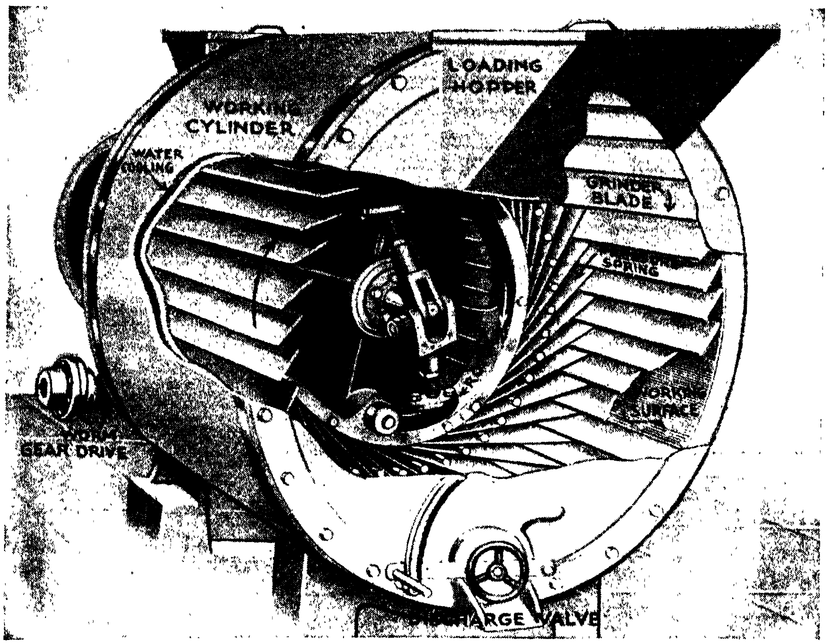

FIG. 6. Cross Section of Bramley Mill.

The reason for this is that it takes concentrated pastes instead of the complete paint. Pastes grind faster and less volume needs to be passed through the mill.

Banbury Mill.[59] This type of mill is not found in the usual paint factory. It is a sort of extra heavy-duty kneading machine in which the material is worked under high pressure. The material charged into the mill is a rather dry mixture of pigment and vehicle. When the batch is done, it is thinned with the balance of the vehicle. A very high degree of dispersion is obtained in this machine.

Edge Runner.[57] This machine consists of a huge stone or iron wheel that runs in a circular trough. Heavy pastes and compositions such as putty are made in it, for which reason it is also called a putty chaser.

Thinning—After the paste has been ground, it is thinned with the balance of the vehicle, either non-volatile or volatile or both, as called for by the formula. In the case of the ball mill, all of the ingredients may have been added at the beginning and nothing need be added. In most cases, this opera-

[59] See also Chapter 39.

tion is done in portable mixers, called change can mixers, in which the final adjustment of the color is also made.

Color Matching—Only rarely do the combinations of pigments and vehicles that are passed through a mill result in the exact color desired so that final adjustment of color must be made by expert tinters either before or after the final thinning.

The paint is then strained to remove lumps or dirt. Certain high grade enamels are passed through centrifuges which remove the coarser particles. The paint is then ready for the containers in which it will be stored or shipped.

PREPARATION OF VARIOUS TYPES OF PAINT

Exterior House Paint—A type of paint that has been used for decades for the exterior walls of wood dwellings, barns, and factories, for fences and other objects is made with a vehicle of raw or boiled linseed oil and thinner, and the pigments, white lead, zinc oxide, titanium oxide pigments, and extenders. In some cases a small percentage of varnish or bodied oil is added to the vehicle. Colored pigments are added as needed to produce light tints. Dark colors have relatively small percentages of the white pigments listed above, and greater percentages of the colored pigments. Over suitable priming coats, house paints may be used on types of structural material other than wood, namely, metal, masonry, and cement-asbestos.

Exterior house paints are composed of approximately two-thirds pigment and one-third vehicle by weight. By volume, the pigment constitutes upwards of 30 per cent of the non-volatile portion.

Until recently, three coats of paint have been considered necessary for the proper protection of exterior surfaces of new wood. In a 3-coat system, the first or priming coat contains an excess of oil to allow for that which is absorbed by the wood. The two additional coats of paint build a film of the required thickness for reasonable durability.

There has now appeared a school of thought that looks upon absorption or penetration as undesirable.[60] First, because it does not contribute anything to the adhesion of the film to the wood. Second, because absorption robs the primer of an indefinite amount of vehicle, thereby making uncertain the relative proportions of pigment and vehicle in the film and nullifying the good results of careful formulation. By the use of a non-penetrating primer, it is concluded that the number of coats may be reduced to two. Because all of the primer remains on the surface, only one additional coat is considered necessary.

Interior Flat Wall Paint—This paint is primarily a decorative medium and the weathering requirements are low.

The vehicle is varnish or bodied oil; the base pigments are primarily the zinc sulfide group and the titanium oxide group, to which are added extenders and colors. The flat finish is produced by a high percentage of pigment in the

[60] Beal, G. F., and Konen, J. C., Paint and Varnish Production Clubs, Official Digest, *186*, 243, May, 1939.
Browne, F. L., Ind. and Eng. Chem., *33*, 900 (1941).
Robertson, D. W., and Jacobsen, A. E., Ind. and Eng. Chem., *28*, 403 (1936).

dry film, so that a layer of oil or varnish does not form on the surface. Consequently, these paints have very low durability on exterior surfaces.

Interior flat wall paints are also made with casein and emulsified resin vehicles.

Proper selection of the color of flat paint for interior walls becomes an important aid in maintaining the proper level of illumination in homes, offices and factories.[61]

The following data indicate the amount of light saved by the use of light colors:

Color	*Diffuse Reflectance (Per cent)*
White	80-90
Cream	65-75
Ivory	60-70
Pink	60-70
Light green	50-60
Light gray	50-65
Light blue	45-60
Buff	50-60
Medium blue	40-50
Orange	15-25
Red	15-25
Dark blue	5-10

Interior Gloss Paints—This is a type of enamel suitable for use on interior surfaces of plaster or wood. It is usually made with a bodied oil vehicle. A gloss paint is more easily washed than a flat paint, and hence is often preferred for kitchens and bathrooms in the home, and for food and other factories where frequent washing is needed. Emulsified resin vehicles may also be used for interior gloss paints, but casein cannot be obtained in concentrations high enough to produce the desired gloss.

Casein Paints—Casein[62] rendered dispersible in water by lime, borates, fluorides or many other reagents, is the binder for this type of paint.[63] Until about 1930 casein paint was sold mostly in the form of a dry powder which was mixed with water by the user, but since then increasing amounts of the paste form are being sold. The casein comprises approximately ten per cent of the dry paint. Casein paints are suitable for use on interior plaster work, where extremely flat finishes are desired. The plaster need not be fully dry when the paint is applied, but must eventually dry, as otherwise a soft film will result and mildew may grow. An important wartime use is for military camouflaging. Casein paints are less resistant to washing than are interior wall paints made with oil or varnish vehicle.

[61] Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors." Chapter 3, 9th Ed., Henry A. Gardner Laboratory, Washington, D. C., 1939.
Gamble, D. L., Trans. Illuminating Eng. Soc., *28*, 326 (1933).

[62] See also Chapter 44.

[63] Sutermeister, E., and Browne, F. L., "Casein and Its Industrial Applications," Chapter 10. Reinhold Publishing Corp. (1939).
Picou, L., Jr., Paint and Varnish Production Clubs, Official Digest, *204*, 129, Mar., 1941.

Emulsified Resin Paint—Some resins, especially the alkyd and the phenol aldehydes,[64] may be dispersed or emulsified in water, and paints using these dispersions as vehicles are made for several purposes.[65] As contrasted with casein, greater concentrations of binder with vehicle can be prepared. As a result, these paints may be made in a wide range of surface characteristics from flat to glossy. The flat finishes are more resistant to washing than are casein paints. The glossy types are suitable for exterior use on masonry.

Calcimine—Calcimine is essentially chalk and glue. It is sold only in the powdered form, ready to be mixed with water. Its principal use is for temporary decoration of interior plaster walls. The paint will not withstand washing. Ordinarily an old coat must be removed before a new coat of calcimine or any other type is applied.

Cement Base Paint—This is a paint consisting essentially of Portland cement, also containing small amounts of pigment, usually white, and hygroscopic salts, such as calcium chloride. It is intended for use both on exterior and interior masonry. The dry film is without gloss, usually less water-repellant than an oil base paint, and becomes temporarily transparent when wet. This paint may be applied to damp masonry; in fact, surfaces should be moistened before it is applied and the film should be kept moist for a day or so after it is applied, in order for the reaction to become complete.

Porch and Deck Paint—A porch and deck paint, or enamel, is called upon to be highly resistant to abrasion as well as to weather. For this reason the vehicle usually is a hard-drying, weather-resistant type. The paint also should be suitable for application on concrete, as many porch floors and most basement floors are made of this material. Varnishes based on rubber resins are among those used for this purpose.

Metal Protective Paints—The fundamental properties of paints for protecting metal are good adhesion, imperviousness to moisture, and the presence of corrosion-inhibiting ingredients. Dry metal will not corrode and hence the first requirement of the paint is moisture resistance. However, since this property is not completely attainable or retained indefinitely, the presence of anticorrosives is necessary to compensate for the deficiency. Anticorrosive properties are imparted by basic pigments, such as red lead, by chromium-containing pigments, such as chrome yellow and zinc yellow, and by metallic pigments such as zinc dust. However, these do not by any means exhaust the list of pigments useful in anticorrosive paints.[66] If the painted object can be baked, a baking-type finish will usually give better protection because of the better moisture resistance developed in such finishes.[67]

[64] See Chapter 31.

[65] Picou, L., Jr., Paint and Varnish Production Clubs, Official Digest, *204*, 129, Mar., 1941.

[66] Sub-Committee XV, A.S.T.M. Comm. D-1, Final Report. Proceedings A.S.T.M. XV, Part I, 214 (1915).

[67] Burns, R. M., and Schuh, A. E., "Protective Coatings for Metal," Chapter 13. Reinhold Publishing Corp. (1939).

Edwards, J. D., and Wray, R. I., Ind. Eng. Chem., *27*, 1145 (1935).

Evans, U. R., J. Oil and Colour Chem. Assoc., *21*, 284-294 (1938).

Nelson, H. A., Trans. Electrochem. Soc., *75*, 37 (1939).

Speller, F. N., "Corrosion—Causes and Prevention," Chapter VIII, 2nd Ed., McGraw-Hill (1935).

Winston, A. W., Reid, J. B., and Gross, W. H., Ind. and Eng. Chem., *27*, 1933 (1935).

Marine Paints—During construction, the hulls of steel vessels receive a temporary coating of an anticorrosive paint. Before the ship is launched, a second coat of the same type paint is often applied. The hull below the water line is then finished with antifouling paint. This paint contains ingredients that are toxic to marine growths, such as barnacles, teredo and the like. These toxic ingredients are usually mercuric oxide and cuprous oxide.

Rapid-drying paints are necessary, in order to avoid long periods of docking when repainting is required. Hence, these paints are usually made with a spirit varnish such as shellac or rosin. Other ingredients include coal tar, pine oil, manganese lineoleate, beeswax, zinc oxide, silica, and Venetian red.[68]

Traffic Paint—Also known as zone-marking paint, enormous quantities of this product are used to mark traffic lanes, parking spaces and the like. They are rapid-drying compositions with vehicles based on either spirit or oleoresinous varnishes. Manila resin spirit varnishes are widely used. The most popular colors are white and yellow. The former is obtained with lithopone or titanium-barium; the latter mostly with chrome yellow. In both cases, substantial percentages of a coarse extender pigment are included in order to improve visibility. Microscopic glass beads have been used in traffic paints in an effort to improve night visibility, but their advantage has not been definitely accepted.

Traffic paints must dry rapidly in order not to hold up traffic for long periods. Paints for heavily traveled roads must be resistant to abrasion, whereas in those for lightly traveled roads, weather resistance is more important.[69]

Bituminous Paints—In addition to natural asphalt, which is one of the oldest, there are several other bituminous materials used in protective coatings. These include the residue from petroleum distillation, coal tar and vegetable oil pitches. The softer types find considerable use as waterproofing coatings for below grade masonry and pipe lines buried in the earth. Roof coatings are mixtures of asphalts with asbestos and other fillers. Harder types of asphalt, such as gilsonite, are used as resins in making both air drying and baking coatings for metal. Many of these coatings are very resistant to acids and alkalis.[70]

Aluminum Paint—This type of paint is widely used as a primer for wood, and as finishing coats for both wood and metal. It is not usually used as a primer for metal. It also finds considerable use as a heat-reflecting paint and as a finish for furnace doors and breechings. The choice of vehicle for aluminum paints is important because of the influence on "leafing." (See section on Bronze Powders.) For exterior purposes, a durable exterior varnish is necessary. For application on hot surfaces, spirit varnishes have been found

[68] Adamson, N. E., "Technology of Ship Bottom Paints," U. S. Navy Dept. C. & R. Bull. 10 (1937). Supt. of Documents, Washington, D. C., 10 cents.
Gardner, H. A., "Importance of Metal Protective Primers as a Base for Antifouling Paints," Nat'l Paint, Varnish and Lacquer Assoc., Scientific Sec. Circ. *611*, Mar., 1941.
ZoBell, C. E., *ibid.*, Circ. *568*, 149, Nov., 1939.

[69] Kopf, C. W., and Mantell, C. L., Paint, Oil and Chem. Review, May 23, 1940, 7 et seq.; June 6, 1940, 44 et seq.; July 4, 1940, 9 et seq.
Shuger, L., Drugs, Oils and Paints, *54*, 343, 413 (1939); Paint Industry Mag., *55*, 12, 127, 229, 378 (1940).

[70] Abraham, H., "Asphalt and Allied Substances," 4th Ed., Chapter XXX. D. Van Nostrand (1938).

best. Early types of aluminum and other bronze powders for interior decorative uses were made with cellulose nitrate lacquers.

Heat-Reflecting Paint—When the visible radiation of the sun is absorbed by an object, it is converted into heat and the temperature of the body is raised. Hence, if an object be coated with a paint that reflects a high percentage of the visible radiation, it will be cooler than one coated with a paint that absorbs the radiation. White and light-tint paints are therefore used where it is desirable to keep objects as cool as possible.[71] Practical applications of this phenomena are white paint for dwellings and white or aluminum paint for gasoline storage tanks.[71]

Fire-Resistant Paint—Although the commonly used paints and varnishes will ignite and burn, they do reduce the flammability of wood and fabrics by coating splinters and fuzzy edges. The greater the percentage of pigment, the greater is this effect. Additional protection against fire is imparted by pigments and compounds that either fuse or give off non-combustible fumes when heated. Among these are borax, zinc borate, and ammonium phosphate. Promising ingredients for fire-resistant paints are synthetic resins.[72]

Wrinkle and Crystal Finishes—A "wrinkle" finish is an example of putting a so-called defect to good use. The immediate cause of wrinkling is the more rapid expansion of the dry surface of a film than of the underlying film.[73] Means of controlling wrinkling have been developed and today many articles such as radios, cameras, and instruments of various kinds are finished in this manner.

A crystal finish is produced by incorporating compounds such as phthalic anhydride in the coating (usually a cellulose nitrate lacquer). As the solvent evaporates, the compounds separate in characteristic crystalline forms.

Chemical-Resistant Finishes—These finishes vary according to the nature of the chemical. Oleoresinous varnishes, especially when baked, are highly resistant to mild mineral acids and alkali. Bituminous varnishes, chlorinated rubber and rubber hydrocarbon compositions, and phenolic dispersion compositions are indicated for the more severe conditions.

Food Container Coatings—To avoid discoloration of the contents or of the tinplate container, the interiors of food and beverage cans are in many cases coated with varnishes. Oleoresinous baking varnishes and vinyl resin spirit varnishes are widely used.

Camouflage Paint—Interest in this type of paint increases tremendously in times of war. The essential requirement is low specular reflection. As camouflaging paints for military purposes must be changed with the season of the year, permanence is not of importance.

Luminous Paint—The basis of luminous paint is a phosphorescent compound such as sulfide of zinc, cadmium, calcium or strontium. The compound,

[71] New, G. F., J. Oil and Colour Chem. Assoc., *19,* 156-164 (1936).
Anon., Nat'l Paint, Varnish and Lacquer Assoc., Scientific Sec. Circ., *562,* July, 1938.
Cottony, H. V., and Dill, R. S., "Solar Heating of Various Surfaces." U. S. Dept. of Commerce, Report BMS 64, Jan., 1941.

[72] Van Kleek, A., "Borax Fire-Retardant Paints," Mimeograph. Forest Products Laboratory, Madison, Wis., April, 1940.
——, Ind. and Eng. Chem., News Ed., *19,* 626 (1941).

[73] Sward, G. G., Nat'l Paint, Varnish and Lacquer Assoc., Scientific Sec. Circ., *261,* Sept., 1936.

in pigment form, is incorporated into a spirit varnish, preferably in a porcelain ball mill. Suitable vehicles include chlorinated rubber, styrol and vinyl compounds, damar and coumarone resins. Luminous paints made with the above-named materials must be activated with near-ultraviolet light in order to glow. However, if minute amounts of radio-active compounds are included in the paint, no previous excitation by light is necessary. The manufacture of luminous pigments and paint is one that requires great care.[74]

Paint Removers—There are two types of removers—organic solvent and caustic. The organic solvent is made up of such liquids as acetone, methanol, benzene, methylene chloride, and so on, and a small amount of paraffin wax. The function of the wax is to retard the evaporation of the remover, which it does by forming a skin over the surface. Cellulose nitrate is sometimes used for this purpose.

The caustic type of remover is made with sodium phosphate, sodium silicate, caustic soda or the like.

Stains—Wood stains regularly used take their names from the type of solvent used for the dye. They are water, spirit and oil. Water, or acid, stains were very widely used until recently because of their fastness to light. However, the grain of the wood is raised by the water and special non-grain-raising spirit stains are displacing the water stains. Spirit (alcohol) stains do not raise the grain of wood as much as water does and combinations of methanol with certain other solvents such as Cellosolve constitute the solvents for non-grain-raising stains. Dyes dissolved in drying oils penetrate deeply and produce a brilliant appearance, but have a tendency to bleed into subsequent coats of varnish.

Glazing liquids are paints, the pigment portion of which is made with relatively transparent pigments. They have special uses for decorating walls or in imitating the grain of wood.

Varnishes colored with dyes are sometimes used to impart transparent colors to impervious surfaces.

Shingle stains are made by adding creosote to oil-pigment paste. Dark colors are customary because of the dark color of commercial creosote. Light colors can be achieved by the use of redistilled creosote or higher homologs or by other wood preservatives such as chlorinated phenols.

Putty—For glazing wood sash and filling holes and cracks in lumber a stiff paste of linseed oil and whiting is commonly used. This composition is the traditional pure putty. It is sometimes modified by the addition of small amounts of white lead in oil. So-called commercial putty contains more or less mineral or other oil instead of linseed oil. Putty for glazing steel sash is made with a varnish vehicle.[75]

Calking compounds for filling joints and cracks around doors and windows should remain elastic as long as possible. Specially treated oils are used as vehicles.[76]

[74] Bryson, H., Paint and Varnish Production Clubs, Official Digest, *193*, 49; *194*, 139 (1940).

[75] Anon., Nat'l Paint, Varnish and Lacquer Assoc., Scientific Sec. Circ., *610*, Feb., 1941.

[76] Tregoning, J. J., Milliken, K. A., Hockman, A., Sligh, W. H., and Kessler, D. W., National Bur. of Standards. Report BMS 33, Jan. 20, 1940.

VARNISHES

Varnishes are of two types—spirit and oleoresinous. A spirit varnish is a solution or dispersion of a resin or other film-forming substance in a volatile solvent. It dries by evaporation of the solvent. Certain synthetic types may require baking. Examples of spirit varnish are shellac and cellulose nitrate lacquer. An oleoresinous varnish is a solution of a mixture (usually cooked) of drying oils and resins in a volatile solvent. This varnish dries by evaporation of the volatile portion, followed by oxidation and polymerization of the residue. Examples are spar varnish and floor varnish.

Raw Materials—The basic raw materials used in the manufacture of varnishes include the many drying oils, dozens of resins,[77] and scores of solvents and driers.

Drying Oils. Practically all of the commercially available drying oils and some of the semidrying oils are used in the manufacture of varnishes, the chief ones being tung, linseed, perilla, oiticica, dehydrated castor, menhaden, sardine, and soybean oils.[78]

Resins. Until the third decade of the twentieth century, the natural products dominated the resin field, but since that time synthetic resins of many types have been developed and used in large amounts.

The principal natural resins entering into varnish manufacture are kauri, Congo, Pontianak, East India, Batu, Manila, and damar. The first two are used almost exclusively in oleoresinous varnishes; the last two almost exclusively in spirit varnishes. Pontianak, East India and Batu are used in both the oleoresinous and spirit types. Lac, the secretion of the lac insect, is usually not discussed with the natural resins, but it is primarily a spirit varnish resin. In addition, there is rosin, widely used as such and also in the form of its glyceride, ester gum.[77] This resin was the first important synthetic resin to be used in varnishes, for the coumarone resins, discovered in 1890, have never attained the prominence achieved by ester gum. The next important synthetic resin was a blend of ester gum and phenol-aldehyde resin. Today synthetic resins for the varnish industry include straight oil-soluble phenol-aldehyde resins, alkyds, maleic acid compositions, chlorinated rubber, polymerized rubber, vinyl derivatives, penta-erythritol esters, terpene polymers, urea-aldehyde, melamine and others.[77] The cellulosic derivatives—cellulose nitrate, cellulose acetate, cellulose acetobutyrate, and ethyl cellulose—may also be included. Strictly speaking, some of these materials should not be classed as resins, and for want of a better name they are classed as film-forming compounds or resinoids. The word "filmogen" [79] used in medicine is hereby suggested as a short word to replace "film-forming compounds."

Solvents and Thinners. The requirements of spirit varnishes for solvents and thinners are more varied than those of oleoresinous varnishes. Most of the needs of the latter are met by turpentine, petroleum spirits, and coal tar

[77] For a complete discussion of the natural resins, see Chapter 40. The synthetic resins are discussed in detail in Chapter 31.

[78] Gardner, H. A., and Scofield, F., Nat'l Paint, Varnish and Lacquer Assoc., Scientific Sec. Circ., *602*, Sept., 1940.

[79] Webster's New International Dictionary, "A vehicle for applying medicine to the skin."

naphtha. Most natural spirit varnish resins are likewise dissolved by these liquids. However, other solvents are needed for lac and for the cellulosic and other spirit type filmogens.

Ethyl alcohol is the solvent for shellac. Butyl acetate, amyl acetate, Cellosolve, butyl alcohol, and acetone are among those used in cellulosic lacquers. Numerous other solvents of lesser importance are used in small amounts.

Driers. These are used only in oleoresinous varnishes. They include inorganic compounds of lead, manganese, and cobalt, such as the oxides, acetates, carbonates, and borates, which are converted to oil-soluble forms when cooked into the varnish. They include also compounds of lead, manganese, and cobalt soluble in oil without further treatment, such as linoleates, resinates and naphthenates.

Manufacture of Spirit Varnishes—This is a simple operation, although considerable knowledge is necessary to select the most suitable and economical ingredients and their proportions in certain types. This refers especially to the cellulosic lacquers and other synthetic filmogens. In the case of a simple product consisting of resin and solvent, the two ingredients are placed in a barrel or other container, and are agitated by stirring or by other means until the resin is completely dispersed or "cut." Best results are obtained by adding the resin to the solvent so that the individual pieces of resin are wet completely.

In other cases, it is desirable to heat the batch to improve dispersion. For example, what is known as gloss oil is made as follows. Rosin is reacted at approximately 400° F. or higher with slaked lime, $Ca(OH)_2$. When the reaction is complete, the hot calcium resinate is thinned with petroleum spirits.

Natural resins, especially the lower grades, contain more or less foreign matter which must be removed by settling, filtration or centrifuging.

The practice of designating the amount of resin in a spirit varnish as the number of pounds of resin dispersed in a gallon of solvent still prevails. A four-pound "cut" of shellac is made by "cutting" four pounds of dry shellac in one gallon of alcohol. However, since the presence of dirt and other insoluble matter makes it necessary to determine the actual amount of non-volatile matter, there is a growing tendency to express the amount of resin on a percentage basis.

Spirit varnishes constitute a large proportion of all varnishes made. They include shellac varnish for floors, natural resin coatings for coating paper, cellulosic automotive lacquers, a large amount of sheet metal coatings, based on alkyd, vinyl, urea and other resins.

Spirit varnishes made with synthetic resins are usually more complex than those made with such natural resins as shellac and Manila. Cellulose nitrate lacquer, which is discussed in a separate section, is an example. Take the case of the recently developed urea-formaldehyde and melamine filmogens. Baking is necessary to develop their excellent property of hardness, but this hardness must be tempered with plasticizers in order to impart satisfactory adhesion. Alkyds are widely used for this purpose.

Vinyl resin, chlorinated rubber, and rubber hydrocarbons are other filmogens that must be modified by the addition of plasticizers or other resins before satisfactory coatings can be made with them.

Manufacture of Oleoresinous Varnish—This is a process which still retains some of the aspects of an art. It consists in cooking resins and drying oils together until they are permanently miscible or until the viscosity has been raised to the desired value. The "bodying" (thickening) of drying oils by heat or by a combination of heat and air belongs to this field.

The processing[80] is done in both set and portable kettles, most of the oleoresinous combinations being processed in the latter.

Portable kettles are of various sizes and shapes, but the usual type has straight sides, is from three to four feet in diameter, and from three to four

FIG. 7. Varnish Kettle with Cover for Fume Removal. (Courtesy Mautz Paint & Varnish Co., Paint, Oil & Chemical Review)

feet deep, and has a capacity of some 200 gallons.[81] Early kettles were made of copper, but today aluminum, stainless steel and Monel metal are extensively used. The kettle is mounted on a low truck by which it can be moved as needed. A thermometer for indicating the temperature and a long metal paddle for stirring are standard accessories.

The source of heat is usually a coke, oil or gas fire, located in a pit below the floor level where the kettle truck can straddle it. Each fire is provided with a flue or stack for carrying off the products of combustion and the fumes from the kettle. In some localities where civic regulations forbid the discharge of fumes into the air, disposal systems must be provided.

Cooking the Varnish. The desired amounts of resin and oil are weighed or measured into the kettle, which is then rolled over the fire pit. The heat is

[80] See also Chapter 40.
[81] Hock, A., Paint and Varnish Production Clubs, Official Digest, *194*, 120-126, Mar., 1940.

applied, usually gently at first, until the resin is melted and then more intensely to bring the batch to the desired temperature. It is usually necessary to pull the kettle off the fire before the top heat is reached, as the exothermic reaction in the varnish releases heat for the last 10 to 25 degrees rise. At the top temperature or some lower point, the batch is held until permanent dispersion of the resin in the oil is assured or until the batch has been thickened (bodied) to the desired degree. The dispersion is tested by noting the clarity of a cooled drop. The body is gaged by the nature of the drip from the paddle, or by the length of the "string" drawn away by a finger applied to a cooled drop. A more scientific method is to withdraw samples, thin them as required and then determine the viscosity with an apparatus such as the Gardner-Holdt Bubble Tubes. Another method is to note the time required for a drop of the batch to form a gel when placed on a hot plate. However, there often is not enough time available for these tests, and the skill and art of the practical experienced varnish cooker is still needed.

When the varnish has been cooked sufficiently, it is pulled to a safe distance from the fire, where it is allowed to cool naturally, or it may be cooled by water directed on the outside of the kettle or even on the hot varnish itself. When the temperature has been reduced to 475° F. or less, the thinner is added cautiously and is thoroughly mixed with the varnish base. The thinned varnish is then clarified by being passed through a filter press or a centrifuge. Finally it is pumped to storage tanks to await packaging.

Driers may be added at some stage of the cooking or may be reserved until the varnish is thinned or cooled. If the varnish has a tendency to form a skin over the surface, the driers may not be added until just before packaging. The commonly used compounds are litharge, basic carbonate of lead, lead acetate, cobalt acetate, manganese acetate, the metallic soaps, and the naphthenates.

In order to inhibit the skinning of some types of varnishes in partially emptied containers in the user's hands, antiskinning agents are often added. These are often phenolic compounds such as guaiacol, catechol, or their derivatives.[82]

The harder types of fossil resins are not miscible with drying oils and must be "run" before they can be used in oleoresinous varnish. This "running" is a severe heat treatment, resulting in a degradation of highly polymerized molecules into simpler ones. A moderate amount of fossil resins is run by the resin manufacturer but probably most of it is run by the varnish manufacturer as he uses it.

The resin is put into a varnish kettle and heated quickly to a temperature of 600° F. or higher. Voluminous foaming takes place, and copious fumes (amounting to about 20 to 30 per cent of the resin) are given off. The running is complete when the foam has subsided and the melt is free from lumps. In some cases, a small percentage of a low-melting-point resin, such as rosin, or some of the oil added to the batch promotes the running. Some effort has been made to use the fumes as a source of chemicals or solvents, but in the great majority of cases they are discharged into the air, unless civic regulations forbid it.

[82] Carrick, L. L., and Beaudine, F., American Paint J., *21*, Nos. 45, 47, 49, 51 (1937).

While the resin is being run, the oil portion of the varnish is being heated in another kettle, and at the proper time it is added to the resin. From this point, the procedure is the same as for synthetic resin or recent resin varnishes.

Indirect Heating. The intense heat on bottom-fired kettles superheats the layer of varnish next to the bottom and causes considerable decomposition of the varnish. One way of avoiding this condition is to heat with electricity. The heaters may be the immersion type or may be elements placed against the outside of the kettle. In both cases the kettle is thoroughly lagged. The temperature is controlled by a thermostat. By taking advantage of non-peak load rates, the cost of electric heating becomes fairly attractive.

Another method is to circulate hot vapors of compounds such as diphenyl (Dowtherm) around jacketed kettles. Kettles holding as much as 1500 gallons have been installed. Coils for circulating cold diphenyl are provided in case cooling is necessary.

Electrically and vapor-heated kettles are usually equipped for vacuum or inert atmospheres above the liquid, and fume disposal systems. However, fume losses are low because decomposition of the varnish is negligible. Very pale products of low acid value are obtained. Moreover, the kettles are equipped with condensers so that losses accompanying thinning at high temperatures are negligible. On account of the initial expense, manufacturers have been slow to adopt these methods, and by far most oleoresinous varnishes are still cooked over direct fires.

Storing the Varnish. Varnish storage tanks are located inside buildings where they can be kept warm in the winter. In some installations, an atmosphere of inert gas is kept over the varnish to prevent skinning or thickening due to oxidation. This gas may be carbon dioxide or, as is more often the case, it is the flue gas produced from special burners.

Reactions in the Varnish Kettle. The chemical reactions occurring in drying oils during varnish cooking are still somewhat obscure, but belong mainly to the polymerization type, the reactions taking place at the double bonds of the fatty acid radicals. The course of the reactions is altered by the presence of resins and driers and by the oxidation which takes place at the surface of the hot varnish. There is some evidence of interchange of acid radicals between the oil and resin molecules of the glyceride or acid types. This interesterification occurs more readily before the acid groups become locked up in polymerized molecules. At any rate, in most cases better miscibility usually results if the resin and oil are cooked and bodied together than if the resin is added to the separately bodied oil.

Tung oil reacts in an interesting manner with certain phenolic resins of the heat-advancing type. One of the characteristics of raw tung oil is its tendency to form a wrinkled film when it dries. This tendency is reduced by heat treatment at temperatures of the order of 550° to 600° F., but during this heat treatment the oil rapidly thickens and the treatment must be stopped before the oil is converted to a gel. However, mixtures of tung oil and certain heat-advancing phenolic resins may be cooked at much lower temperatures (450° F.) to yield varnishes that do not wrinkle.

Oiticica oil resembles tung oil in its varnish-making properties, but does not equal it in resistance to water and alkali.

Dehydrated castor oil is obtained by heating castor oil with a catalyst, whereby the hydroxyl group attached to the twelfth carbon atom and hydrogen from an adjacent carbon atom are evolved in the form of water. A doubly conjugated group is thereby formed. The resulting product has some of the properties of tung oil.

Perilla oil resembles linseed oil, but bodies more rapidly when heated or blown with air. It dries faster and harder than linseed oil.

Soybean oil bodies very slowly in the varnish kettle and if cooking is continued until the usual body is reached, losses by volatilization are likely to be high. Soybean oil varnishes tend to dry more slowly than most other types, but if sufficient time is available before adverse conditions are encountered, excellent service may be expected.

Sardine oil is another oil that tends to give relatively soft, slow-drying varnishes, but, as in the case of soybean oil, the varnishes are very serviceable.

Types of Varnish—The proportions of oil and resin in an oleoresinous varnish are usually expressed as the number of gallons of oil per 100 pounds of resin. Thus a 10 gallon varnish is made with 10 gallons of oil and 100 pounds of resin. If the proportion of oil to resin is, say, 12 gallons or under, the varnish is classed as a "short" oil type. A "long" oil varnish is one containing 25 or more gallons of oil to 100 pounds of resin.

Spar Varnish. On account of its suitability for coating the spars, masts and rails of ships, long oil water-resisting varnishes are called spar varnishes. Early types were made with fossil resins and linseed oil, but today straight or modified phenolic resins and tung oil are widely used.

Interior Varnish. These are usually of medium oil length and do not have the elasticity requirements of long oil varnishes when exposed outdoors.

Furniture Varnish. These are short in oil and are made with a wide variety of resins.

Baking Varnishes. These are not readily classified as to oil length or type of resin. They are hardened by baking and the drier content is greatly reduced or eliminated entirely. Baking temperatures range from 150° F. upwards to over 300° F. If artificial heat below 150° F. is used, the operation is called "forced drying" rather than baking.

CELLULOSE LACQUERS [83]

Cellulose nitrate was first made in 1833 and the first recorded use of its film-forming properties was about 1850. In a mixture of alcohol and ether, it gives a solution called collodion. With the discovery of amyl acetate in 1878, its industrial use as a coating material began to develop. This "banana oil" was used to coat metals such as copper and brass to prevent tarnishing for some fifty years before the next and greatest advance which came about as follows. At the end of the First World War, huge stocks of butyl alcohol and guncotton were on hand. The problem of diposal of these materials was solved by converting the guncotton into a soluble type, suitable for use in coatings, by reducing the nitrogen content and by converting the butyl alcohol into butyl acetate which is a solvent for the soluble cotton.

[83] See also Chapter 31 and Chapter 38.

Cellulosic lacquers are a distinct advance in the art and science of spirit varnishes, as they are compounded of several ingredients which require careful selection in order to produce the properties desired in the final film.

By themselves, the cellulosic compounds do not make good films for most purposes. They lack adherence and distensibility, properties which are imparted by resins and plasticizers. In some cases so great a proportion of these are used that the cellulosic ingredients constitute only a small portion of the material and might themselves be considered to be the modifying ingredients.

The ingredients used in lacquers are the cellulosic derivatives, usually the nitrate, resins, plasticizers, and solvents or diluents.

Cellulose Nitrate—The manufacture of this material is treated elsewhere in this book.[83] For use in lacquers, it is made in several types, classed according to the viscosity of standard solutions, e.g., ¼ second, ½ second, 5 seconds, etc. It is also classed according to the type of solvent required.

R.S. (Regular Soluble), cellulose nitrate, the most widely used type, is soluble in esters, ketones, mixtures of ether and alcohol, etc. Solutions of R.S. cellulose nitrate will tolerate considerable dilution with hydrocarbons.

A.S. (Alcohol Soluble) cellulose nitrate is similar in its solubility to the R.S., except that its solution does not tolerate dilution with hydrocarbons, but does tolerate alcohols.

S.S. (Special Soluble) cellulose nitrate is made for use with S.D. Alcohol No. 1. Small percentages of esters are desirable and hydrocarbons are also compatible.

Cellulose Acetate—More powerful solvents, such as ketones, are required to dissolve cellulose acetate. Its principal advantage is non-flammability, for which it is preferred for airplane dope.

Cellulose Aceto-butyrate—This material is also non-flammable. It is somewhat more weather resistant than cellulose nitrate and thus is used in clear coatings for metals.

Resins—To increase the solids content so that thicker films can be laid down, resins are incorporated in lacquer. A very great increase in adhesion is also imparted by some resins. Gloss is also enhanced. The principal resins used include ester gum, shellac, damar, elemi, and alkyds.

Plasticizers[84]—This type of ingredient is added to soften or to render the film more ductile and flexible. Many of them are slowly evaporating solids or liquids. One way of classifying them is by source; e.g., natural or chemical. The natural type includes camphor and various treated oils such as raw castor, blown castor, blown linseed and blown soybean oils. The chemical plasticizers include tricresyl phosphate, dibutyl phthalate, diethyl phthalate, diamyl phthalate, and sebacic acid esters.

Solvents[85]—Selecting the best solvents for cellulose nitrate lacquers is an interesting problem in the balancing of physical properties and cost accounting, because the better solvents are the more costly ones. Solvents may be divided into two main classes—true solvents and diluents.[86] An intermediate class, called latent solvents or co-solvents, is recognized by most technologists. Per-

[84] See also Chapter 31.
[85] For a discussion of manufacture of solvents, see Chapter 30.
[86] Doolittle, A. K., Ind. and Eng. Chem., *27*, 1169 (1935).

haps the most important true solvent is normal butyl acetate. Others are ethyl acetate, amyl acetate, acetone, methyl ethyl ketone, Cellosolve and its various derivatives. Diluents comprise toluene, xylene and high solvency naphthas. These liquids are solvents for the resins but not for the cellulosic compounds, except ethyl cellulose, but are tolerated in substantial amounts by solutions of cellulosic esters in other liquids. They are important in reducing the cost. Ethyl, butyl, and other alcohols when used alone have no solvent power for the cellulosic compounds, but when mixed with true solvents they become effective and are known as latent solvents.

The first large outlet for cellulosic lacquers was in finishing automobiles which still take enormous amounts. Other large outlets are airplanes, furniture, fabrics, lighting fixtures, toys, and many others.

PAINTING METHODS

Unlike some other commodities such as rubber, paste or liquid paint is not a finished product. An automobile tire, a bag, glove or other article of rubber is fabricated completely under controlled conditions. But a paint is not in its final form until it has become converted to a solid film under circumstances over which the paint manufacturer has no control. This control is usually satisfactory for factory-finished articles such as automobiles, refrigerators and furniture. It is not so satisfactory for exterior house paint, floor varnish, interior flat wall paint and countless other jobs. Surfaces may not be properly prepared; the weather may be favorable or unfavorable; workmanship may be good, poor or indifferent.

Types of paint and their uses have already been described in a preceding section. At this place will be given a brief outline of the preparation of surfaces and the application of the paint. Detailed instructions for practical painting are to be found in books on this subject.[87]

Wood—Wood should be dry. Moisture up to the saturation of the fibre is not harmful, but no free moisture should be present. Exterior surfaces of buildings are usually smooth enough, but interior trim often requires smoothing. Furniture especially must be made smooth before paint is applied. After the wood is prepared, stains, if desired, are applied. The pores of open grain wood are filled with a paste filler. Nail and other holes are filled with putty after the priming coat has been applied. Light rubbing with abrasive paper or steel wool is often necessary between coats.

Metal—Metal must be free from rust, grease or dirt. Mill scale and rust may be removed from iron and steel by acid pickling, sand blast, wire brush, scraper, or flame. Grease is removed by solvent. As soon as possible after cleaning, the painting should be done, since rust immediately re-forms. Be-

[87] Lawrance, J., "Painting from A to Z," 2nd Ed., The Sutherland Publishing Co., Ltd., London (1938).
Miskella, W. J., "Practical Japanning and Enameling," Finishing Research Laboratories, Inc., Chicago (1928).
Pattou, A. B., and Vaughn, C. L., "Furniture, Furniture Finishing, Decoration and Patching," Frederick J. Drake & Co., Chicago (1931).
Vanderwalker, F. N., "Wood Finishing, Plain and Decorative," Frederick J. Drake & Co., Chicago (1925).

fore being painted, vast amounts of iron, steel, aluminum and magnesium are given chemical pre-treatments known as Bonderizing, chromatizing, Cronaking and the like.[88] These processes comprise treatment with phosphates and chromates. They impart corrosion resistance but must themselves be protected by paints.

The first coat of paint on iron or steel should contain a rust-inhibitive pigment, such as chrome orange, zinc yellow or red lead. Subsequent coats may be varied according to the conditions of exposure.

Zinc, such as galvanized iron, may be allowed to weather for three to six months to etch the spangles, or it may be etched with acid, or it may be sand-blasted.[89] Substantial amounts of zinc dust in the primer also improve adhesion.

The painting of copper requires no special treatment other than removal of grease and very slight roughening of the surface.

Masonry—In the presence of water, the lime in plaster and concrete reacts with sodium or potassium compounds that are almost invariably present, to form hydroxides which saponify some types of oil or varnish base paints. Hence, before being finished with such paints, new plaster or concrete should be allowed to dry for several months or until the relative humidity of the air in contact with it is under approximately 65 per cent.[90] If painting must be done before the masonry is dry, special alkali-resistant finishes should be used. These usually contain a water-resisting varnish. Such a varnish may be added to the priming coat of house paint that is to be used on masonry. Treating the masonry with an aqueous solution of zinc sulfate is sometimes successful in rendering the alkali harmless.

Casein and emulsified resin paints may be applied to young plaster and concrete successfully, provided the masonry dries out with reasonable speed. Otherwise these coatings will remain soft and may even fail to harden eventually. Paints based on Portland cement are useful in such cases. This paint is widely used for both exterior and interior masonry.

Basement floors of concrete are sometimes damp because of moisture in the ground. This moisture exerts a hydrostatic pressure that blisters all impervious coatings. A type of coating that is being used in such cases is a thin penetrating stain containing some pigment.

Certain hard-drying floor paints, such as chlorinated rubber, do not adhere to smooth, well-troweled concrete floors. Such floors should be etched with hydrochloric acid before they are painted.

Applying Paint—Three main ways of applying paint are brushing, spraying, and dipping. Other ways are by roller coating and tumbling.

Brushing. Brushes are made in many types and sizes, for use with ordinary paint, varnish, sign paint, stencil paint, bituminous roof coatings, cement

[88] Darsey, Van E., Ind. and Eng. Chem., *33*, 222 (1941).
Edwards, J. D., and Wray, R. I., Ind. and Eng. Chem., *27*, 1145 (1935).
Speller, F. N., Ind. and Eng Chem., *30*, 1152 (1938).
Winston, A. W., Reid, J. B., and Gross, W. H., Ind. and Eng. Chem., *27*, 1333 (1935).
[89] Nelson, H. A., and Kittelberger, W. W., Ind. and Eng. Chem., *25*, 27 (1933).
[90] Bonnell, D. R. G., and Watson, A., Chem. and Ind., *57*, 183 (1938).

base paints, casein paints, and so on. Bristles are Chinese or Siberian hog, squirrel (so called camel's hair), and other animal, vegetable and synthetic fibres.

Spraying. Spraying is very widely used in industrial finishing.[91] It is a time-saving method for such articles as automobiles, refrigerators and furniture. There is, however, considerable loss of material which does not strike the article. Spraying is done in booths that exhaust the fumes and in many cases systems for recovering the finish from the exhaust are in use.[92] A recent innovation is the spraying of hot lacquers,[93] for which special equipment is needed. Advantages of hot lacquers are a saving in the number of coats by virtue of the increased percentage of solids in the lacquer. Also less volume of the material must be handled.

Another innovation is spraying in a high voltage electrostatic field, similar to that described in the next section. The article is attached to the positive pole. Spray from a gun tends to be attracted to the article and even travels around corners and edges and coats areas not directly covered by the gun.

Dipping. Regularly shaped articles without crevices or pockets are conveniently coated by dipping into a tank of the finishing material. Enameled wire is coated by this method in a continuous process. After withdrawal from the dipping tank, the wire passes through ovens where the coating is baked.

In order to reduce tears and beads as much as possible, the article is withdrawn from the tank at a speed approximately equal to that at which it flows. A novel means of eliminating beads and tears from dipped articles has been described by Ransburg.[94] In this process, the article is made one electrode of high voltage electrostatic field, which repels the excess material.

Roller Coating. Roller coating is a very economical means of coating objects in the form of flat sheets. Sheet metal for containers, automobile license tags, and metal signs are among the articles coated by this means.

Tumbling. Small articles, especially when made of wood, are most conveniently and economically coated by tumbling. The articles and the required amount of finishing material are put in a barrel which is then rotated for the required time. They are then spread on drying trays. After drying, they may be polished in a similar machine.

Baking of Finishes. Such properties as adhesion, hardness, and resistance to water, chemicals and other destructive forces, are invariably improved by baking the finish. Temperatures range from 150° to 400° F. In addition to modifying the chemical reactions in a filmogen, the elevated temperatures relieve strains in the film, permit it to flow into the irregularities of the support and to eliminate pinholes formed by escaping solvent.

The principal vehicles used for baking finishes will include oleoresinous varnishes, alkyds, dispersion resins, melamine, and urea-formaldehyde. However, it may also be used to accelerate the drying of straight spirit varnishes.

[91] Gross, B., Metal Cleaning and Finishing, *8*, No. 7, No. 8 (1936).
[92] Saunders, S. G., Ind. and Eng. Chem., *33*, 230 (1941).
[93] Bogin, C., U. S. Patent 2,150,096, March 7, 1939.
Nelson, H. H., Ind. and Eng. Chem., *31*, 70 (1939).
[94] Ransburg, H. P., "Dipping as Augmented by Electric Tear Drop Eliminator." Presented at Meeting of Paint and Varnish Division, Amer. Chem. Soc., St. Louis, Mo., April, 1941.

Most baking is done in convection ovens of the steam or gas-fired type. In some gas-fired ovens, the products of combustion pass directly through the oven.

Recently, infra-red lamps [95] have been adopted as a source of heat for baking films. Its principal advantage is saving time, and to a lesser degree, space. It is especially adapted for use with metal articles made of thin stock, as much of the energy used to heat the metal is lost so far as baking the film is concerned. However, the method is not limited to metal articles.

Repainting. Smooth, shiny surfaces of old paint should be roughened so as to provide a tooth for the new paint. Loose powder (chalk) on surfaces should be brushed off. Paint that has cracked and scaled should be wire-brushed to remove all loose portions. Complete removal with paint and varnish remover or by burning off may be necessary if the scaling is bad.

SOME ECONOMIC ASPECTS OF THE PAINT INDUSTRY

Until the middle of the nineteenth century, every painter made his own paint from dry pigments and oil, but about that time a few painters and dealers in paint materials were preparing liquid paint for their customers.[96]

TABLE 2—SOME GENERAL STATISTICS FOR PAINT, VARNISH AND RELATED PRODUCTS (N.P.V. & L.A. 1941)

Year	*No. of Establishments*	*Wage Earners Average for Year*	*Wages and Salaries*	*Value of Products*	*Value Added* [b] *by Manufacture*
1849 [a]	4	22	$5,000	$77,000	$71,000
1869	202	3,355	1,819,000	21,923,000	7,143,000
1889	522	8,189	4,302,000	54,234,000	21,497,000
1909	791	14,240	8,271,000	124,889,000	45,874,000
1919	830	21,507	24,118,000	340,346,000	123,234,000
1925	923	25,490	35,419,552	470,736,264	176,793,224
1929	1,063	29,211	78,169,695	568,975,838	234,843,773
1935	1,082	27,686	56,658,657	416,999,566	185,016,614
1939 [c]	1,254	28,167	64,740,625	518,824,601	229,881,349

a Data for 1849 for paints only.
b Value of products less cost of materials, etc.
c Figures for 1939 obtained by adding preliminary figures for establishments primarily manufacturing paints, varnishes and lacquers to preliminary figures for establishments primarily manufacturing colors and pigments, to obtain uniform basis of comparison with previous biennial census years.

Also according to Heckel [97] the first patent on ready-mixed paint was issued to a D. R. Averill of Newbury, Ohio, in 1867. This, however, may not have been the first ready-mixed paint, for at a fair sponsored by the Maryland Institute in 1848 one of the exhibits was a "patent anti-corrosive paint . . . a

[95] Goodell, P. H., Electrical Eng., *60,* 3 (1941).
McCloud, J. L., Ind. and Eng. Chem., *33,* 225 (1941).
[96] Heckel, G. B., "The Paint Industry—Reminiscences and Comments," p. 22 The American Paint Journal Co., St. Louis, Mo. (1931).
[97] *Ibid.,* p. 16.

metallic preparation, not so heavy as lead in bulk, and when properly applied it will spread over a much larger surface than lead." [98]

Heckel also states that the first varnish factory in the United States was that of Christian C. Schrack who began business in Philadelphia in 1815. Varnish is not included in the 1849 Census of Manufactures, but is included in the subsequent years.

The paint industry of America originated in the Mid-Atlantic and North Eastern States, and most of the output and establishments are east of the Mississippi and north of the Ohio Rivers. However, paint and varnish factories have followed the furniture industry into Virginia and the Carolinas. The Pacific Coast States are also well represented.

The growth of the industry, including the manufacture of pigments, is shown in the accompanying table which is an abridged one, prepared from a larger table compiled by the National Paint, Varnish and Lacquer Association.[99] The data originated in the Bureau of the Census.

From the modest start of 1849, the industry has shown steady progress. Although the 1939 business was less than in 1929, the relative standing among all manufactures improved, as may be seen from the following data.

TABLE 3—RELATIVE STANDING OF THE PAINT INDUSTRY

	1929			*1939*		
	All Manufactures	*Paint*		*All Manufactures*	*Paint*	
	Millions of Dollars	*Millions of Dollars*	*Per Cent of Total*	*Millions of Dollars*	*Millions of Dollars*	*Per Cent of Total*
Value of products	68,000	569	.80	57,000	519	.91
Value added by manufacture	31,000	235	.76	25,000	230	.92

Technologic advances have operated in the paint industry as well as in others to lower costs. At the same time most of the properties of the products have been improved. High grade industrial (factory applied) finishes for automobiles, refrigerators, furniture and the like are more durable than ever. High grade trade sales products, such as interior and exterior house paints, are brighter (in the case of white) and have more opacity.

Although it is true that the costs of prepared paint and varnish are relatively low, it must be remembered that the cost of the dry film on a surface is a different thing and is largely influenced by the cost of labor of application. In the case of industrial finishes, labor is estimated to represent approximately 60 per cent of the finished job. In the case of paints applied by the house painter, labor may represent 80 per cent or more.

Probably the most important property of today's finishes is rapid-drying. The development of rapid-drying cellulose nitrate lacquers and the introduction of the spray gun were life savers of the automobile industry after the First World War. Since then other rapid-drying spirit varnishes have been de-

[98] Hartung, W. H., "Early Chemistry in Maryland." Baltimore Association of Commerce, p. 45, Mar., 1939.
[99] Nat'l Paint, Varnish and Lacquer Assoc., The Open Door, VII, No. 2, Feb. 3, 1941.

veloped, but no single one has dominated the market as cellulose nitrate lacquers did for a few years. The extensive use of tung oil shortened the drying time of oleoresinous varnishes.

Foreign trade in finished paints and varnishes is not an important factor, exports being from 5 to 10 million dollars a year, less than 2 per cent of the total industry. Imports are negligible. Paint and varnish factories have been built in many foreign countries in the past 15 years, and consequently exports have tended to decline.

On the other hand, imports of raw materials are substantial, totaling some $50,000,000 per year. War conditions are changing the picture, but otherwise the largest single commodity is tung oil, of which 100,000,000 or more pounds are imported annually. Other drying oils that are wholly imported are oiticica and perilla. According to the U. S. Department of Commerce, imports of these oils in 1939 and 1940 were:

	1939		*1940*	
	Pounds	*Value*	*Pounds*	*Value*
Tung oil	78,717,634	$11,724,253	97,048,595	$20,274,412
Perilla oil	51,284,120	2,204,815	11,347,270	873,054
Oiticica oil	18,866,689	1,708,045	15,536,623	2,218,264

Considerable quantities of ochre, sienna, red iron oxides, and chalk are imported, but the quantities of other colors and of the white pigments are insignificant. Lac from India, and natural resins from the East Indies, New Zealand, and Africa are valued at some 5 or 10 million dollars a year. In spite of the increasing production of synthetic resins, natural resins are still in great demand.

READING LIST

GENERAL

"Symposium on Accelerated Laboratory Tests and Service Tests on Protective and Decorative Coatings," American Society for Testing Materials, Philadelphia (1938).

"Symposium on Paint and Paint Materials," American Society for Testing Materials, Philadelphia (1935).

Bearn, J. Gould, "The Chemistry of Paints, Pigments and Varnishes," Ernest Benn, Ltd., London (1923).

"Paint and Varnish Technology Course," Mimeograph, Thirty Lectures, Case School of Applied Science, Dept. of Chemical Engineering. Cleveland, Ohio (1940).

Gardner, Henry A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," ninth edition, second printing (1940). Henry A. Gardner Laboratory, Washington, D. C.

Heaton, Noel, "Outlines of Paint Technology," Charles Griffin & Co., Ltd. (1928). Second edition (1940), J. B. Lippincott Co., Philadelphia.

Lawrance, James, "Painting from A to Z," second edition, The Sutherland Publishing Co., Ltd., Manchester (1938).

Mattiello, Joseph J., Editor. "Protective and Decorative Coatings." Volume I. John Wiley & Sons, Inc., New York (1941).

New England Paint and Varnish Production Club, Lectures of 1939-40, American Paint Journal Co., St. Louis, Mo. (1940).

Toch, Maximilian, "The Chemistry and Technology of Mixed Paints," third edition, second printing, D. Van Nostrand Co., New York (1932).

Uebele, Charles L., "Paint Making and Color Grinding," National Painters Magazine, New York (1913).

VARNISHES

Barry, T. Hedley, and Dunster, F. W., "Varnish Making," Leonard Hill, Ltd. (1935).

Huff, Ralph H., "Scientific Methods of Varnish Manufacture," American Paint Journal Co. (1940).

Krumbhaar, Wilhelm, "The Chemistry of Synthetic Surface Coatings," Reinhold Publishing Co., New York (1937).

Morrell, Robert Selby, "Varnishes and Their Components," Henry Frowde and Hodder & Stoughton, London (1923).

Oil and Colour Chemists Assoc., "Symposium on Varnish Making," Chemical Publishing Co., New York (1940).

LACQUERS

Jones, A., "Cellulose Lacquers, Finishes and Cements," C. Griffin & Co., Ltd. (1937).

Martin, Ray C., "Lacquer and Synthetic Enamel Finishes," D. Van Nostrand Co., New York (1940).

Wilson, Samuel P., "Pyroxylin Enamels and Lacquers," second edition, D. Van Nostrand Co., New York (1927).

PIGMENTS

Curtis, C. A., and Fyleman, Ernest, "Artificial Organic Pigments," Sir Isaac Pitman & Sons, New York (1930).

Faloon, D. B., "Zinc Oxide, History, Manufacture and Properties as a Pigment," D. Van Nostrand Co., New York (1925).

Mattiello, Joseph J., Editor, "Protective and Decorative Coatings," Volume II, John Wiley & Sons, Inc., New York (1942).

Wagner, Hans, "Die Körperfarben," second edition, Wissenschaftliche Verlagsgesellschaft, m.b.H., Stuttgart (1939).

MISCELLANEOUS

Abraham, Herbert, "Asphalts and Allied Substances," Chapter 30, fourth edition. D. Van Nostrand Co., New York (1938).

Bennett, E. F., "A Review of Driers and Drying," Paint Technology (1940).

Edwards, Junius D., "Aluminum Paint and Powder," second edition, Reinhold Publishing Corp., New York (1936).

Miskella, William J., "Practical Japanning and Enameling," Finishing Research Laboratories, Inc., Chicago (1928).

Simonds, Herbert R., "Finishing Metal Products," Metal Products Exhibits, Inc. (1935).

Sutermeister, Edwin, and Browne, Frederick L., "Casein and Its Industrial Applications," Chapter 13, Reinhold Publishing Corp., New York (1939).

CHAPTER 26

WHITE LEAD

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The name white lead applies to a compound consisting of lead carbonate and lead hydroxide. It is a commercial name distinctive of a product often referred to as basic carbonate white lead. It is one of the oldest white pigments in current use today. The generally accepted chemical formula for white lead is given as $2PbCO_3 \cdot Pb(OH)_2$, corresponding to the composition shown here:

Lead carbonate	68.9%	Lead oxide (PbO)	86.3%
Lead hydroxide	31.1%	Carbon dioxide (CO_2)	11.4%
	100.0%	Combined water (H_2O)	2.3%
			100.0%

However, the commercial white leads of today vary considerably in their chemical composition, the range of lead carbonate being from 62 per cent to 75 per cent. If the lead carbonate content exceeds 68.9 per cent, the presence of normal lead carbonate is evident. The recent white leads of lower lead carbonate content range from 62 per cent to 66 per cent—resulting in greater basicity—and are characterized by finer particle size, higher hiding power and increased paint thickening properties. The lower lead carbonate content white lead, that is, with a lead carbonate content approximating 62 per cent, predominates in a basic carbonate white lead having a chemical formula which may be written as $4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$, corresponding to the following composition:

Lead carbonate	60.2%	Lead oxide (PbO)	88.1%
Lead hydroxide	27.2%	Carbon dioxide (CO_2)	9.9%
Lead oxide (PbO)	12.6%	Combined water (H_2O)	2.0%
	100.0%		100.0%

It is evident, therefore, that basic carbonate white lead may have a chemical composition range in terms of lead carbonate from 60.2 per cent to 68.9 per cent, and we have within this range of chemical composition a mixture of two basic carbonate white leads. As the lead carbonate is increased above the theoretical 68.9 per cent, free or normal lead carbonate will be present. However, if the total lead carbonate does not exceed 75 per cent, the quality of the pigment is not impaired, but above 75 per cent total lead carbonate content, the quality of the pigment suffers as a result of the high normal lead carbonate content.[1] There-

[1] Anderson, A. W., Ind. Eng. Chem., *26*, 1047 (1934).

fore, white leads showing more than a limited excess of normal lead carbonate are not considered desirable pigments.

ECONOMIC ASPECTS

White lead maintains its position of importance as a white paint pigment despite the fact that chemical research has provided newer pigments possessing certain valuable characteristics to a high degree. Furthermore, manufacturing improvements and economies have enhanced the apparent value of these newer pigments. The annual production of white lead in this country for the past 30 years is shown in Figure 1.

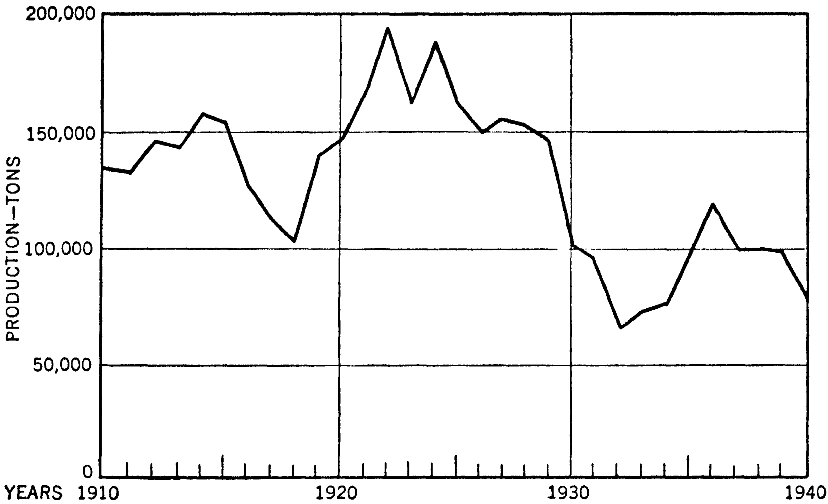


FIG. 1. Annual Production of White Lead in United States.

Fluctuations in price of white lead follow as a general rule the fluctuations in the price of metallic lead, the principal raw material from which it is manufactured. This is natural since lead comprises about 80 per cent of the finished product.

THE RAW MATERIALS FOR WHITE LEAD

Lead, which is the principal raw material, is usually found as an ore in combination with sulfur as lead sulfide or galena. Galena is usually associated with other minerals, from which it must be separated, smelted and refined.[2] The refining process is carried on until copper, silver, bismuth and other impurities have been removed and lead of refined grade, termed corroding lead, is obtained.[3] Purity of the lead used is very important to the physical properties of white lead, particularly in those processes where the lead is converted or corroded directly

[2] For a discussion of smelting and refining of lead see Chapter 24.
[3] Specifications for corroding pig lead will be found in A. S. T. M. Specification B-29-35.

into basic carbonate white lead, since even traces of certain metals other than lead will result in discolored white lead. For this reason, in these processes, only refined lead is used and the use of impure lead is not practicable.

When white lead is mixed into paint form and applied on an exterior surface, the paint wears away in a very gradual manner, by chalking. The original metallic lead from which the white lead was made is not recoverable. There is no return or recirculation of the lead used for this purpose as there is when lead is fabricated into storage batteries, cable coverings, alloys and other products, where, after their period of usefulness is ended, the scrap metal may be recovered and refined for reuse. This is, of course, advantageous for the miners and refiners of lead, but it also means that a considerable portion of the world's lead is irrecover-

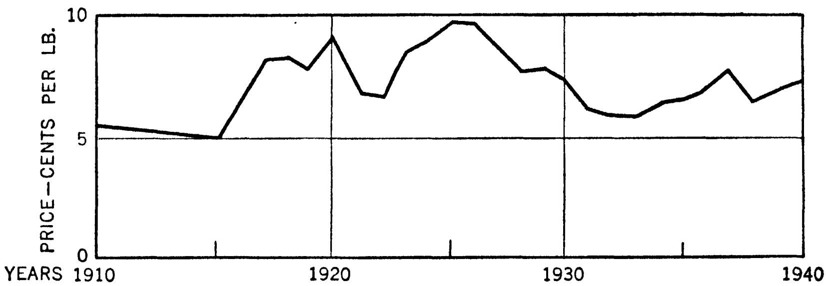


FIG. 2. Price of White Lead over Three Decades.

Data 1910 to 1935 from U. S. Bureau of Mines, Minerals Yearbook. Data 1936 to 1939 from Chemical Industries Buyers Guide. Data for 1940 from Oil, Paint and Drug Reporter, Feb. 10, 1941.

ably consumed in paint. This holds true, obviously, for all pigments used in paint. However, the reserves of lead in the various parts of the world are so tremendous that there is no prospect of depletion of the supply available for white lead manufacture for many years to come.

Carbon dioxide used in white lead manufacture is obtained in various ways, depending on the process used. In the Dutch process the carbon dioxide is obtained by the fermentation of tan bark. The combustion of coke or coal or other fuel is used as a source in the Carter and other processes.

Acetic acid is used in most white lead processes and although only a small amount is present in the product, it has an important part in the conversion of the metallic lead to basic carbonate white lead.

REACTIONS IN MAKING WHITE LEAD

Finely divided metallic lead is easily and readily oxidized in the presence of acetic acid and moisture, forming basic lead acetate:

$$Pb + O + 2HC_2H_3O_2 \rightarrow Pb(C_2H_3O_2)_2 + H_2O$$
$$Pb + O + Pb(C_2H_3O_2)_2 + H_2O \rightarrow 2Pb(OH)(C_2H_3O_2)$$

This product is readily converted to basic lead carbonate, in the presence of water, by the action of carbon dioxide.

$$6Pb(OH)(C_2H_3O_2) + 2CO_2 \rightarrow 2PbCO_3 \cdot Pb(OH)_2 + 3Pb(C_2H_3O_2)_2 + 2H_2O$$

This is the simple basic reaction involved in most of the processes used for the commercial manufacture of basic lead carbonate white lead.

Today in the United States there are several processes in commercial operation; however, of these the Dutch and Carter processes account for the greater proportion of the output.

THE DUTCH PROCESS

Corroding—The Dutch process is one of slow corrosion wherein pig lead is changed to basic lead carbonate white lead by the action of gases produced by the fermentation of tan bark. Special buildings known as corroding or "stack" houses are provided for this purpose. These buildings are divided into a number of compartments or stacks generally about 30 feet high with a floor space of about 20 by 40 feet. Since the process of corrosion takes several months, the various compartments or stacks are started in rotation so that in any stack house, stacks are being filled or set simultaneously, others are in the process of corrosion, and still others being torn down and stripped. In this way a continuous supply of completed white lead can be maintained.

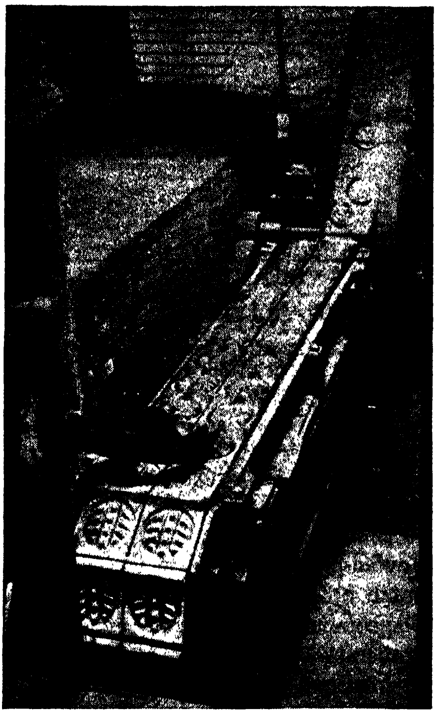


FIG. 3. Automatic Casting Machine for Making Lead Buckles.

The floor of the stack building, which is ordinarily of earth, is covered with a layer of tan bark about 20 inches thick. On this layer is placed a layer of corroding pots, covering the entire floor. These pots are of substantial glazed stone ware construction and measure about a foot high and 8 inches in diameter. They somewhat resemble large flower pots but there is no hole in the bottom and the pots are designed so as to provide a shelf or shoulder about one-third of the way from the bottom. The lower part, in other words, forms a sort of compartment or well in which about one-half pint of dilute acetic acid (2.5 per cent-3.0 per cent) is placed. The amount of acetic acid used does not exceed 0.4 per cent of the total weight of the lead.

The pots are then filled with lead buckles which are perforated discs of lead about 6 inches in diameter. The casting of these metallic discs or buckles is really the first step in the process of manufacturing white lead. An automatic casting machine, such as is shown in the accompanying photograph, Figure 3, is used in the casting of the discs or buckles and they are then conveyed directly to the floor of the stack building. The process of loading the pots with buckles is shown in Figure 4. The buckles fill the top or larger compartment of the pot so that they are separated from the acetic acid in the bottom part or well. Buckles are of various designs, but all designs provide for the circulation of the corroding gases and also provide somewhat greater surface for chemical action. Figure 5 shows some typical designs.

Fig. 4. Loading the Corrosion Pots.

On the top of the layer of pots a layer of boards is placed, making a false floor. On top of this is placed another layer of tan bark, then another layer of pots filled in a similar manner to the first layer. The completed stack contains eight or ten such layers or tiers.

A certain amount of ventilation is necessary so that moisture and generated gases may escape, so a ventilating pipe, generally of wood, is provided, connecting with each tier and usually running up through the center of the stack. At the top of the vent pipe or flue is an outlet which may be opened or closed as desired. In operation the vent pipe is used for partial control of the process of corrosion. At the start the vent pipe is closed to hold in the gases and heat and thus accelerate the start of the fermentation action of the tan bark. After the stack has started to "work," that is, the temperature has risen to about 180° F., indicating that the action has started, then the vent is opened somewhat to allow normal corrosion to continue.

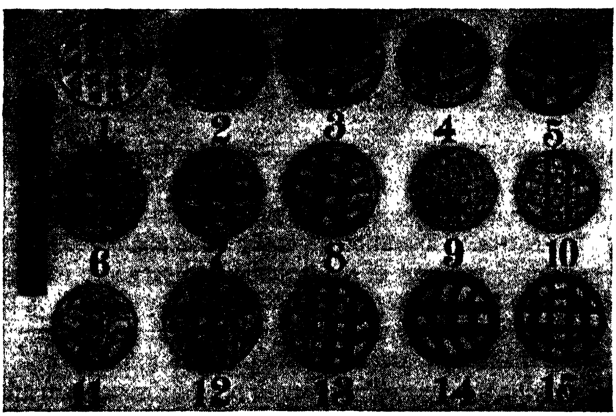


Fig. 5. Typical Designs of Lead Buckles.

Chemical Change—When the stack has been built, the tan bark ferments liberating carbon dioxide and generating heat. The heat causes the acetic acid to volatilize. The fumes attack the lead buckles and since oxygen and moisture are present, the surface of the lead oxidizes to a hydrated lead oxide and becomes coated with basic lead acetate. At the same time, the carbon dioxide generated by the fermenting tan bark decomposes the basic lead acetate forming basic lead carbonate or white lead, and normal lead acetate. This normal lead acetate reacts under the existing conditions with more metallic lead forming more basic lead acetate which in turn is converted to basic carbonate by the action of more carbon dioxide. This cycle is repeated until most of the lead is converted to white lead

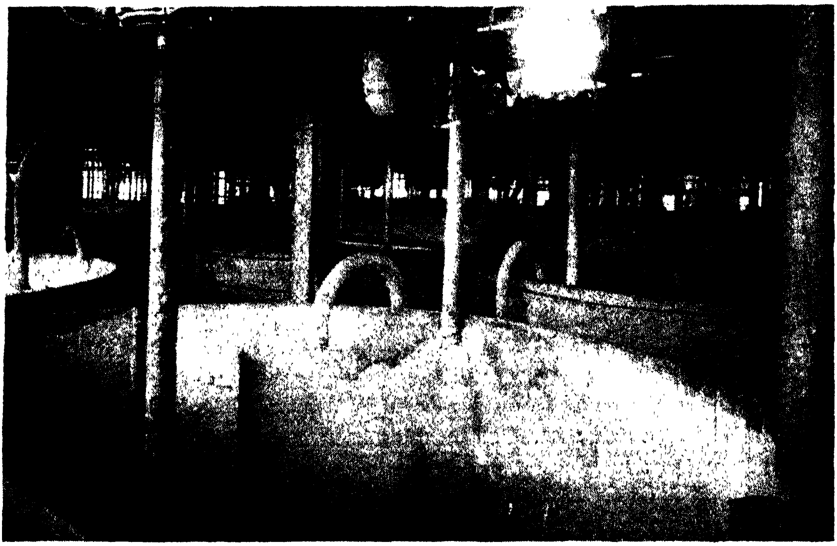


FIG. 6. Settling Tanks for White Lead.

so that a relatively small amount of acetic acid or lead acetate acts as a corroding catalyst for the manufacture of a large tonnage of white lead.

When the corrosion has proceeded to the proper point, the stack is taken down and stripped. The corrosion operation generally takes about 100 to 120 days and after this time about 80 per cent of the metallic lead cast into buckles will have been converted into a hard white crust of white lead with only a thin core of metal left in the center of the buckle. These corroded buckles are then taken out of the pots by hand and are transferred to the grinding mill. Here the white lead buckles with their metallic cores are passed through a tumbling screen which separates most of the metal portion, which is returned to the stack house to be used in subsequent corrosions. After passing the tumbler screen the white lead is passed through a set of rolls. These crush the white lead into a powder but flatten out the residual metallic lead so that it may be easily separated on a fine screen. The white lead is now ready for grinding.

Grinding—The unground white lead is mixed with water to form a thin pulp. This is ground through high speed buhrstone water mills and then generally carried through a system of rake tubs, settling tanks, and drag boxes, in which the coarser particles are separated and returned for regrinding. Finally the finished, ground material is passed through fine silk bolting cloth which is about equivalent to a 325-mesh screen. At the end of the grinding process the particle size averages about 2 microns, average diameter by surface mean. After grinding, the finished slurry is pumped to large settling tanks (Figure 6), where the white lead settles to the bottom, forming a thick pulp.

Water Pulp White Lead—White lead at this stage may be processed in either of two ways. It may be filtered, dried, disintegrated, packed and sold as

FIG. 7. Festoon Dryer for White Lead.

dry white lead, or it may be mixed with linseed oil to form a heavy oil paste and sold as white lead in oil. The production of dry white lead is a simple process. The heavy settled water pulp, with as much of the water removed as possible, is filtered by means of a vacuum filter generally of the continuous, rotating drum type.[4] The filter cake is dried in a continuous traveling belt type steam heated dryer. In most cases the dryer is what is known as a festoon dryer, where the filter cake is fed and pressed into the meshes of a wire screen belt which hangs in loops or festoons while traveling through a long drying compartment (Figure 7). Some plants have recently adopted a type of dryer in which the cake is partially dried and formed into small sticks, which lie loosely on a traveling screen through which hot dry air is blown.

After the white lead is dried it is passed through a mill or disintegrator which breaks up any lumps which may have formed in the drying process. The fin-

[4] For a discussion of filtration see Chapter 2.

ished product, generally packed in wooden barrels, is a fine dry white powder free from lumps or agglomerates.

White Lead in Oil—For the manufacture of white lead in oil the dry white lead may be mixed with linseed oil in large chaser mills and then thoroughly ground in buhrstone or roller mills. This procedure has been largely replaced by the process of flushing the white lead water pulp directly with the linseed oil. The white lead water pulp is mixed with the linseed oil in tall cylindrical tanks equipped with powerful agitators better known to the white lead manufacturer as pulpers. After a short while the basic carbonate white lead, due to a greater chemical affinity for the oil, which contains free fatty acids, leaves the water phase entirely and clear water, free from white lead, can be separated. White lead in oil made by this method may contain a small amount of residual moisture, but this is in no way detrimental to the product. However, the moisture content may be reduced, if desired, to a few hundredths of one per cent by transferring the paste white lead to low temperature vacuum mixers. Making paste white lead by taking advantage of the affinity of linseed oil for white lead has the advantage over dry grinding of being considerably cheaper, the entire drying cost being saved. Also, it entails much less hazard to the workmen since the handling of dry white lead is eliminated. After the white lead has been pulped in oil, it is thoroughly ground in buhrstone or high speed roller mills to insure a perfectly dispersed and homogeneous product.

THE CARTER PROCESS

Chemically, white lead manufactured by the Carter process is essentially the same as that manufactured by the Dutch process. In each case the refined metallic lead is oxidized to lead monoxide or hydrated lead monoxide and subsequently converted into basic lead acetates which are acted upon by carbon dioxide to form basic carbonate of lead or white lead.

Pig lead of the same purity as used in the Dutch process is required in the Carter process.

The first step in this process is to atomize the metallic lead, the method being substantially the same as atomizing a liquid in an ordinary atomizer. The pig lead is melted in a kettle to which is affixed a nozzle through which the molten lead flows by gravity or under pressure. At the outlet it is struck by a jet of compressed air, which atomizes or blows the lead into very fine particles, which are slightly oxidized.

The atomized lead, in charges of about 4000 pounds, is then placed in wooden cylinders (Figure 8) about 6 feet in diameter and 10 feet long, which revolve very slowly. The metallic lead in the cylinders is treated with water, dilute acetic acid and carbon dioxide. Water and a very weak solution of the acetic acid are sprayed into the cylinders at alternate intervals. The carbon dioxide is admitted through the center of the cylinder head and is produced by combustion, with excess air, of carefully selected coke. The coke is burned under boilers, to utilize its heat value. The lead in the cylinders is kept moist with water during corrosion and a certain per cent of oxygen (air) passes into the cylinders with the carbon dioxide.

The action of water and acetic acid upon an excess of metallic lead and lead oxide under these conditions produces various basic lead acetates. The carbon dioxide acting on the basic acetates forms basic lead carbonate or white lead.

The normal lead acetate, freed by the carbon dioxide acting on the basic lead acetate, acts again on the excess of metallic lead in the presence of oxygen, with the formation of more basic lead acetate. The cycle is repeated until corrosion is complete.

As the cylinders slowly revolve, the atomized lead is carried upward on the inside wall of the cylinder and rolls down to the bottom continually exposing new surfaces to the corroding agents. The heavy mass also performs most efficiently

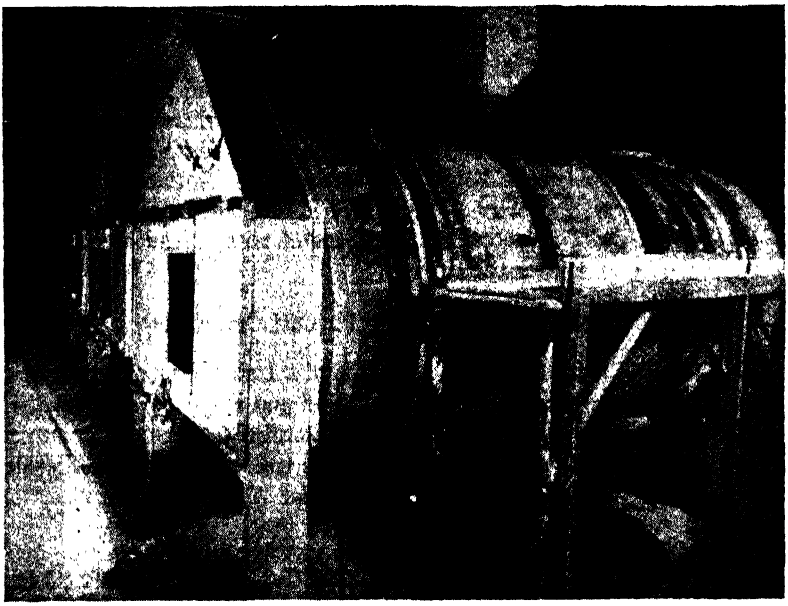


FIG. 8. Oxidizing Cylinders for Carter Process White Lead.

the functions of a tube mill, grinding the carbonate off the metallic particles as fast as it is formed and reducing it to an exceedingly fine powder.

By the Carter process corrosion is completed in from 8 to 12 days. No artificial heat is required, sufficient heat being generated by the chemical reaction to maintain the contents of the cylinder at about 150° F. during corrosion.

At the proper stage, the cylinders are emptied and the white lead is then washed and agitated in water, removing residual lead acetate. It is then floated in water to remove the small particles of coarse lead, if there are any, and is then pumped into storage tubs, where the white lead settles in the form of a thick pulp. After the water has been removed by filtering and drying, the product is commercial dry white lead. This is ground or disintegrated in a manner similar to the handling of Dutch white lead. Either the dry or the pulp white lead is mixed with linseed oil as with Dutch process white lead, and ground to produce a similar paste.

EUSTON PROCESS [5]

The Euston process for the manufacture of white lead is in its essential features a modification and development of the old French Thenard process. It involves, first, the solution of highly refined metallic lead and then the precipitation of white lead of rigidly controlled pigmentary characteristics from this lead solution. Metallic lead is usually considered as a material very resistant to atmospheric oxidation or corrosion, because a film of oxide rapidly forms on the surface of the lead which protects the surface from further oxidation. If, however, this film of oxide is removed, the lead surface, on being again exposed to air, will be rapidly oxidized again until a new protective film is formed. Advantage of this phenomenon is taken in the Euston process.

In making these solutions, highly refined metallic lead having a purity of about 99.9 per cent is melted and run into cool water where it solidifies into a mossy, spongy mass of feathered lead. This gets the lead into a condition having a large surface exposed to oxidation and solution. The feathered lead is placed in large tanks where it is oxidized on the surface through the action of air. The lead oxide so formed is dissolved off by means of normal lead acetate solution. The approximate reaction involved is:

$$2PbO + Pb(C_2H_3O_2)_2 = Pb(C_2H_3O_2)_2 \cdot 2PbO$$

This basic lead acetate which is formed is of a high degree of purity as most of the impurities are unattacked, remain behind and are removed from the system. The basic lead acetate solution is then clarified to remove any suspended matter and is run to the carbonators where it is treated with carbon dioxide gas to form white lead. The approximate reaction is:

$$3Pb(C_2H_3O_2)_2 \cdot 2PbO + 2H_2O + 4CO_2 = 2(2PbCO_3 \cdot Pb(OH)_2) + 3Pb(C_2H_3O_2)_2$$

While this reaction is unquestionably simple, numerous side reactions may occur in the operation of treating basic lead acetate solutions with carbon dioxide which substantially affect the composition and characteristics of the precipitate. By suitable methods, however, the reaction can be so handled as to produce a white lead of any composition, even up to pure lead carbonate, which is usually considered useless as a pigment. In the Euston process the reaction is carefully controlled, to enable the uniform production of several grades of white lead.

It will be noted from the above reaction that the normal lead acetate is unchanged by the carbonation and when the reaction is complete, the white lead is suspended in a normal lead acetate solution. This suspension is pumped to a settling tank where the white lead settles to the bottom as a thick slurry and the normal lead acetate solution overflows the top and is reused to dissolve more lead oxide to make basic lead acetate solution. It will thus be seen that the neutral lead acetate solution is unchanged in the process, but is simply used as a solvent for the lead oxide and a carrier for the white lead. The CO_2 gas used in this process is produced by burning sulfur free fuel under strictly controlled condi-

[5] Written by P. E. Sprague, Vice President, The Glidden Co.

tions so that a high percentage of carbon dioxide is obtained. The gas is thoroughly washed and purified so that it is entirely free from any foreign matter.

The heavy slurry on the bottom of the settling tank is pumped to the filters where it is filtered and thoroughly washed to remove all mother liquor. The filtered white lead is dried in steam heated dryers which are so constructed that no dust can escape into the atmosphere. The dried white lead from the dryers is run through a pulverizer to break up any lumps which may be formed during the drying. The several grades are then packed into barrels and sold as dry white lead basic carbonate or ground in linseed oil and sold as pure white lead-in-oil.

SPERRY PROCESS [6]

The process [7] which is operated by the White Lead Department of the International Smelting and Refining Company, East Chicago, Indiana, was developed at the beginning of the present century in the Research Laboratory of Elmer A. Sperry. Two of his many developments in this field were the Sperry and Townsend [8] cells. The former can be used to produce any insoluble salt of any metal. To date it has been used to produce white lead, lead arsenate, litharge, lead borate, copper oxide and carbonate, and lead chromate.

The Sperry Cell—The Sperry cell, as operated to produce white lead, consists of a concrete cell tank in which are suspended lead anodes and insoluble iron cathodes. (See Figure 9.) The cathodes are incased in porous fabric envelopes which act as diaphragms to separate the electrolytes. The catholyte is circulated through the compartment formed by the envelope diaphragms. This electrolyte contains from ·1 to 3 per cent sodium acetate, from 7 to 14 per cent sodium carbonate, and approximately ½ per cent sodium hydroxide. The cell tank is filled with the anolyte which circulates around the submerged anodes and the outer surface of the diaphragms. The anolyte contains from 3 to 5 per cent sodium acetate and only a trace of sodium carbonate and sodium bicarbonate. Each electrolyte is maintained in rapid circulation about its electrode and the circulation system of each is entirely independent of the other. The only communication that exists between these two electrolytes is through the diaphragms of the cells.

The Cell Reaction—When direct current is passed through the cell carbonate and hydroxide ions migrate under the influence of the current from the catholyte through the diaphragm to the anolyte. At the same time, electrochemical equivalent amounts of lead ions dissolve from the surface of the lead anodes and pass momentarily into solution in the anolyte. Since the anions are more mobile than the cations the plane in which the ions meet is quite close to the surface of the anode. In this plane precipitation takes place, and white lead is formed. Due to a slight seepage of catholyte through the diaphragm the anions are transferred to the anolyte in amounts in excess of the reaction requirements. This results in complete precipitation of the lead ions dissolved from the anode. A study of the cell reactions indicates that the formula for white lead should be written

[6] Written by Wm. J. Knox, Jr., White Lead Plant Superintendent, International Smelting and Refining Co., East Chicago, Ind.
[7] Bowman, R. G., Trans. A. I. M. E. 73. 146 (1926).
[8] For the use of the Townsend cell see Chapter 12.

$Pb(CO_3PbOH)_2$ and that this compound is formed through the reactions of the intermediate compounds $Pb(CO_3H)_2$ and $Pb(OH)_2$.

Cell Performance—Practically no difference is found between theoretical and actual production of this cell. An ampere efficiency of 100 per cent is used in all production calculations. The theoretical production of white lead of theoretical

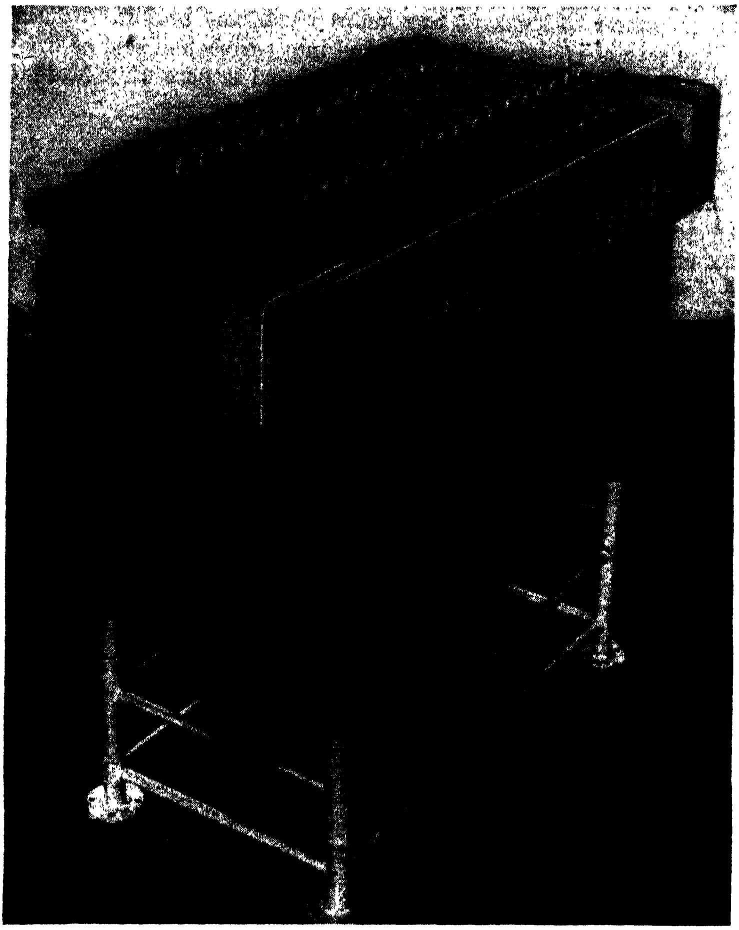


FIG. 9. Sperry Cell for the Production of White Lead.

composition (11.344 per cent CO_2) per ampere, per 24 hours, is 0.25505 pound. The cells have a total anode area of 140 square feet. The voltage drop per cell when operating at 30 amperes per square foot of anode surface is approximately 2.8 volts.

The continuous flow of anolyte removes the white lead from the cell as fast as it is formed. From the cell the anolyte flows to a settler where the white lead is removed and clear overflow from the settler is returned continuously to the cell. The catholyte, in its circulation external to the cell, is carbonated to replenish the carbonate ions and neutralize excessive hydroxide ions formed at surface of the cathode.

The settled white lead is removed continuously from the bottom of the settler to a filter where it passes through a counter-current washing cycle to remove and recover the anolyte solution. The washed white lead pulp is dried, ground and air floated, and is then barrelled in a dry pulverulent form.

Properties of Electrolytic White Lead—The outstanding characteristics of electrolytic white lead—exceptional purity, brilliant whiteness, and uniformity—are due to the ease with which cell reactions can be controlled and to the fact that in the cell only the lead is dissolved from the surface of the lead anode, other metals remaining on the anode surface in the form of a hard film.

The physical properties of electrolytic white lead can be varied over a wide range to meet changing specifications. This is accomplished by changing the operating constants of the cell, which in turn will change the chemical composition of the particle and the composition of the particle's surface, also the size and shape of the particles. Uniformly large or small particles or various mixtures of large and small particles can be produced. The uniformity of the various grades produced is the result of the positive control of the chemical reactions taking place in the cell.

THOMPSON-STEWART PROCESS

This process has been developed recently by the National Lead Company, and at the present time is in operation at two of its plants.

The starting material is a mixture of finely divided lead oxide and metallic lead. To form this, the pig lead is melted and fed into a small furnace inside which the molten lead is agitated causing the formation of metallic lead fume. This fume oxidizes rapidly, although not completely, resulting in a mixture of finely divided metallic lead and lead oxide. A charge of this partially oxidized lead product is placed in a tank and mixed with water to form a slurry. As a reacting agent, with a function similar to that in the Dutch or Carter processes, a small percentage of acetic acid is added. The batch is agitated, aerated and carbonated and basic carbonate white lead is formed by reactions similar to those discussed previously.

Carrying Out the Reactions—Carbonation is effected by means of a specially designed carbonating system, wherein the slurry is continuously drawn from the tank, reacted with carbon dioxide in a gas tight, continuous absorption system and then returned to the main tank. This absorption system is so efficient that practically all of the carbon dioxide fed in is converted into basic lead carbonate of definite chemical composition. The velocity and volume of both the lead slurry and carbon dioxide gas are maintained at predetermined ratios.

The reaction end point is controlled by an electrometric conductivity method which indicates precisely the point at which the carbonation has reached a predetermined value; that is, when white lead of the desired chemical composition has been formed. The product consists, in the main, of basic lead carbonate having the following empirical formula:

$$4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$$

Basic lead carbonate white lead manufactured by this method contains a larger percentage of total lead than the average commercial white lead and is the most basic of lead carbonate white leads in commercial production. However, the process, being flexible in operation, may produce a combination of basic carbonate white lead within the empirical formula range of $4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$ and $2PbCO_3 \cdot Pb(OH)_2$. The outstanding characteristics of white lead made by this process are extremely fine particle size, superior hiding power, and desirable paint thickening properties.

PROPERTIES OF WHITE LEAD

The relative merits of the various processes used in the manufacture, and the relative merits of the white leads they produce, are subjects of somewhat controversial nature. Most of the white lead produced is used in paint. Long life, continued good appearance and adequate protection of the surface are the prime requisites of all good paint.

Although the ultimate value of a paint, or of its essential ingredients, cannot be fully appraised by initial appearance, it can, through carefully conducted chemical and physical tests made at the time of manufacture, be appraised within certain reasonable, practical limits.

White leads made by various processes have varying characteristics and, especially with the newer processes, the control of pigment properties is much more precise. The development of precision control methods was necessary because of the demand, on the part of consumers, for more and more special grades of white lead meeting rigid specifications involving both physical and chemical properties. The data of Table 1 on the physical properties of basic carbonate white lead give an idea of the range of variation.

TABLE 1—PROPERTIES OF WHITE LEAD

Specific Gravity	6.7 to 6.8
Bulking Values:	
Pounds per solid gallon	56 to 57
Gallons per pound	0.0175 to 0.0179
Refractive Index	1.94 to 2.09
Brightness (in glycerine)	80% to 92%
Oil Absorption* (pounds of oil per 100 pounds pigment)	8 to 15
Hiding Power (Complete hiding in linseed oil paint over black background)	13 sq. ft. to 25 sq. ft. per lb.
Fineness:	
Portion retained on a No. 325 sieve: Less than	0.1% to 0.2%
Particle size. Average diameter by surface mean	0.9 to 2.3 microns
Paint Consistency †.	
Per cent pigment in 30 second paint	63 to 82
Pounds of pigment in one gallon of 30 second paint	10.5 to 21.5

* A.S.T.M. Standard Method D-281-31.

† Determined by Gardner Mobilometer—120 gram system—10 cm. fall—70° F. Test paint composed of pigment and refined linseed oil having acid number of 2.5.

In general it may be said that careful chemical control in manufacture insures good quality and uniform characteristics for basic carbonate white leads made by all of the processes described.

INDUSTRIAL USES OF WHITE LEAD

By far the largest proportion of the white lead produced is used for the manufacture of paint. As a white paint pigment, white lead is unique in its ability to impart to the paint, by itself, all of the properties necessary to successful paint performance. Because of its chemical affinity for paint vehicles, white lead becomes more of an integral part of the paint film than do other white pigments which are non-reactive in paint vehicles. Basic carbonate white lead is a primary white pigment which actually reinforces the paint, providing tough, flexible films which are exceptional in their resistance to embrittlement.

White lead finds its way into paint in two forms. As the dry powder, it is used by paint manufacturers, either alone or in combination with other pigments, to produce prepared paints of various types. In the form of "paste lead," or "lead-in-oil," which contains about 10 per cent linseed oil, it is supplied to the painter, who is able to prepare from it the majority of the paints which he uses.

White lead is exceptional in the versatility of its uses in paints. It is used in priming paints and undercoaters because of its adhesion, flexibility and lack of porosity. In interior flat wall paints, it provides solidity and washability. Paints which have to meet rigorous performance requirements employ white lead extensively.

Exterior paints, which are subjected to the severe conditions of weather exposure, contain a considerable proportion of white lead. Basic carbonate white lead is the only white pigment which can be used to constitute the entire pigment portion of an exterior paint. It is characterized by its consistent performance, on various types of materials and under various climatic conditions. The performance record indicates, in brief, extreme ultimate durability, coupled with moderate, gradual chalking, good tint and color retention, good covering power, easy brushing, and relative freedom from cracking and scaling. A paint possessing these qualities provides an ideal surface for repainting, when this becomes necessary, because it establishes a surface that does not require any special preparation.

The combination of properties for paints, listed above, is found particularly in basic carbonate white lead. However, other pigments may display one or more of these properties in such a marked degree that their inclusion in the paint, in moderate amounts, may appreciably alter the characteristics of the paint in one or more particulars. Even though such pigments cannot be used by themselves to produce satisfactory exterior paints, they are nevertheless satisfactorily used, in combinations, with basic carbonate white lead as the base pigment, for special purposes, or to achieve certain effects.

In addition to its use in paint, basic carbonate white lead is of value to the paint industry as a base for putty. It materially improves the straight whiting and linseed oil putty, insuring better adherence and longer life, even under adverse conditions.

The ceramic industry absorbs a considerable tonnage of basic carbonate white lead annually. Lead is used as an essential ingredient of many glazes, and although lead compounds other than white lead are also used to supply the percentage of lead required, basic carbonate white lead is found a particularly convenient form to use, by the glaze maker, because it is non-reactive or stable in water, and its particle size gives it valuable suspension properties in slurries, or water suspensions with other ingredients.

There are many other uses [9] for which basic carbonate white lead has been found highly desirable because of its physical and chemical characteristics; for example, certain lubricating greases, and protective temporary machine coatings made with non-drying greases and oils, are reinforced with basic carbonate white lead. Special adhesives, designed to be exceptionally strong and water resistant, are made with basic carbonate white lead as an important ingredient.

WHITE BASIC LEAD SULFATE

Basic lead sulfate is a lead compound which is quite widely used as a paint pigment. Commercially, it is called "white basic lead sulfate," "basic sulfate white lead," and "sublimed white lead."

White basic lead sulfate was first made in 1855 by E. O. Bartlett, who made some on an experimental basis in Birmingham, Pa. Bartlett was at that time making zinc oxide directly from zinc ores by the American process, and he applied the same principles to the production of a lead pigment from lead ore and found that it was possible by heating a lead ore under proper conditions to produce a white powder having pigment properties.

The commercial production of basic lead sulfate was transferred to Missouri where there were deposits of lead ore which were sufficiently free from other metals. The first plant was built in 1876 in Joplin, Missouri.

Composition—The composition of basic lead sulfate may be represented by the empirical chemical formula $2PbSO_4 \cdot PbO$.

The ores which were used prior to 1930 contained some zinc and the basic lead sulfate which was made from them contained 4 to 6 per cent zinc oxide. Commercial basic lead sulfate now being made by either fume or chemical processes does not contain zinc oxide; therefore it more closely conforms to the empirical formula.

The lead monoxide (PbO) content of basic lead sulfate, chemically combined with the lead sulfate ($PbSO_4$), is largely responsible for many of the good properties exhibited by this pigment. Normal lead sulfate, which contains no combined lead monoxide, has poor hiding power and is not a very satisfactory paint pigment. The various grades and types of white basic lead sulfate cover a range of 72 per cent to 85 per cent lead sulfate and 15 per cent to 28 per cent lead oxide.

Manufacture—White basic lead sulfate is made by two types of processes—the fume process and the chemical process.

Two fume processes are in use, differing chiefly in the raw materials which are used. In one fume process selected lead sulfide ore (galena) is subjected to a high temperature in an oxidizing atmosphere in a special furnace. In the other, molten lead is sprayed into a jet of ignited fuel gas and air in a special furnace, into which sulfur dioxide gas is also introduced.

In both fume processes the white basic lead sulfate is formed in the furnace

[9] Gregory, T. C., "Uses and Applications of Chemicals and Related Materials," p. 343, Reinhold Publishing Corp., New York (1940).

as a fume which is drawn off, and passed through a cooling and collecting system.

In the chemical process metallic lead is first atomized, and the finely divided metallic lead, or metallic lead and lead oxide, is then mixed with water. Sulfuric acid is added, under controlled conditions, to form white basic lead sulfate which closely approximates in composition the empirical formula $2PbSO_4 \cdot PbO$. The details of the recent chemical process are given in U. S. Patent No. 2,249,330. The conditions under which the crystals of basic lead sulfate are formed are such that the particles are needle-like or acicular in shape.

Properties—White basic lead sulfate is an opaque white pigment which resembles basic lead carbonate in many of its properties but is not equal to basic carbonate white lead in performance. It is slightly lower in specific gravity. As manufactured today, the color of basic lead sulfate equals that of the whitest basic carbonate white lead. White basic lead sulfate has strong affinity for linseed oil, and is easy to grind.

INDUSTRIAL HAZARDS

The lead industry, as an outstanding example, proves the value of safeguarding the health of the worker. In modern plants, every precaution is taken to insure the continued good health of every employe. Efficient methods of dust and fume collection and disposal, adequate sanitary facilities, periodic health examinations, thorough education of the worker in the proper handling of lead and lead products, and rigidly enforced rules for personal cleanliness have radically changed the old conception of industrial hazard in this industry. Therefore, lead poisoning, as such, is practically non-existent in the properly equipped and efficiently managed industrial activities of today.

Section VII

PRODUCTS OF ORGANIC SYNTHESIS

The lustiest child of the chemical industry of recent decades has probably been the synthetic organic chemicals. This Section VII, at best, represents only a very rough classification. Some small parts of the material dealt with here involve inorganic rather than organic chemistry. Some of the processes, such as fermentation for solvents, are not truly chemical synthesis. Again, some parts of the pharmaceutical field involve extraction or slight modifications of natural materials—not synthesis. Also, many instances of organic synthesis are discussed in the chapters of other sections of the book. Nevertheless, the material covered here represents the most important aspects of the organic chemical industry.

CHAPTER 27

INDUSTRIAL ORGANIC CHEMICALS

ALEXANDER LOWY
Late Professor of Organic Chemistry, University of Pittsburgh

Because of the immensity of the field of industrial organic chemistry, it is necessary to have a definite compilation of the essential information of the chemical reactions [1] involved, if one is to arrive at any clear picture of the industry. The most essential information is presented in tabular form in this chapter. It does not simplify a field that is so complicated that it cannot be simple but it assembles the information in a state of some order.

The information in this chapter is particularly apropos to the material in the following chapters which deal with the group of industries based directly on organic syntheses. However, many industries which fall outside that group, particularly those which deal with natural plant and animal products, utilize many phases of the chemical knowledge presented here.

ORGANIC TYPE FORMULAS

Organic chemistry has many features of nomenclature and formulation which are specific in the field, so a compilation of the essentials is presented in Table 1.

THE ORGANIC UNIT PROCESSES

The information on the group of reactions now commonly known as the Organic Unit Processes, such as nitration, sulfonation, etc., has evolved into a system of compilation of a chemical engineering, rather than a strictly chemical character. Consequently, this group of reactions is treated in the first section of the book which deals with the engineering fundamentals. See Chapter 3.

ORGANIC TYPE REACTIONS

During the long course of a century of research many types of organic reactions have become associated with investigators' names. Some of these reactions are summarized in Table 2. There is considerable overlapping of this classification with that of the unit processes but since both systems are in common use both should be presented.

[1] See Chapter 3.

INDUSTRIAL PRODUCTS

Probably the outstanding characteristic of organic chemistry is the fact that a tremendous number of products may be obtained from one, or a very few, raw materials. In order to aid the visualization of the interrelationships between various raw materials and products a series of charts, which are essentially abbreviated flow sheets, have been prepared to cover several of the more important organic chemical industries. They are presented as Tables 3, 4, 5, 6, and 7.

These tables should be studied in conjunction with the various chapters which cover the various industrial products.

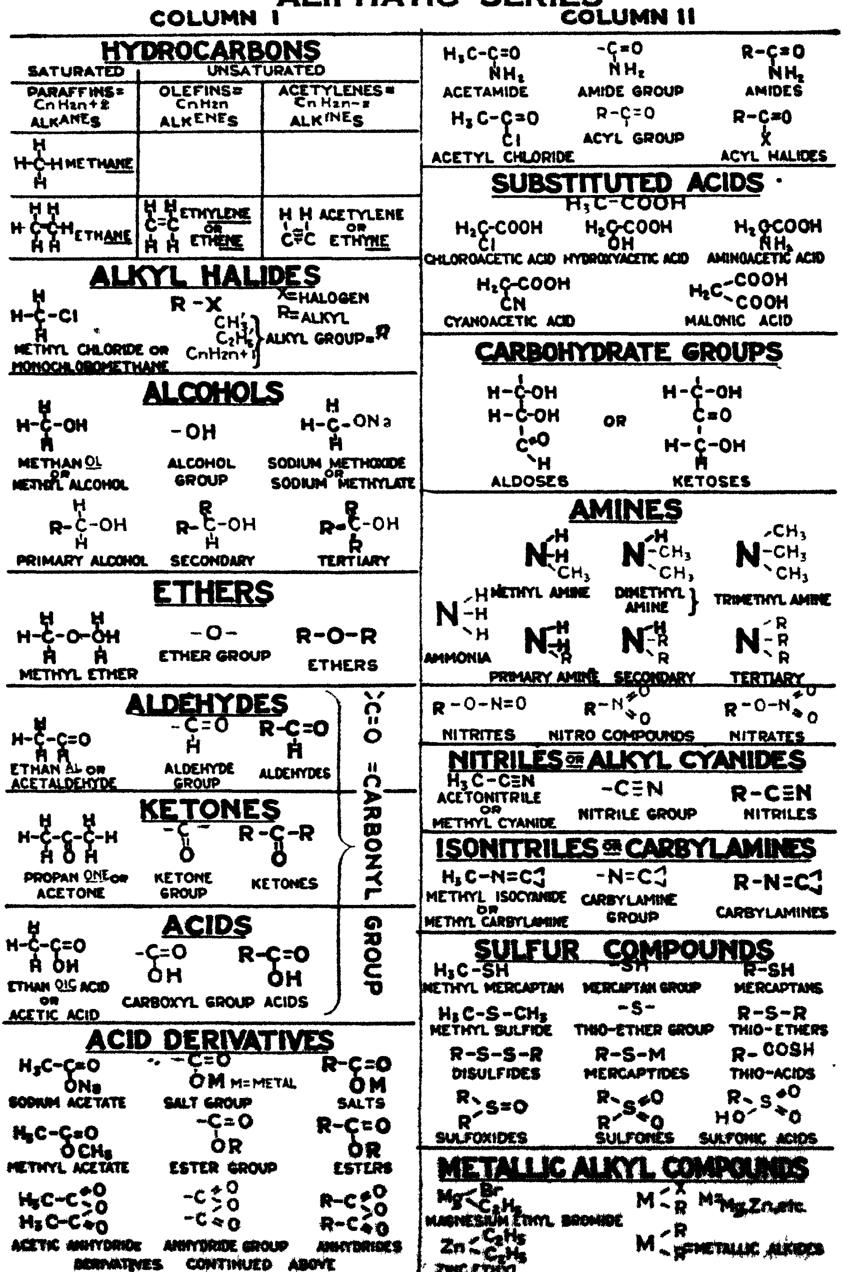
Although these tables give an overview of a few branches of the industry they do not begin to cover the field. Since it is almost impossible to list all of the organic compounds in use in industry today, the more important ones, with their scientific and common names, formulas, general methods of preparation and uses are arranged and tabulated, and follow under the five headings below.

Table 8—Aliphatic Compounds
Table 9—Benzene Derivatives
Table 10—Naphthalene Derivatives
Table 11—Anthracene Derivatives
Table 12—Heterocyclic Compounds

Table 1

ORGANIC TYPE FORMULAS

ALIPHATIC SERIES

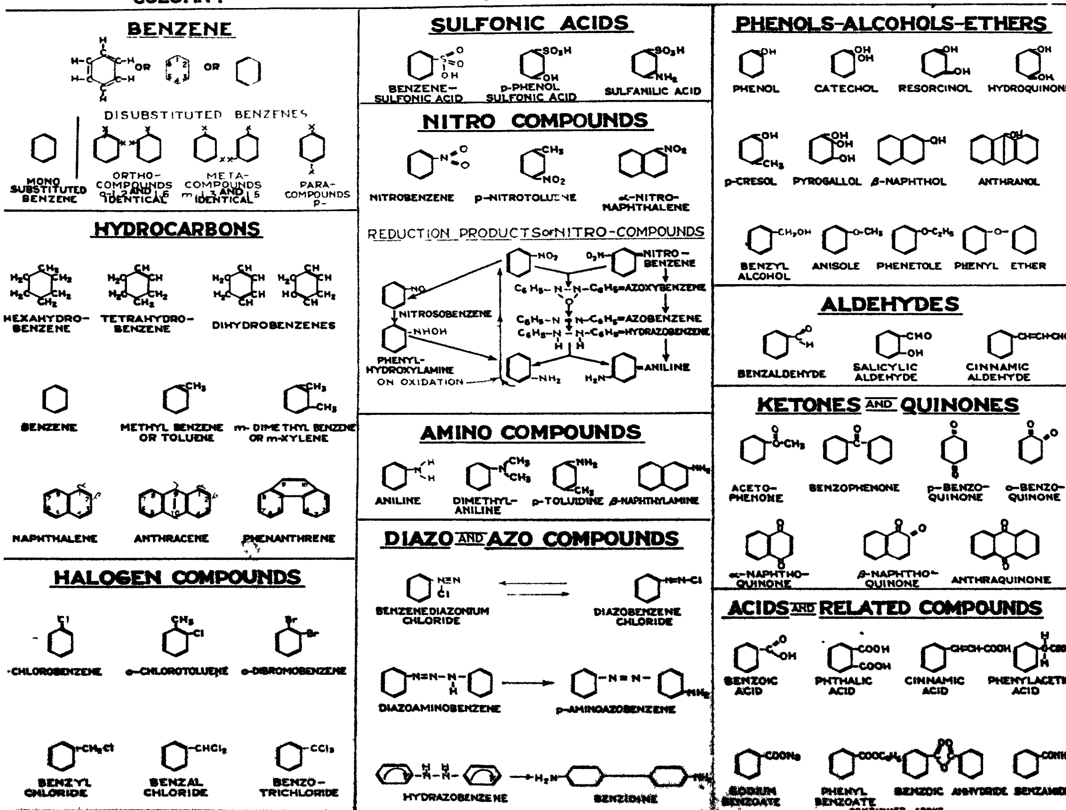


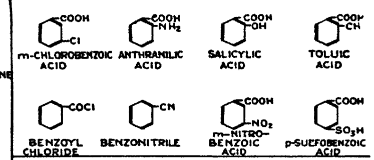
Compiled by

ALEXANDER LOWY

ORGANIC TYPE FORMULAS

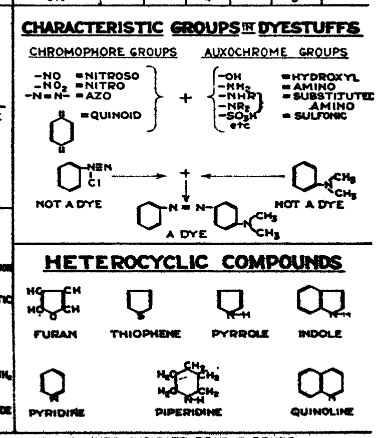
AROMATIC SERIES





RULES FOR SUBSTITUTION

PRESENT IN POSITION 1	POSITION ENTERED BY SUBSTITUENTS					
	ALKYL	Cl	Br	I	NO_2	SO_3H
ALKYL	4(2)	4(2)	4(2)	4(2)	4(2)(3)	4(2)(3)
Cl	4(2)	4(2)(3)	4(2)(3)	4	4(2)	4
Br	4(2)	4(2)(3)	4(2)(3)		4(2)	4
I		4	4	4	4(2)	4
OH	4(2)	4(2)	4(2)	4(2)	4(2)	4(2)
NH_2	4(2)	4(2)	4	4	4(2)	4(2)
NO_2	4(2)	3	3		3(2.4)	3(2 4)
SO_3H	4(2)		3		3(2 4)	3(4)
COOH	4(2)	3	3	3	3(2 4)	3(4)
CN			4		3	



LIGHT LINES INDICATE SINGLE BONDS

HEAVY LINES INDICATE DOUBLE BONDS

Compiled by ALEXANDER LOWY

Table 2

ORGANIC TYPE REACTIONS

KNOWN BY THEIR ORIGINATORS' NAMES

SABATIER-SENDERENS' REACTION

Passing vapors of substances to be reduced mixed with hydrogen over finely divided nickel or certain other metals (catalyzers) at an optimum temperature

$CO + 3H_2 \xrightarrow{\text{at } 250^\circ} CH_4 + H_2O$

$CO_2 + 4H_2 \xrightarrow{\text{at } 300^\circ} CH_4 + 2H_2O$

C_6H_6 (Benzene) $+ 3H_2 \xrightarrow{\text{at } 180^\circ} C_6H_{12}$ (hexahydrobenzene)

WURTZ' REACTION

Synthesis of Aliphatic hydrocarbons.

$R\boxed{X + 2Na + X}R \longrightarrow R\text{-}R + 2NaX$

Alkyl halide — Alkyl halide — Hydrocarbon

$CH_3\boxed{I + 2Na + I}C_2H_5 \rightarrow CH_3\text{-}C_2H_5 + 2NaI$

Methyl iodide — Ethyl iodide — Propane

WILLIAMSON'S REACTION

Synthesis of ethers. Action of alkoxides on alkyl halides.

$RO\boxed{Na + X}R \longrightarrow R\text{-}O\text{-}R + NaX$

Sodium Alcoholate — Ether

$C_2H_5O\boxed{Na + I}C_3H_7 \rightarrow C_2H_5\text{-}O\text{-}C_3H_7 + NaI$

Sodium Ethylate — Propyl iodide — Ethylpropyl ether

GRIGNARD'S REACTIONS

For preparation of hydrocarbons, secondary alcohols, tertiary alcohols, acids, etc.

$RX + Mg \longrightarrow Mg{<}^{R}_{X}$ (Magnesium {alkyl / aryl} halide)

Hydrocarbons: $Mg{<}^{\boxed{CH_3 \quad H}OH}_{I} \longrightarrow CH_4 + Mg{<}^{OH}_{I}$ (Basic Magnesium iodide)

Secondary Alcohols: $R\text{-}C{\lessgtr}^{O}_{H} + RMgX \rightarrow R\text{-}C{\lessgtr}^{R}_{H}\boxed{OMgX + H}OH \rightarrow R\text{-}C{\lessgtr}^{R}_{H}OH + Mg{<}^{OH}_{X}$

Aldehydes

Tertiary Alcohols: $R\text{-}C{\lessgtr}^{O}_{R} + RMgX \rightarrow R\text{-}C{\lessgtr}^{R}_{R}\boxed{OMgX + H}OH \rightarrow R\text{-}C{\lessgtr}^{R}_{R}OH + Mg{<}^{OH}_{X}$

Ketones

Acids: $RMgX + C{\lessgtr}^{O}_{O} \longrightarrow R\text{-}C{\lessgtr}^{O}\boxed{OMgX + H}OH \rightarrow R\text{-}C{\lessgtr}^{O}_{OH} + Mg{<}^{OH}_{X}$

HOFMANN'S REACTION

For preparation of primary amines from acid amides.

$RCONH_2 + O \longrightarrow RNH_2 + CO_2$

$CH_3CONH_2 + Br_2 + KOH \longrightarrow CH_3CONHBr + KBr + H_2O$

Acetamide — Acetbromamide

$CH_3CON\boxed{HBr + KOH} \longrightarrow KBr + H_2O + CH_3\text{-}C{\lessgtr}^{O}_{N} \xrightarrow{\text{Rearranges}} CH_3\text{-}N{=}C{=}O$

Methyl isocyanate

$CH_3\text{-}N{=}C{=}O + 2KOH \longrightarrow CH_3NH_2 + K_2CO_3$

Methylamine

MENDIUS' REACTION

For preparation of primary amines by reducing nitriles.

$CH_3\text{-}C{\equiv}N + 2H_2 \xrightarrow{\text{Na + Alcohol}} CH_3\text{-}C{\lessgtr}^{H}_{H}N{<}^{H}_{H}$

Acetonitrile — Ethyl Amine

HOFMANN'S CARBYLAMINE REACTION

Test for primary amines and preparation for carbylamines.

$C_2H_5\text{-}N{<}\boxed{^{H}_{H} + ^{Cl}_{Cl}}{>}C{<}^{Cl}_{H} + 2KOH \longrightarrow C_2H_5\text{-}N{=}C{<}\boxed{^{Cl}_{H} + KOH} \rightarrow C_2H_5\text{-}N{=}C + 3KCl + 3H_2O$

CLAISEN'S EXPLANATION OF THE ACETOACETIC ESTER SYNTHESIS

$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$

$CH_3\text{-}C{\lessgtr}^{O}_{OC_2H_5} + NaOC_2H_5 \longrightarrow CH_3\text{-}C{\equiv}^{ONa}_{OC_2H_5,\ OC_2H_5}$

$CH_3\text{-}C{\equiv}^{ONa}\boxed{^{OC_2H_5}_{OC_2H_5} + ^{H}_{H}}{>}CHCOOC_2H_5 \rightarrow CH_3\text{-}C{\lessgtr}^{ONa}{=}CHCOOC_2H_5 + 2C_2H_5OH$

Sodium acetoacetic ester

$CH_3\text{-}C{\lessgtr}^{ONa}{=}CHCOOC_2H_5 + CH_3COOH \longrightarrow CH_3\text{-}C{\lessgtr}^{OH}{=}CHCOOC_2H_5 + CH_3COONa$

Acetoacetic ester

Tautomeric forms. $CH_3\text{-}C{\lessgtr}^{OH}{=}CHCOOC_2H_5 \rightleftharpoons CH_3\text{-}C{\lessgtr}^{O}\text{-}CH_2COOC_2H_5$

Enolic — Ketonic

Ketonic Hydrolysis. $CH_3COCH_2\,CO\,OC_2H_5$ (H OH / H OH) $\xrightarrow[\text{Acids or Alkalies}]{\text{Dil Aqueous or Alc}} CH_3COCH_3 + CO_2 + C_2H_5OH$

Acid Hydrolysis: $CH_3\,CO\,CH_2\,CO\,OC_2H_5$ (HOH, HOH) $\xrightarrow[\text{Conc Aqueous KOH}]{\text{Conc Alc KOH}} CH_3COOH + CH_3COOH + C_2H_5OH$

FITTIG'S REACTION

For preparation of aromatic hydrocarbons.

$C_6H_5\boxed{X + 2Na + X}R \longrightarrow C_6H_5\text{-}R + 2NaX$

Aryl Halides — Alkyl or aryl halides — Hydrocarbons

$C_6H_5\boxed{Br + 2Na + Br}CH_3 \rightarrow C_6H_5\text{-}CH_3 + 2NaBr$

Bromobenzene — Methylbenzene

$C_6H_5\boxed{Br + 2Na + Br}C_6H_5 \rightarrow C_6H_5\text{-}C_6H_5 + 2NaBr$

Diphenyl

$C_6H_5\text{-}CH_2\boxed{Cl + 2Na + Cl}H_2C\text{-}C_6H_5 \longrightarrow$

Benzyl Chloride

$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}C_6H_5 + NaCl$

Dibenzyl

FRIEDEL-CRAFTS' REACTION

For preparation of aromatic hydrocarbons and ketones. Elimination of HX in presence of anhydrous $AlCl_3$. The H atom being linked to a carbon in a ring, while the X atom must be linked to a carbon not in a ring.

$C_6H_5\text{-}\boxed{H + X}\text{-}C_2H_5 \rightarrow C_6H_5\text{-}C_2H_5 + HX$

Ethyl Benzene

$CH_3C_6H_4\boxed{H + Cl}CH_3 \rightarrow CH_3\text{-}C_6H_4\text{-}CH_3 + HCl$

Xylene

$C_6H_5\boxed{H + Cl}H_2C\text{-}C_6H_5 \rightarrow C_6H_5CH_2C_6H_5 + HCl$

Diphenylmethane

$\begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\boxed{\begin{matrix} H & & Cl \\ H & + & Cl \\ H & & Cl \end{matrix}}{\gtrless}CH \rightarrow (C_6H_5)_3CH + 3HCl$

Triphenylmethane

$C_6H_5\boxed{H + Cl}OCCH_3 \rightarrow C_6H_5\text{-}CO\text{-}CH_3 + HCl$

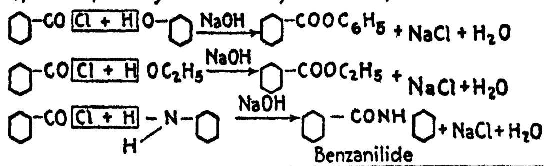
Acetophenone

Compiled by
ALEXANDER LOWY

Table 2 (Continued)

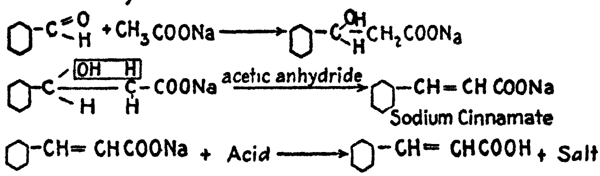
SCHOTTEN-BAUMANN'S REACTION

For preparation of esters and substituted amides. Consists in mixing acid chlorides with alcohols, phenols, primary or secondary amines in presence of a strong base (NaOH).



PERKIN'S REACTION

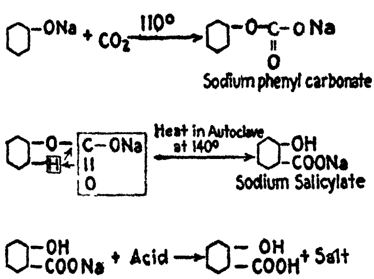
For preparation of unsaturated aromatic acids and derivatives. Consists in heating together a mixture of an aldehyde (either aliphatic or aromatic), the Na salt of a fatty acid and its anhydride.



Condensation always takes place at the carbon atom adjoining the COONa Group

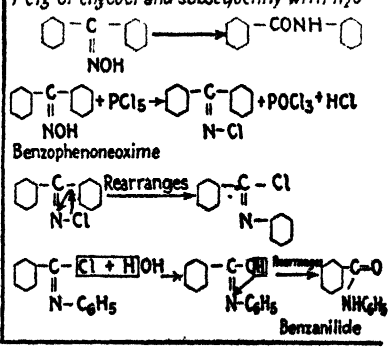
KOLBE-SCHMITT'S REACTION

For preparation of aromatic hydroxy (phenolic) acids. Action of CO_2 on phenolates.



BECKMANN'S REARRANGEMENT

Molecular transformation of Ketoximes to substituted amides when treated with PCl_5 or CH_3COCl and subsequently with H_2O



SKRAUP'S REACTION

For preparation of quinolines and derivatives. Consists in heating a mixture of aniline, glycerol, H_2SO_4 (dehydrating agent) and nitrobenzene (oxidizing agent).

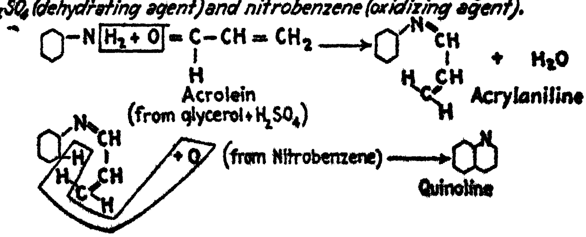
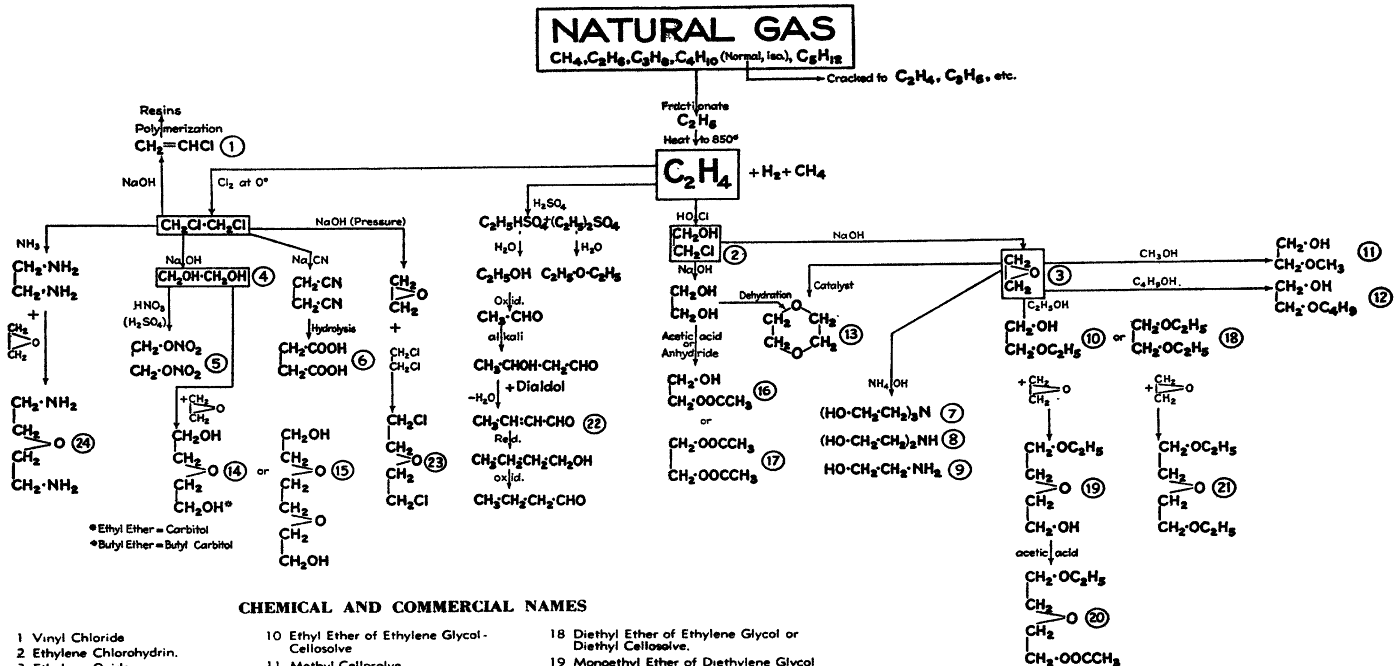


Table 3



CHEMICAL AND COMMERCIAL NAMES

1 Vinyl Chloride
2 Ethylene Chlorohydrin.
3 Ethylene Oxide.
4 Ethylene Glycol.
5 Ethylene Dinitrate - Glycol Dinitrate. –
6 Succinic Acid.
7 Triethanolamine.
8 Diethanolamine
9 Monoethanolamine.
10 Ethyl Ether of Ethylene Glycol - Cellosolve
11 Methyl Cellosolve
12 Butyl Cellosolve.
13 1,4-Dioxan.
14 Diethylene Glycol.
15 Triethylene Glycol.
16 Glycol Monoacetate.
17 Glycol Diacetate.
18 Diethyl Ether of Ethylene Glycol or Diethyl Cellosolve.
19 Monoethyl Ether of Diethylene Glycol or Carbitol.
20 Carbitol Acetate.
21 Diethyl Ether of Diethylene Glycol or Diethyl Carbitol.
22 Crotonaldehyde.
23 β,β' - Dichloroethyl Ether.
24 β,β' - Diaminoethyl Ether.

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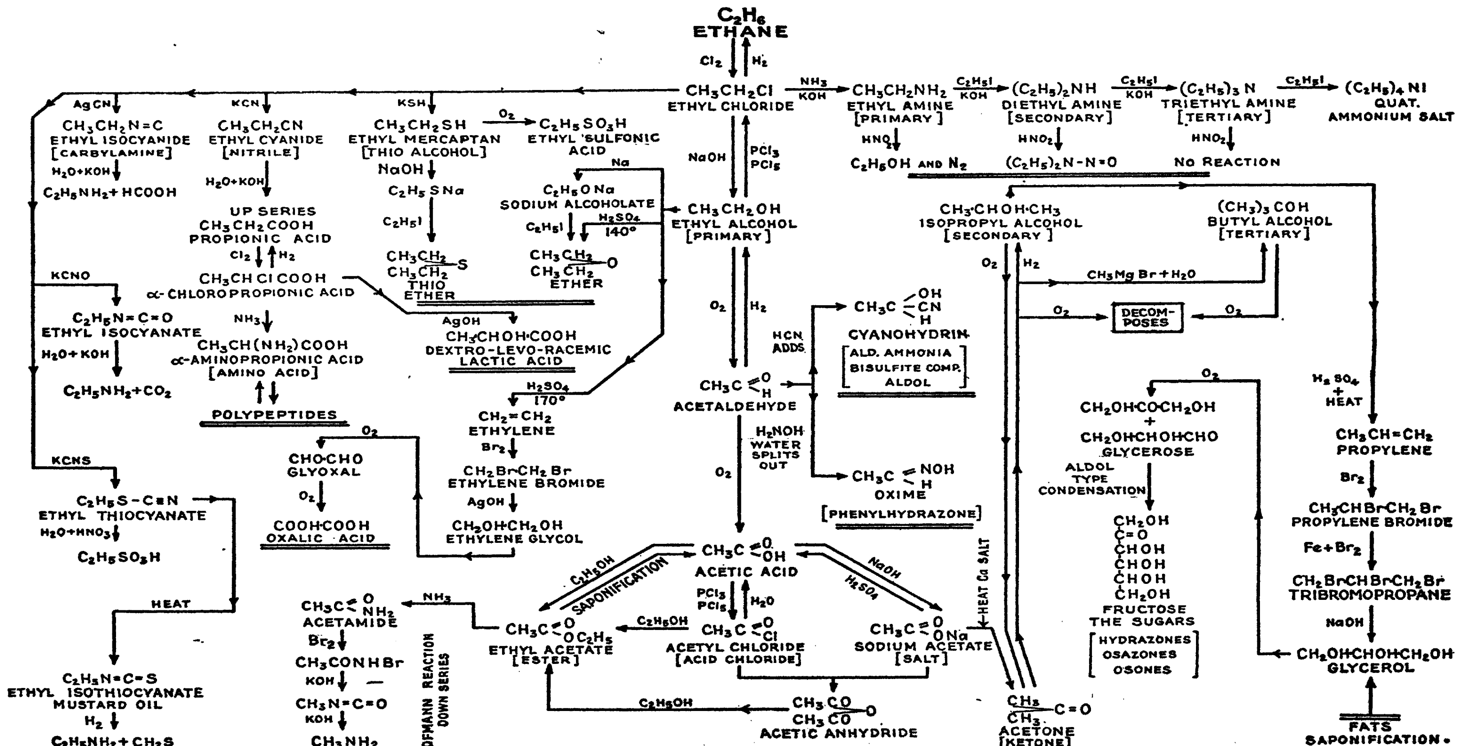
Table 4

ORGANIC CHEMICAL TRANSFORMATIONS

ALIPHATIC SERIES



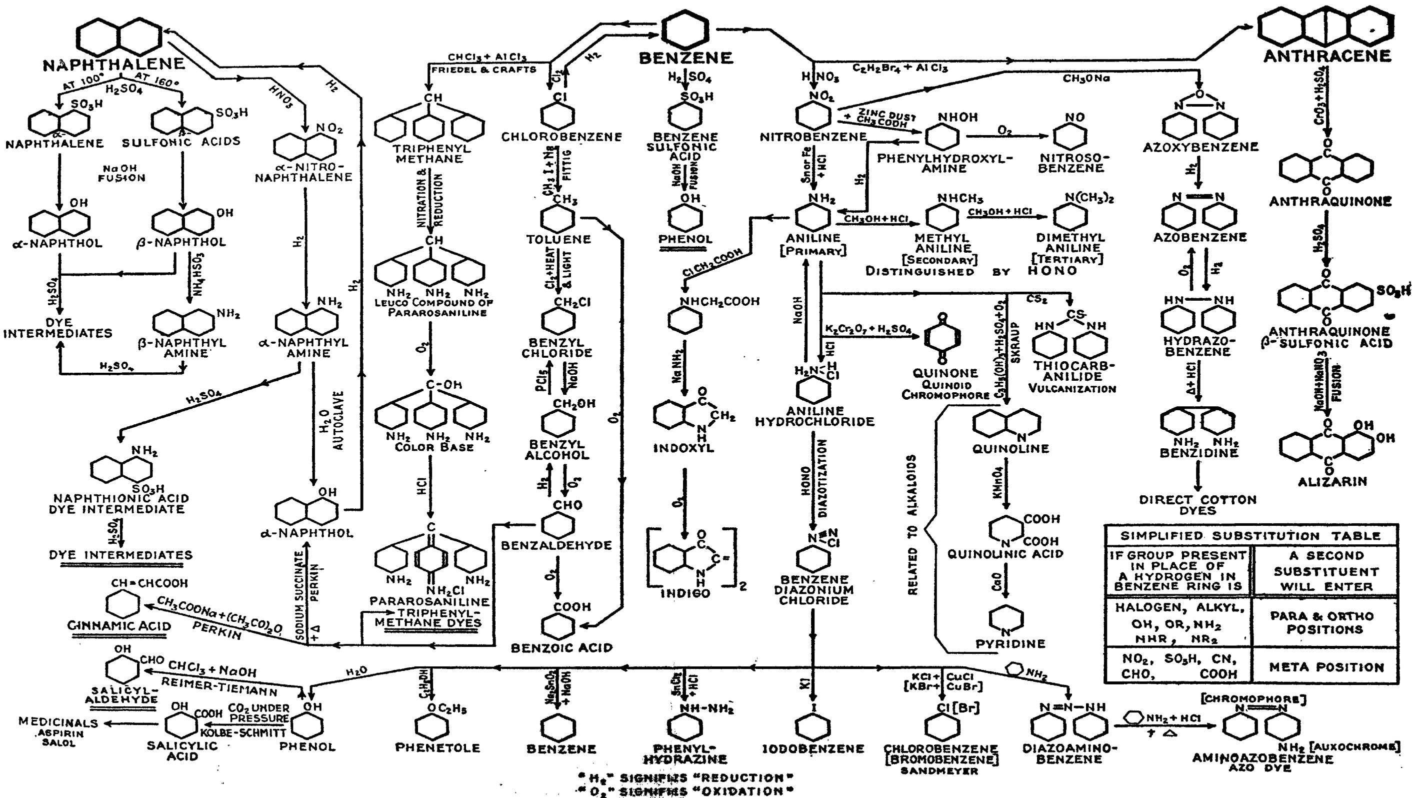
"H_2" SIGNIFIES "REDUCTION"
"O_2" SIGNIFIES "OXIDATION"

Compiled by

LUCIUS A. BIGELOW, Ph.D. and KURWIN R. BOYES

Table 5

ORGANIC CHEMICAL TRANSFORMATIONS
AROMATIC SERIES



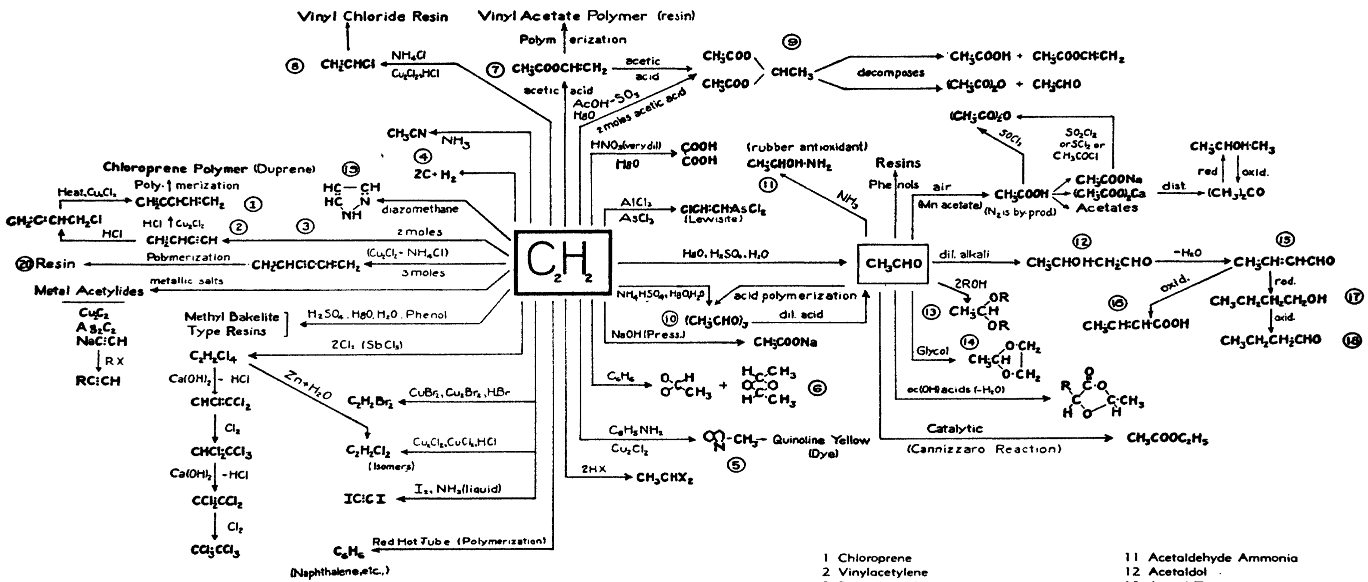
SIMPLIFIED SUBSTITUTION TABLE	
IF GROUP PRESENT IN PLACE OF A HYDROGEN IN BENZENE RING IS	A SECOND SUBSTITUENT WILL ENTER
HALOGEN, ALKYL, OH, OR, NH_2 NHR, NR_2	PARA & ORTHO POSITIONS
NO_2, SO_3H, CN, CHO, COOH	META POSITION

"H_2" SIGNIFIES "REDUCTION"
"O_2" SIGNIFIES "OXIDATION"

Compiled by
LUCIUS A. BIGELOW, Ph.D. and KURWIN R. BOYES

Table 6

CHART OF PRODUCTS DERIVED FROM ACETYLENE



1 Chloroprene
2 Vinylacetylene
3 Divinylacetylene
4 Acetylene Black
5 Quinaldine
6 Dimethyldihydroanthracene
7 Vinyl Acetate
8 Vinyl Chloride
9 Ethylidene Acetate
10 Paraldehyde
11 Acetaldehyde Ammonia
12 Acetaldol
13 Acetal Type
14 Ethylidene Ether of Glycol
15 Crotonaldehyde
16 Crotonic Acid
17 n-Butanol
18 Butyraldehyde
19 Pyrazole
20 Synthetic Drying Oil (S.D.O.)

Compiled by
ALEXANDER LOWY

Table 7

COAL PRODUCTS CHART

Compiled by
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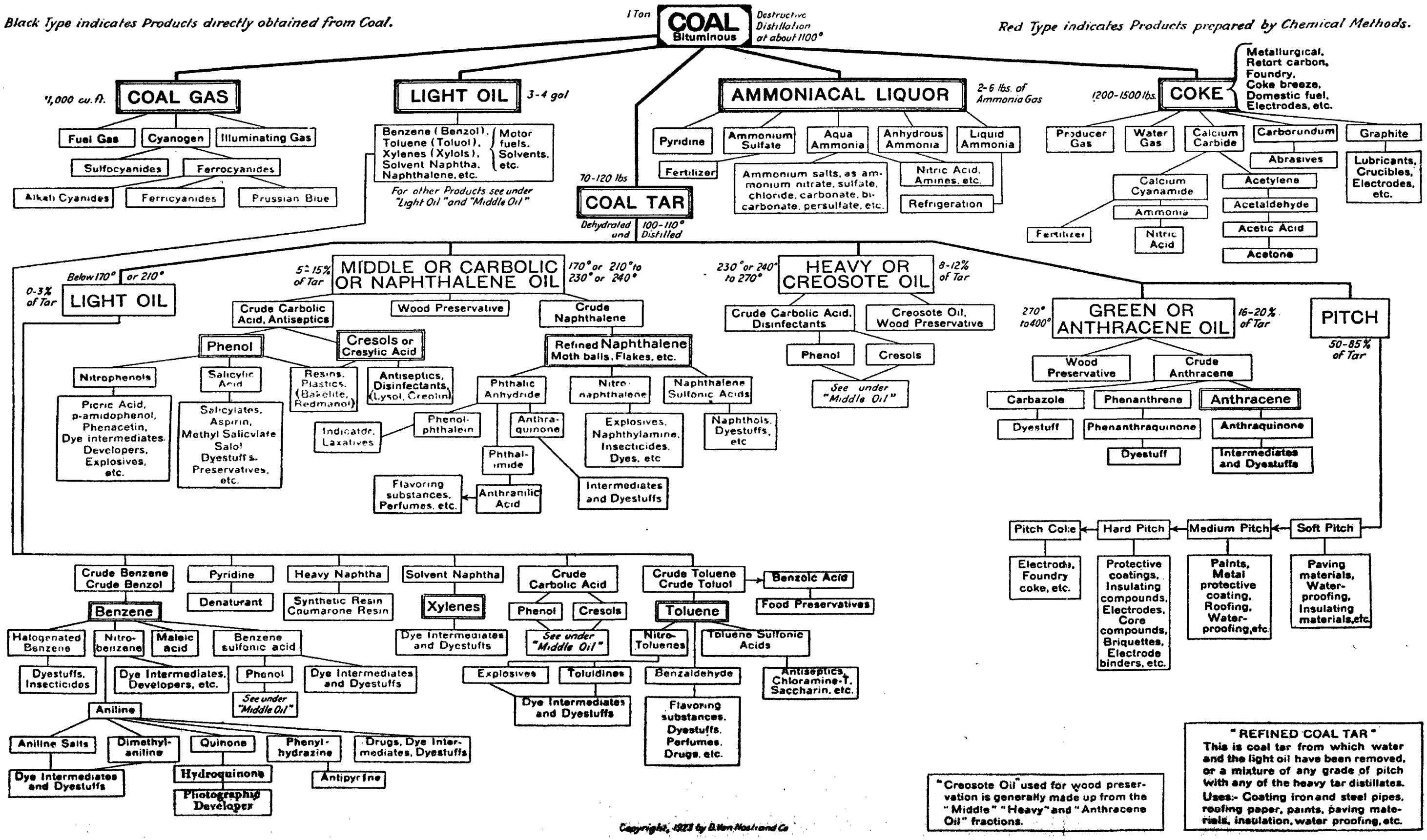
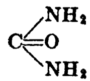


TABLE 8—ALIPHATIC COMPOUNDS

Name	*Formula*	*Preparation*	*Uses*
1. Acetaldehyde **Aldehyde**	$CH_3 \cdot CHO$	Passing acetylene into dilute H_2SO_4 in presence of a catalyst (Hg salts)	Paraldehyde, organic syntheses, preparation of rubber accelerators, phenolic resins, synthetic drugs, synthetic acetic acid (see C_2H_2 chart)
2. Acetaldehyde ammonia **Aldehyde Ammonia**	$CH_3 \cdot CHOH \cdot NH_2$	Action of ammonia on acetaldehyde	Rubber accelerator
3. Acetamide	$CH_3 \cdot CO \cdot NH_2$	Action of NH_3 on ethyl acetate or heating ammonium acetate under pressure	Solvent, plasticizer, hygroscopic agent, organic syntheses, soldering flux
4. **Acetic acid**	$CH_3 \cdot COOH$	Distillation of calcium acetate with HCl or H_2SO_4; oxidation of ethyl alcohol; $C_2H_2 \rightarrow CH_3 \cdot CHO \rightarrow CH_3 \cdot COOH$	Dyes, white lead, esters, metallic acetates, cellulose acetate, textile industry, organic syntheses, etc.
5. Acetic anhydride	$(CH_3 \cdot CO)_2O$	Heating ethylidene acetate or action of acetyl chloride and sodium acetate	Acetylating agent, organic syntheses
6. Acetyl chloride	$CH_3 \cdot COCl$	Action of SO_2Cl_2 on sodium acetate	Acetylating agent, organic syntheses
7. **Acetylene**	C_2H_2	Action of H_2O on CaC_2 (see Chapter 56)	Welding, steel cutting, acetaldehyde, organic syntheses, illumination (see chart) (see Chapters 31, p. 1215, and 19, p. 760)
8. **Adipic acid**	$(CH_2)_4 \begin{cases} COOH \\ COOH \end{cases}$	Oxidation of hexahydrophenol	Resins, organic syntheses (see Chapter 31)
9. Amyl acetate	$CH_3 \cdot COOC_5H_{11}$	Esterification of acetic acid and amyl alcohol	Solvent, lacquer compositions, flavors (see Chapter 30)
10. Amyl alcohol	$C_5H_{11}OH$	Refined from fusel oil or synthesized from pentane— $C_5H_{12} \rightarrow C_5H_{11}Cl \rightarrow C_5H_{11}OH$ (see Chapter 30)	Amyl acetate and other esters, solvent flotation agent (see Chapters 24, p. 919, 30, p. 1176)

11. **Amylamines**	mono—$C_5H_{11}\cdot NH_2$ di—$(C_5H_{11})_2NH$ tri—$(C_5H_{11})_3N$	Action of NH_3 on $C_5H_{11}OH$	Salts, soaps, solvents, organic syntheses
12. **Amyl butyrate**	$C_3H_7\cdot COOC_5H_{11}$	Esterification of butyric acid and amyl alcohol	Solvent, flavors
13. **Amyl propionate**	$C_2H_5\cdot COOC_5H_{11}$	Esterification of propionic acid and amyl alcohol	Solvent, flavors
14. **Butane**	C_4H_{10}	Separated from natural gas	Fuel, refrigerant, low boiling solvent, organic syntheses
15. *n*-**Butanol**	C_4H_9OH	Fermentation of corn by the Weizmann process or hydrogenation of crotonaldehyde	Esters, organic syntheses, solvent and vehicle in the varnish, paint and pyroxylin industries (see Chapter 30)
16. **Butyl acetate**	$CH_3\cdot COOC_4H_9$	Esterification of acetic acid and butyl alcohol	Solvent for nitrocellulose, flavors (see Chapter 30)
17. **Butyl alcohol (secondary)**	$CH_3\cdot CHOH\cdot CH_2\cdot CH_3$	Butylene is reacted with H_2SO_4. The resulting isobutyl hydrogen sulfate is hydrolyzed	Lacquers and lacquer thinners, esters, organic syntheses
18. **Butyl lactate**	$CH_3\cdot CHOH\cdot COOC_4H_9$	Esterification of lactic acid and butyl alcohol	Solvent, flavors
19. **Butyl propionate**	$C_2H_5\cdot COOC_4H_9$	Esterification of propionic acid and butyl alcohol	Solvent for nitrocellulose
20. **Butyl stearate**	$C_{17}H_{35}\cdot COOC_4H_9$	Esterification of stearic acid and butyl alcohol	Plasticizer, cosmetics
21. **Butyraldehyde** **Butalyde**	$C_3H_7\cdot CHO$	Oxidation of n-butanol	Rubber accelerator, butyric acid, organic syntheses (see Chapter 31)
22. **Calcium acetate** **Acetate of lime**	$(CH_3\cdot COO)_2Ca$	Neutralization of acetic acid of pyroligneous acid with $Ca(OH)_2$	Acetone, acetic acid, mordant in dyeing and printing textiles

TABLE 8—ALIPHATIC COMPOUNDS—*Continued*

Name	*Formula*	*Preparation*	*Uses*
23. Carbamide **Urea**		NH_3 and CO_2 in presence of catalysts form ammonium carbamate. This is heated in an autoclave at 150° and yields urea and H_2O; hydrolysis of cyanamide under pressure	Synthetic resins (glass substitute), manufacture of rubber accelerators, organic syntheses, fertilizers (see Chapters 31, p. 1211)
24. Carbon disulfide	CS_2	Heating sulfur and carbon in an electric furnace (see Chapter 12, p. 490)	Solvent, organic syntheses, rayon, insecticide, CCl_4 (see Chapter 38, p. 1450)
25. Carbon tetrachloride	CCl_4	Action of Cl_2 on carbon disulfide in presence of catalyst or chlorination of methane of natural gas (see Chapter 11, p. 467)	Dry cleaning, fire extinguishers, solvent (see Chapter 11, p. 469)
26. Carbonyl chloride **Phosgene**	$COCl_2$	Passing Cl_2 and CO over charcoal (see Chapter 33, p. 1269)	Dyes, war gas, organic syntheses (see Chapters 33, p. 1270, 11, p. 465)
27. Cellulose	$(C_6H_{10}O_5)_x$	Derived from the cell walls of plants, the main source being cotton, wood, etc.	Cellulose acetate, nitrocelluloses, ethyl cellulose, rayon, paper, textiles, etc.
28. Cellulose acetates	Triacetate —$C_{12}H_{16}O_8$ Tetracetate—$C_{14}H_{18}O_9$ Pentacetate—$C_{16}H_{20}O_{10}$	Acetylation of cellulose with acetic anhydride (see Chapter 31, p. 1203)	Rayon, non-flammable photographic and motion picture films, lacquers and varnishes, non-shatterable glass (see Chapter 31, p. 1204)
29. Cellulose ethyl ethers **Ethyl cellulose**	Various percentages of ethoxy groups in cellulose	Action of ethyl chloride on soda cellulose	Transparent films, paints, varnishes, paper coating, artificial silk
30. Cellulose nitrates **Nitrocellulose**	Mononitrate—$C_6H_9O_4(NO_3)$ Dinitrate —$C_6H_8O_3(NO_3)_2$ etc.	Nitration of cellulose with mixed acid (see Chapters 38, p. 1452, 32, p. 1233)	Explosives, production of collodion, celluloid, lacquers, etc. (see Chapters 32, p. 1235, 31, p. 1202)

31. **Cellulose xanthate**	$C(=S)(SNa)(O\cdot\text{Cellulose})$	Action of CS_2 and NaOH solution on cellulose (see Chapter 38, p. 1451)	Rayon (see Chapter 38, p. 1450)
32. **Chloral hydrate**	$CCl_3\cdot CHO\cdot H_2O$	Chlorination of ethyl alcohol	Organic syntheses, as hypnotic and sedative in medicine
33. Chloroacetic acid	$CH_2Cl\cdot COOH$	Passing Cl_2 into boiling glacial acetic acid containing some I, S or P (catalyst)	Organic syntheses, manufacture of indigo, in medicine
34. Chloroacetyl chloride	$CH_2Cl\cdot COCl$	Chlorination of acetyl chloride	Organic syntheses
35. **Chloroprene**	$CH_2 : CCl\cdot CH : CH_2$	Addition of HCl to Vinyl acetylene	Polymerizes to synthetic rubber-like substance (Neoprene) (see Chapter 39, p. 1486)
36. **Chloropicrin Nitrochloroform**	$CCl_3\cdot NO_2$	Action of bleaching powder on picric acid	Fumigant, insecticide, poison gas (see Chapter 33, p. 1261)
37. **Citric acid**	$HO\cdot C(COOH)(CH_2\cdot COOH)_2$	Extracted from lemons or by the fermentation of glucose or sucrose by certain mold or fungi	Calico printing, medicine, dyeing, blue printing, beverages, citrates
38. **Crotonaldehyde**	$CH_3\cdot CH : CH\cdot CHO$	Elimination of 1 mol of water from aldol	Quinaldine, preparation of rubber accelerators, organic syntheses, warming agent
39. Cyanamide (calcium salt)	$CN\cdot NH_2$ $CaCN_2$	$CaCN_2$ is produced by heating CaC_2 to about 1000° and passing N_2 into it. Cyanamide is prepared by the action of NH_3 on $CN\cdot Cl$	Fertilizer, syntheses
40. Dextrin	$(C_6H_{10}O_5)_x$	Hydrolysis of starch	Adhesives, textile printing, sizing paper, confectionery

TABLE 8—ALIPHATIC COMPOUNDS—*Continued*

Name	*Formula*	*Preparation*	*Uses*
41. Dichlorodifluoromethane	CCl_2F_2	$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} 3CCl_2F_2 + 2SbCl_3$	Refrigerant
42. Dichloroethyl ether **Chlorex**	$(CH_2Cl\cdot CH_2)_2O$	Dehydration of 2 mols of ethylene chlorohydrin (see Chapter 11, p. 473)	Solvent, degreasing textiles, syntheses, purification of lubricating oils (see Chapter 14, p. 571)
43. Dicyandiamide	$NH{=}C(NH_2)NH\cdot CN$	Heating cyanamide to 150°	Fertilizers, organic syntheses
44. Diethylene glycol	$CH_2\cdot OH$ | CH_2 ⟩O CH_2 | CH_2OH	Hydrolysis of β, β'—dichlorethyl ether or the combination of ethylene oxide with ethylene glycol	Solvent for nitrocellulose, gums, resins, in manufacture of composition cork, penetrant in dyeing (see Chapter 31)
45. Diethylene glycol monobutyl ether **Butyl carbitol**	$CH_2\cdot OH$ | CH_2 ⟩O CH_2 | $CH_2\cdot OC_4H_9$	Action of ethylene oxide on ethylene glycol monobutyl ether	Baking lacquers, nitrocellulose solvent, as lubricant in textile industry
46. Diethylene glycol monoethyl ether **Carbitol**	$CH_2\cdot OH$ | CH_2 ⟩O CH_2 | $CH_2\cdot OC_2H_5$	Action of ethylene oxide on ethylene glycol monoethyl ether	Baking lacquers, nitrocellulose solvent, in textile industry as lubricant
47. Diethylene glycol monomethyl ether **Methyl carbitol**	$CH_2OH\cdot CH_2{-}O{-}CH_2\cdot CH_2\cdot OCH_3$	Action of ethylene oxide on ethylene glycol monomethyl ether	Preparation of methyl carbitol acetate, solvent (see carbitol)

48. Diethyl oxalate	$COOC_2H_5$ | $COOC_2H_5$	Esterification of oxalic acid and ethyl alcohol	Solvent for nitrocellulose, organic syntheses
49. Diethyl sulfate	$(C_2H_5)_2SO_4$	Action of conc. H_2SO_4 on ethyl alcohol or $C_2H_4 + H_2SO_4$	Ethylating agent, organic syntheses (see Chapter 31, p. 1205)
50. Dimethylamine	$(CH_3)_2NH$	Decomposition of boiling p-nitrosodimethylaniline hydrochloride by means of NaOH solution	Organic syntheses, preparation of rubber accelerators, gasoline stabilizer
51. Dimethyl ketone **Acetone**	$CH_3 \cdot CO \cdot CH_3$	Distillation of calcium acetate, the fermentation of corn by the Weizmann process and the dehydrogenation of isopropyl alcohol	Solvent, acetylene gas absorbent, alcohol denaturant, celluloid, chloroform, plastics, dyes, varnish, organic syntheses
52. Dimethyl sulfate	$(CH_3)_2SO_4$	CH_3OH and fuming H_2SO_4 distilled in vacuo	Methylating agent for amines and phenols
53. Dipropyl ketone **Butyrone**	$C_3H_7 \cdot CO \cdot C_3H_7$	Dry distillation of calcium butyrate	Solvent for nitrocellulose lacquers, rosin, gums, waxes and synthetic resins; organic syntheses
54. Ethane	C_2H_6	Separated from natural gas	Organic syntheses, fuel
55. Ether, ethyl ether **Sulfuric ether**	$C_2H_5 \cdot O \cdot C_2H_5$	Action H_2SO_4 on ethyl alcohol and subsequent distillation of product formed with additional ethyl alcohol at 130°, or $2C_2H_5OH—H_2O$ by catalysis	Solvent, fuel, anesthetic, organic syntheses
56. Ethyl acetate **Acetic ether**	$CH_3 \cdot COOC_2H_5$	Esterification of acetic acid and ethyl alcohol	Solvent, flavors, lacquers
57. Ethyl acetoacetate **Acetoacetic ester**	$CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5$	Condensation of C_2H_5OH with diketene or the action of sodium ethylate on dry ethyl acetate	Solvent, flavors, pyrazolone dye syntheses

TABLE 8—ALIPHATIC COMPOUNDS—*Continued*

Name	*Formula*	*Preparation*	*Uses*
58. Ethyl alcohol **Grain alcohol** **Cologne spirit** **Wine spirit**	C_2H_5OH	Fermentation of sugars derived from starch, molasses and the Weizmann fermentation method (butanol, acetone and ethyl alcohol in the ratio of 6:3:1); $C_2H_4 + H_2O$ in presence of H_2SO_4 (see Chapter 30)	Solvent, perfumery, medicine, flavors, fuel, pharmacy, organic syntheses, anhydrous ethyl alcohol is used as solvent for lacquers (see Chapter 30)
59. Ethyl alcohol (denatured)		Addition of denaturants such as methanol, pyridine, benzene, acetone, etc., to grain alcohol	Solvent for industrial purposes, medicated alcohols, fuel, etc.
60. Ethyl butyrate	$C_3H_7 \cdot COOC_2H_5$	Esterification of butyric acid and ethyl alcohol	Solvent, flavors
61. Ethyl chloride	C_2H_5Cl	Addition of HCl to ethylene (see Chapter 11, p. 472)	Anesthetic, refrigeration, organic syntheses, lead tetraethyl
62. Ethylene	$CH_2 : CH_2$	Pyrolysis of ethane, propane, etc.	Organic syntheses, illuminant, anesthetic, artificial ripening of fruits
63. Ethylene dibromide	$CH_2Br \cdot CH_2Br$	Action of Br_2 on ethylene	Added to "ethyl gas" to vaporize the $PbBr_2$, organic syntheses
64. Ethylene chlorohydrin	$CH_2Cl \cdot CH_2OH$	Action of HOCl on ethylene (see Chapter 11, p. 473)	Organic syntheses, early sprouting of plants, manufacture of ethylene glycol (see chart)
65. Ethylenediamine	$\begin{array}{ll} CH_2 - & CH_2 \\ \vert & \vert \\ NH_2 & NH_2 \end{array}$	Ethylene dichloride and ammonia	Preparation of medicinals, dyes, rubber accelerators, organic syntheses
66. Ethylene dichloride	$CH_2Cl \cdot CH_2Cl$	Action of Cl_2 on ethylene (see Chapter 11, p. 472)	Solvent, fumigant (see chart)
67. Ethylene dinitrate	$CH_2ONO_2 \cdot CH_2ONO_2$	Action of mixed acid on glycol	Low-freezing dynamite

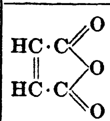
68. Ethylene glycol **Glycol**	$HOCH_2 \cdot CH_2OH$	Hydrolysis of ethylene chlorohydrin with $NaHCO_3$ or the action of H_2O on ethylene oxide in presence of a catalyst (see Chapter 30)	Ethers of glycol, ethylene dinitrate, "anti-freeze" compounds, cosmetics, solvent, food preservative (see chart)
69. Ethylene glycol monobutyl ether **Butyl cellosolve**	$CH_2—OC_4H_9$ $\vert$ $CH_2—OH$	Action of ethylene oxide on butanol	Solvent for nitrocellulose, gums, and resins
70. Ethylene glycol monoethyl ether **Cellosolve**	$CH_2—OC_2H_5$ $\vert$ $CH_2—OH$	Action of ethylene oxide on ethyl alcohol	Solvent for nitrocellulose, dye penetrant
71. Ethylene glycol monomethyl ether **Methyl cellosolve**	$CH_2—OCH_3$ $\vert$ $CH_2—OH$	Action of ethylene oxide on methanol	Solvent for cellulose acetate, nitrocellulose, gums, and resins
72. Ethylene glycol monoethyl ether monoacetate **Cellosolve acetate**	$CH_2—OC_2H_5$ $\vert$ $CH_2—O \cdot OCCH_3$	Acetylation of ethylene glycol monoethyl ether with glacial acetic acid	Lacquers, nitrocellulose solvent
73. Ethylene oxide	$O\langle{}^{CH_2}_{CH_2}$	Elimination of HCl by means of alkali from ethylene chlorohydrin	Organic syntheses, fumigant (see chart)
74. Ethyl formate	$H \cdot COOC_2H_5$	Esterification of formic acid and ethyl alcohol	Fumigant, larvacide, flavors, synthesis of vitamin B_1 (see Chapter 34, p. 1300)
75. 2-Ethyl hexanol **Octyl alcohol**	$C_4H_9 \cdot CH \cdot CH_2OH$ $\vert$ C_2H_5	Dehydration and hydrogenation of the aldol type condensation product from 2 moles of n-butyraldehyde	Solvent for nitrocellulose, gums, waxes, resins, fats; esters, anti-foaming agent
76. Ethylidene diacetate	$CH_3 \cdot CH\langle{}^{OOC \cdot CH_3}_{OOC \cdot CH_3}$	Passing C_2H_2 into glacial acetic acid in presence of $HgSO_4$ as catalyst	Preparation of acetic anhydride and acetaldehyde (see Chapter 31, p. 1203)
77. Ethyl lactate	$CH_3 \cdot CHOH \cdot COOC_2H_5$	Esterification of lactic acid and ethyl alcohol	Solvent for nitrocellulose, cellulose acetate, and resins

TABLE 8—ALIPHATIC COMPOUNDS—*Continued*

Name	*Formula*	*Preparation*	*Uses*
78. Ethyl methyl ketone **Methyl acetone**	$CH_3 \cdot CO \cdot C_2H_5$	By-product in the fermentation process for the manufacture of acetone	Solvent, organic syntheses
79. Ethyl mercury chloride **Ceresan**	$C_2H_5 \cdot HgCl$	Reaction of mercury diethyl and $HgCl_2$	Fungicide
80. Ethyl nitrite	C_2H_5ONO	Action of HONO on ethyl alcohol	Medicine, organic syntheses, solvent
81. Formaldehyde **Formalin is 35 to 40% solution in water**	$H \cdot CHO$	Passing a mixture of methanol vapor and air over hot copper	Organic syntheses, synthetic resins, photography, disinfectant, preservative, etc., paraformaldehyde, dyestuffs
82. **Formic acid**	$H \cdot COOH$	CO at 6 or 7 atmospheres pressure passed over powdered NaOH at 150° to 170° yields HCOONa. HCOONa + acid yields HCOOH	Formates, esters, organic syntheses, dyeing, tanning, CO preparation, etc.
83. **Fumaric acid**	$HOOC \cdot CH : CH \cdot COOH$	Heating or treatment with traces of reagents converts maleic acid to fumaric acid.	Salts, esters, organic syntheses
84. **Gluconic acid**	$CH_2OH \cdot (CHOH)_4 \cdot COOH$	Oxidation of glucose electrolytically or with HOBr	Vegetable tanning of leather, metal polish, calcium gluconate in calcium therapy
85. **Glucose** **Grape sugar** **Corn sugar**	$C_6H_{12}O_6$	Hydrolysis of starch-containing substances by means of dilute mineral acids	Confectionery, ethyl alcohol, food, sweetening agent, diluent for dyes
86. **Glycerol** **Glycerin**	$HOCH_2 \cdot CHOH \cdot CH_2OH$	Hydrolysis of fats and oils, chlorination of propene (see Chapters 14, p. 575, 42, 11, p. 474)	Nitroglycerin, medicine, cosmetics, solvent, food preservative, inks, glycero-phosphates, synthetic plastics, "anti-freeze," etc. (see Chapters 32, p. 1233, and 31, p. 1214)

87. Glyceryl triacetate **Triacetin**	$(CH_3COO)_3C_3H_5$	Action of acetic anhydride on glycerol	Plasticizer for cellulose esters
88. Glycerophosphoric acid	$C_3H_5(OH)_2O \cdot PO_3H_2$	Action of glycerol on phosphoric acid	Nerve tonic in medicine, glycerophosphates
89. Glyceryl nitrate **Nitroglycerin**	$CH_2—ONO_2$ / $CH—ONO_2$ / $CH_2—ONO_2$	Action of mixed acid ($HNO_3 + H_2SO_4$) on glycerol	Explosives, medicine
90. Hexachlorethane	$CCl_3 \cdot CCl_3$	Addition of Cl_2 to C_2Cl_4 or chlorination of $C_2H_2Cl_4$	Fireworks, smoke devices
91. Hexamethylenetetramine **Hexamine, formin, urotropine**	$(CH_2)_6N_4$	Action of ammonia on formaldehyde	Rubber accelerator, medicine, synthetic resins (see Chapters 39, p. 1465, 31, p. 1213)
92. *n*-Hexanol	$CH_3 \cdot (CH_2)_4 \cdot CH_2OH$	Condensation of butyraldehyde with acetaldehyde and reduction of the resultant product	Organic syntheses to introduce the hexyl group
93. Hydrocyanic acid **Prussic acid**	HCN	Action of H_2SO_4 on NaCN	General fumigation, insecticides, military poison gas, stimulant in medicine (see Chapter 33, p. 1261)
94. 2-Hydroxy-4-butanal **Aldol acetaldol**	$CH_3 \cdot CHOH \cdot CH_2 \cdot CHO$	Action of dilute alkali on acetaldehyde	Preparation of rubber accelerator, crotonaldehyde
95. 4-Hydroxy-2-keto-4-methylpentane **Diacetone alcohol, Diacetone**	$CH_3 \cdot CO \cdot CH_2 \cdot C(CH_3)(OH) \cdot CH_3$	Condensation of 2 molecules of acetone by NaOH at low temperature	Paint and varnish remover, solvent for cellulose nitrate and cellulose acetate
96. α-Hydroxypropionic acid **Lactic acid**	$CH_3—C(H)(COOH)(OH)$	Fermentation of starch, milk, sugar or hydrolysis of α-hydroxypropionitrile	Salts of lactic acid, dyeing and calico printing, leather and textile industry, medicine, esters, etc.

TABLE 8—ALIPHATIC COMPOUNDS—*Continued*

Name	*Formula*	*Preparation*	*Uses*
97. Hydroxy succinic acid **Malic acid**	OH — $CH{-}COOH$ — $CH_2{-}COOH$	Hydration of maleic acid	Foodstuffs, synthetic fruity acid
98. Isobutyl alcohol	$(CH_3)_2C(H){-}CH_2OH$	Fractionation of fusel oil	Esters, organic syntheses
99. Isopropyl acetate	$CH_3 \cdot COOC_3H_7(i)$	Esterification of acetic acid and isopropyl alcohol	Solvent, flavors
100. Isopropyl alcohol	$CH_3 \cdot CHOH \cdot CH_3$	Reduction of acetone or hydrolysis of isopropyl acid sulfate	Solvent, organic syntheses, esters, rubbing alcohol (see Chapter 30)
101. Isopropyl ether	$(i)\ C_3H_7{-}O{-}C_3H_7(i)$	Dehydration of 2 moles of isopropyl alcohol	Solvent for animal, vegetable and mineral oils, fats, waxes, resins; used in many cases instead of ethyl ether
102. **Lactose** **Milk sugar**	$C_{12}H_{22}O_{11} \cdot H_2O$	Separated from milk	Food, confectionery, medicine
103. Lead tetraethyl	$Pb(C_2H_5)_4$	Action of ethyl chloride on lead sodium amalgam	"Anti-knock" compound (see Chapter 14, p. 532)
104. **Maleic acid** **Toxilic acid**	$HOOC \cdot CH : CH \cdot COOH$	Catalytic (air) oxidation of benzene vapor	Organic syntheses, assistant for dyeing and printing textiles, resins, malic acid, succinic acid
105. **Maleic anhydride**		Catalytic (air) oxidation of benzene vapor	Maleic acid, esters, alkyd resins (see Chapter 31, p. 1214)

106. **Mannitol**	$CH_2OH \cdot (CHOH)_4 \cdot CH_2OH$	Electrolytic reduction of glucose	Resins, nitromannitol, oxidation inhibitor, printing pastes, organic syntheses
107. Mercuric fulminate	$(CNO)_2Hg$	Action of strong nitric acid on Hg and alcohol	Detonators for explosives
108. **Mesityl oxide**	$(CH_3)_2C : CH \cdot CO \cdot CH_3$	Dehydration of diacetone alcohol	Organic syntheses, solvent
109. Methane **Marsh gas**	CH_4	Main constituent of natural gas	Fuel, carbon tetrachloride
110. Methanol **Columbian spirit** **Methyl alcohol** **Wood alcohol**	CH_3OH	Destructive distillation of wood; combination of $CO + 2H_2$ under pressure in the presence of a catalyst (ZnO); also from $CO_2 + 3H_2$ (see Chapter 30)	Formaldehyde, solvent, denaturant for ethyl alcohol, dimethylaniline, organic syntheses, etc. (see Chapter 30)
111. Methyl acetate	$CH_3 \cdot COO \cdot CH_3$	Esterification of acetic acid and methyl alcohol	Solvent for cellulose esters and ethers
112. Methyl chloride **Artic**	CH_3Cl	Trimethylamine from the residues of beet root molasses is treated with HCl. Thermal decomposition of $(CH_3)_3N \cdot HCl$; action of HCl on CH_3OH	Refrigerant, methylating agent (see Chapter 11, p. 469)
113. Methyl methacrylate	$CH_2{=}C(CH_3){-}COOCH_3$	Esterification of methacrylic acid with methanol	Polymerizes to colorless resins, film for laminated glass, etc. (see Chapter 31, p. 1216)
114. Nitromethane Nitroethane Nitropropanes	$CH_3 \cdot NO_2$ $C_2H_5 \cdot NO_2$ $C_3H_7 \cdot NO_2$	Vapor phase nitration of hydrocarbons	Organic syntheses
115. Oleic acid **Red oil**	$CH_3(CH_2)_7CH{=}CH(CH_2)_7 \cdot COOH$	Hydrolysis of oils and fats	Soap stock, greases, dry cleaning, emulsification, flotation agent (see Chapter 24, p. 919)
116. **Oxalic acid**	$(COOH)_2 \cdot 2H_2O$	Heating sawdust with NaOH at 240° or by heating sodium formate	Salts and esters, dyestuffs, bleaching agent, metal polish, tanning, etc.

TABLE 8—ALIPHATIC COMPOUNDS—*Continued*

Name	*Formula*	*Preparation*	*Uses*
117. **Paraformaldehyde, trioxymethylene** **Paraform**	$(H \cdot CHO)_x$	Evaporation of formaldehyde solution with H_2SO_4	Disinfectant, organic syntheses, fungicide
118. **Paraldehyde**	$(CH_3 \cdot CHO)_3$	Polymerization of acetaldehyde with mineral acids	Generating acetaldehyde, preparation of rubber accelerators and synthetic resins, organic syntheses, solvent, medicine
119. Potassium acid tartrate **Cream of tartar**	$KOOC \cdot (CHOH)_2 \cdot COOH$	Purification of argol	Baking powders, dyeing, medicine
120. **Potassium xanthate**	$C(=S)(SK)(OC_2H_5)$	Action of potassium ethoxide ($KOH + C_2H_5OH$) on CS_2	Flotation of ores
121. Propane	C_3H_8	Separated from natural gas	Fuel, refrigerant, organic syntheses
122. Propylene	$CH_3 \cdot CH : CH_2$	Pyrolysis of hydrocarbons	Organic syntheses, reactions analogous to ethylene (see chart)
123. Propylene dichloride	$CH_3 \cdot \underset{\mid \atop Cl}{CH} \cdot \underset{\mid \atop Cl}{CH_2}$	Action of Cl_2 on propylene	Solvent for oils, fats, waxes, gums, resins; reactions analogous to ethylene dichloride (see chart), dry cleaning
124. Sodium potassium tartrate **Rochelle salt**	$CHOH \cdot COONa$ $\mid$ $CHOH \cdot COOK \cdot 4H_2O$	Neutralization of cream of tartar with Na_2CO_3	Silvering mirrors, medicine, glass industry
125. **Sorbitol**	$CH_2OH \cdot (CHOH)_4 \cdot CH_2OH$	Electrolytic reduction of glucose	Resins, synthesis of vitamin C, humectant, cosmetics, medicine (see Chapter 34, p. 1302)

126. **Starch**	$(C_6H_{10}O_5)_x$	Extraction from corn, potatoes, arrowroot and other cereals	Food, dextrin, glucose, adhesives, laundry, pharmacy, nitrostarch, *etc.*
127. **Stearic acid**	$C_{17}H_{35}\cdot COOH$	Hydrolysis of fats and oils	Soap stock, greases, pharmacy, candles, cosmetics, stearates
128. **Succinic acid**	$HOOC\cdot CH_2\cdot CH_2\cdot COOH$	Reduction of maleic acid; or by $C_2H_4Cl_2 \rightarrow C_2H_4(CN)_2 \rightarrow C_2H_4(COOH)_2$	Salts, esters, resins (see Chapter 31)
129. **Sucrose** **Cane sugar** **Beet sugar**	$C_{12}H_{22}O_{11}$	Extraction from sugar cane and sugar beet	Food, sweetening agent, confectionery, alcohol
130. **Tartaric acid**	$CHOH\cdot COOH$ | $CHOH\cdot COOH$	Action of milk of lime on cream of tartar and subsequent treatment with H_2SO_4	Salts and esters, beverages, medicine, dyeing
131. Tetrachloroethane	$C_2H_2Cl_4$	Combination of $2Cl_2$ with acetylene in presence of a catalyst ($SbCl_5$) (see Chapter 11, p. 470)	Solvent, denaturant for alcohol, insecticide
132. Tetrachlorethylene Perchloroethylene	$CCl_2 : CCl_2$	Heating pentachloroethane with $Ca(OH)_2$	Solvent, detergent compositions, liquid medium in transformers, drycleaning
133. **Tetramethyl thiuram disulfide** **Thiurams**	$(CH_3)_2NSO\cdot S\cdot S\cdot CSN(CH_3)_2$	Oxidized condensation product of $(CH_3)_2NH$ and CS_2	Ultra-accelerator for rubber (see Chapter 39, p. 1465)
134. **Tributyl phosphate**	$(C_4H_9)_3PO_4$	Esterification of phosphoric acid and butanol	Plasticizer for nitrocellulose lacquers, plastics and cellulose acetate
135. **Trichloroethylene**	$CHCl : CCl_2$	Heating tetrachloroethane with $Ca(OH)_2$ (see Chapter 11, p. 471)	Solvent, laundries and textile industry, degreasing metals

TABLE 8—ALIPHATIC COMPOUNDS—*Concluded*

Name	*Formula*	*Preparation*	*Uses*
136. Trichloromethane **Chloroform**	$CHCl_3$	Action of bleaching powder (Cl_2) upon alcohol or acetone. Reduction of CCl_4 (see Chapter 11, p. 470)	Solvent, medicine, organic syntheses, dry cleaning
137. Triethanolamine Diethanolamine Monoethanolamine	$N(CH_2\cdot CH_2OH)_3$ $HN(CH_2\cdot CH_2OH)_2$ $H_2N(CH_2\cdot CH_2OH)$	Action of NH_4OH on ethylene oxide or ethylene chlorohydrin + NH_3	Soaps, emulsions, gas purification for acid gases, dye solvent and penetrant
138. Triiodomethane **Iodoform**	CHI_3	Warming iodine with ethyl alcohol and Na_2CO_3	Medicine
139. Vinyl acetate	$CH_3\cdot COOCH : CH_2$	Reaction of vinyl chloride upon sodium acetate or $CH_3COOH + C_2H_2$	Polymerizes to resins which are used in lacquers and molding compositions (see Chapter 31, p. 1215)
140. Vinyl acetylene	$CH_2 : CH\cdot C \vdots CH$	Polymerization of 2 moles of acetylene ($Cu_2Cl_2 + NH_4Cl$, catalyst)	Preparation of chloroprene (see Chapter 39, p. 1486)
141. Vinyl chloride	$CH_2 : CHCl$	Action of NaOH on ethylene dichloride or $HCl + C_2H_2$ (see Chapter 11, p. 471)	Organic syntheses, resins by polymerization (see Chapter 31, p. 1216)

TABLE 9—BENZENE DERIVATIVES

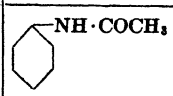
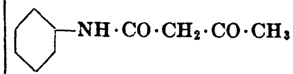
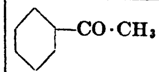
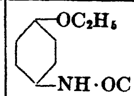
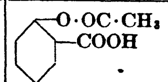
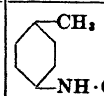
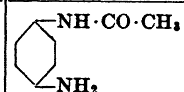
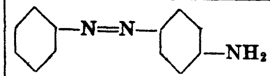
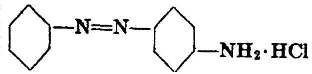
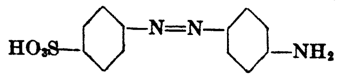
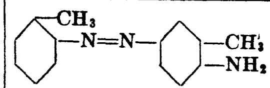
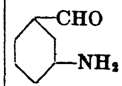
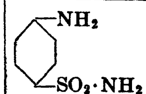
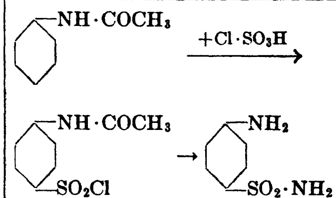
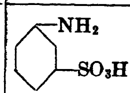
Name	*Formula*	*Preparation*	*Uses*
142. **Acetanilide** **Antifebrin**		Action of glacial acetic acid or acetic anhydride on aniline (see Chapter 34, p. 1306)	Preparation of p-nitroaniline, p-nitroacetanilide, p-phenylenediamine; antipyretic in medicine, stabilizer of H_2O_2, vulcanization accelerator
143. Acetoacetanilide		Condensation of aniline with aceto-acetic ester	Dyes of the Hansa color series, organic syntheses
144. **Acetophenone** **Hypnone**		Treating benzene with acetyl chloride in presence of $AlCl_3$	Perfumery, medicine, organic syntheses
145. **Acetyl-p-phenetidine** **Phenacetin**		Heating p-phenetidine, glacial acetic acid and fused sodium acetate	Analgesic and antipyretic in medicine
146. Acetyl salicylic acid **Aspirin**		Action of acetyl chloride or glacial acetic acid on salicylic acid	Analgesic, antirheumatic and antipyretic in medicine
147. Acetyl-p-toluidine		Acetylation of p-toluidine with acetic anhydride	m-nitro-p-toluidine
148. p-Aminoacetanilide		Reduction of p-nitroacetanilide with iron and acetic acid	Azo dyes

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
149. p-Aminoazobenzene		Molecular rearrangement of diazoaminobenzene in presence of aniline hydrochloride	Azo dyes
150. p-Aminoazobenzene hydrochloride		Action of HCl on p-aminoazobenzene	Azo dyes
151. p-Aminoazobenzene-p-sulfonic acid		Sulfonation of p-aminoazobenzene	Azo dyes
152. o-Aminoazotoluene		Molecular rearrangement of diazoaminotoluene (o-toluidine and diazotoluene chloride)	Azo dyes
153. m-Aminobenzaldehyde		Reduction of m-nitrobenzaldehyde with $Na_2S_2O_4$	Preparation of m-hydroxybenzaldehyde
154. p-Aminobenzenesulfonamide **Sulfanilamide**			Medicine (hemolytic streptococcic infection) (see Chapter 34, p. 1312)
155. m-Aminobenzenesulfonic acid **Metanilic acid**		Reduction of m-nitrobenzenesulfonic acid	Azo and triphenylmethane dyes

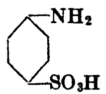
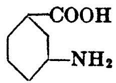
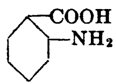
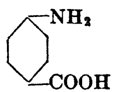
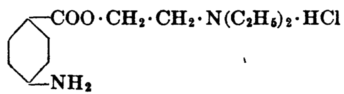
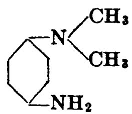
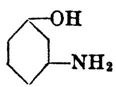
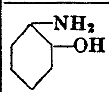
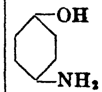
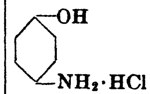
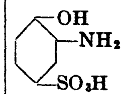
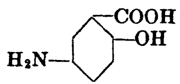
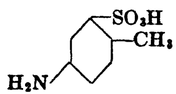
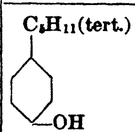
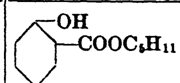
156. p-Aminobenzenesulfonic acid **Sulfanilic acid**		Heating aniline with H_2SO_4 at 200°	Pyrazolone and azo dyes, organic syntheses
157. m-Aminobenzoic acid		Reduction of m-nitrobenzoic acid with iron and acetic acid	Azo dyes
158. o-Aminobenzoic acid **Anthranilic acid**		Action of sodium hypochlorite on phthalimide	Dyes; its esters used in perfumery and flavors
159. p-Aminobenzoic acid		Reduction of p-nitrobenzoic acid	Esters are important local anesthetics
160. p-Aminobenzoyldiethylaminoethane HCl **Novocaine**		Action of diethylamine on chloroethyl-p-nitrobenzoate and the subsequent reduction of the nitro group	Local anesthetic
161. p-Aminodimethylaniline		Reduction of p-nitrosodimethylaniline with Zn and HCl	Thiazine dye, photographic developers, rubber accelerator (see Chapter 39, p. 1465)
162. m-Aminophenol		Fusion of metanilic acid with NaOH	Dyes and dialkyl m-aminophenol
163. o-Aminophenol		Reduction of o-nitrophenol	o-anisidine

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
164. p-Aminophenol		Rearrangement of phenylhydroxylamine or reduction of p-nitrosophenol with Na_2S	Photographic developer, stilbene, azo and sulfur dyes
165. p-Aminophenol hydrochloride		Action of HCl on p-aminophenol	Photographic developer and dyes
166. 2-Amino-1-phenol-4-sulfonic acid		Reduction of 2-nitro-p-phenolsulfonic acid by Na_2S	Azo dyes
167. 5-Aminosalicylic acid		Reduction of nitrosalicylic acid or reduction of benzene-azo-salicylic acid	Azo and triphenylmethane dyes
168. 5-Amino-o-toluenesulfonic acid		Heating p-toluidine sulfate	Azo dyes
169. p-tert.-Amyl phenol **Pentaphen**		Condensation of amylene with phenol	Manufacture of oil soluble resins, germicide
170. Amyl salicylate		Esterification of amyl alcohol and salicylic acid	Flavors, perfumes

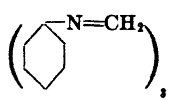
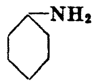
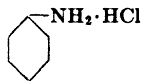
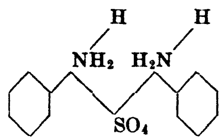
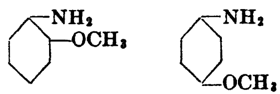
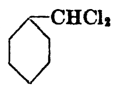
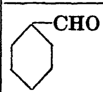
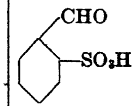
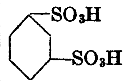
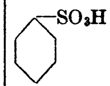
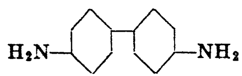
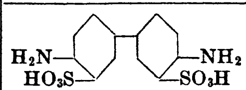
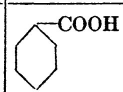
171. **Anhydroformaldehydeaniline** **Formaniline**		Condensation of aniline and formaldehyde	Triphenylmethane dyes and rubber accelerator
172. **Aniline** **Aniline oil**		Reduction of nitrobenzene with Fe turnings and HCl (see Chapter 28, p. 1110)	Intermediates and dyes, pharmaceuticals, acetanilide, rubber accelerator, etc. (see Chapters 39, p. 1465, 28, p. 1127)
173. **Aniline hydrochloride** **Aniline salt**		Aniline and HCl	Dyes and intermediates, dyeing and printing fabrics with aniline black
174. **Aniline sulfate**		Aniline and H_2SO_4	Rubber accelerator, dyes and intermediates
175. **o-Anisidine** **p-Anisidine**		Reduction of the corresponding nitroanisole with Fe and HCl	Azo dyes
176. Benzal chloride		Chlorination of boiling toluene in sunlight or ultra-violet light	Benzaldehyde, organic syntheses
177. Benzaldehyde **Artificial oil of bitter almonds**		Hydrolysis of benzal chloride with $Ca(OH)_2$	Organic syntheses, flavors, triphenylmethane dyes, perfumery, soap ingredient, toilet preparations, etc.

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
178. Benzaldehyde-o-sulfonic acid		Heating o-chlorobenzaldehyde with Na_2SO_3 under pressure	Triphenylmethane dyes
179. Benzene **Benzol**		Fractional distillation of "light oil" fraction from destructive distillation of coal (see Chapters 15 and 16)	Solvent, dry cleaning, paints, varnishes, motor fuel, organic syntheses
180. m-**Benzenedisulfonic acid**		Sulfonation of benzene	Resorcinol, organic syntheses
181. Benzenesulfonic acid		Sulfonation of benzene	Phenol, organic syntheses
182. Benzidine		Reduction of nitrobenzene with Zn and NaOH and the rearrangement of the resulting hydrazobenzene with strong acid	Disazo dyes
183. Benzidinedisulfonic acid (2,2′-or 3,3′-)		Heating benzidine sulfate with H_2SO_4	Disazo dyes
184. Benzoic acid		Hydrolysis of benzotrichloride with $Ca(OH)_2$ or the oxidation of toluene	Dyestuffs, esters in perfumes and flavors, pharmaceuticals, benzoates, antibactericide in medicine, Na salt as food preservative

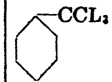
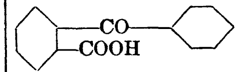
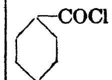
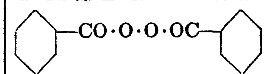
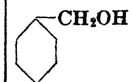
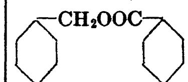
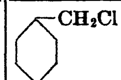
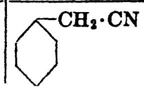
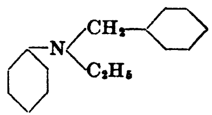
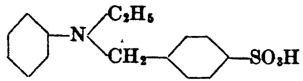
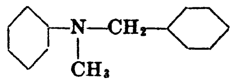
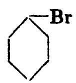
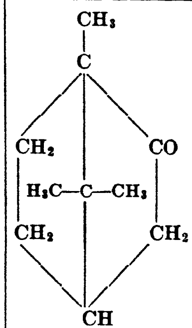
185. Benzoquinone **Quinone**		Oxidation of aniline with chromic acid acid	Hydroquinone
186. Benzotrichloride		Chlorination of boiling toluene in sunlight or ultra-violet light	Benzoic acid, dyes, organic syntheses
187. o-Benzoylbenzoic acid		Condensation of phthalic anhydride with benzene in the presence of $AlCl_3$	Synthesis of anthraquinone
188. Benzoyl chloride		Action of SO_2Cl_2 on benzoic acid or action of Cl_2 on benzaldehyde	Benzoylating agent, dyes
189. Benzoyl peroxide **Lucidol**		Reaction of benzoyl chloride and Na_2O_2	Oxidizing and bleaching agent
190. Benzyl alcohol		Reduction of benzaldehyde or hydrolysis of benzyl chloride	Manufacture of lacquers, perfumery, medicine, esters
191. Benzyl benzoate		Action of benzyl chloride on sodium benzoate	Fixative for perfumes and flavors, solvent, medicine
192. Benzyl chloride		Partial chlorination of boiling toluene in sunlight or ultra-violet light	Benzyl alcohol, organic syntheses, benzyl cellulose
193. Benzyl cyanide		Action of NaCN on benzyl chloride	Phenylacetic acid, organic syntheses

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
194. **Benzylethylaniline**		Condensation of ethyl aniline and benzyl chloride	Triphenylmethane dyes
195. **Benzylethylanilinesulfonic acid**		Sulfonation of benzylethylaniline	Triphenylmethane dyes
196. **Benzylmethylaniline**		Condensation of methylaniline and benzyl chloride	Triphenylmethane dyes
197. **Bromobenzene**		Bromination of benzene in presence of Fe	Organic syntheses
198. **Camphor**		Distillation of the wood of the camphor laurel tree; synthetic method	Celluloid, insecticides, medicine, plasticizer, moth preventative (see Chapter 31, p. 1202)

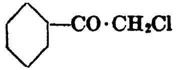
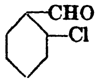
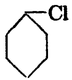
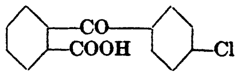
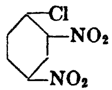
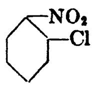
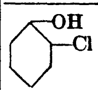
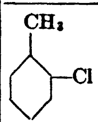
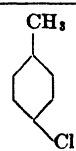
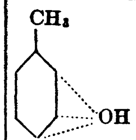
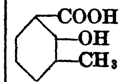
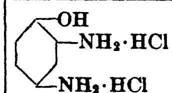
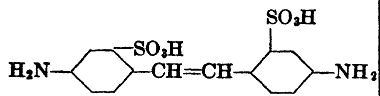
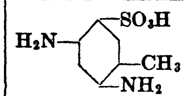
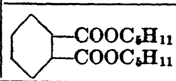
199. **Chloroacetophenone "CN"**		Action of chloroacetyl chloride on benzene in presence of $AlCl_3$ (see Chapter 33, p. 1267)	Tear gas (see Chapter 33, p. 1259)
200. o-Chlorobenzaldehyde		Oxidation of o-chlorobenzyl alcohol with HNO_3	Triphenylmethane dye
201. Chlorobenzene		Chlorination of benzene in presence of Fe as a catalyst (see Chapter 11, p. 475)	o- and p-chloronitrobenzene, chlorodinitrobenzene, phenol
202. Chlorobenzoyl-o-benzoic acid		Condensation of chlorobenzene with phthalic anhydride ($AlCl_3$)	Production of chloroanthraquinone
203. Chloro-2,4-dinitrobenzene		Nitration of chlorobenzene with mixed acid	Sulfur dyes
204. poly-Chlorodiphenyls **Aroclors**	Various isomers	Chlorination of diphenyl	Lacquers, fire-retarding paint and lacquer films, dielectric
205. o-Chloronitrobenzene		Nitration of chlorobenzene	Organic syntheses
206. o-Chlorophenol		Chlorination of phenol	Anthraquinone derivatives such as alizarin, catechol
207. o-Chlorotoluene p-Chlorotoluene	 	Chlorination of toluene (catalytic)	Organic syntheses, dye intermediates

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
208. o-m-p-Cresols **Cresylic acid**		Fractional distillation of coal tar (see Chapter 16, p. 661)	Disinfectant, dyes, soap, explosives, organic syntheses, resins, tricresyl phosphate, flotation agent (see Chapter 24, p. 919)
209. **2,3-Cresotic acid** **o-Cresotic acid** **o-Cresotinic acid**		Action of CO_2 on sodium-o-cresolate under pressure	Azo and triphenylmethane dyes
210. Cyclohexane	$(CH_2)_6$	Catalytic reduction of benzene	Solvent
211. p,p′-Diaminodiphenylamine		Oxidation of a mixture of p-phenylenediamine and aniline and subsequently reducing the indamine formed	Aniline black dyes, rubber antioxidant (see Chapter 39, p. 1465)
212. 2,4-Diaminophenol dihydrochloride **Amidol**		Reduction of 2,4-dinitrophenol and treatment with HCl	Photographic developer
213. 4,4′-Diamino-2,2′-stilbenedisulfonic acid **Diaminostilbenedisulfonic acid**		By boiling the Na salt of p-nitrotoluene-o-sulfonate with NaOH solution, subsequently reducing the stilbene derivative.	Disazo dyes
214. 4,6-Diamino-m-toluenesulfonic acid		Heating m-tolylenediamine sulfate with oleum	Disazo dyes
215. Diamyl phthalate		Action of amyl alcohol on phthalic anhydride	Solvent for nitrocellulose, plasticizer and softener

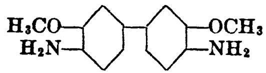
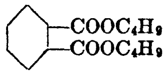
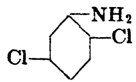
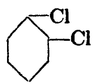
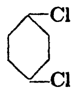
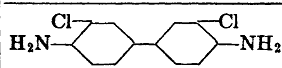
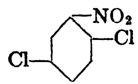
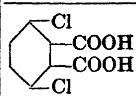
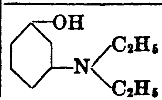
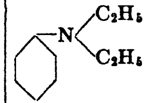
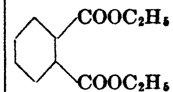
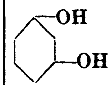
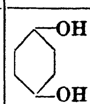
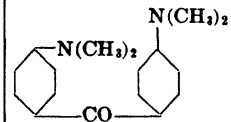
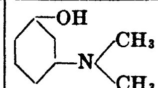
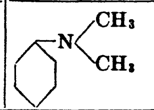
216. **o-Dianisidine**		Reduction of o-nitroanisole with Zn dust and NaOH to hydrazoanisole. This rearranges to o-dianisidine with strong acid	Disazo dyes
217. Dibutyl phthalate		Action of butyl alcohol on phthalic anhydride	Plasticizer in synthetic rubber nitrocellulose and cellulose acetate lacquers. Fixative in perfumery (see Chapter 39, p. 1485)
218. 2,5-Dichloroaniline		Reduction of 2,5-dichloronitrobenzene with Fe and HCl	Azo dyes
219. o-Dichlorobenzene		Chlorination of benzene in presence of Fe (see Chapter 11, p. 477)	Organic syntheses, insecticides, paint remover
220. p-Dichlorobenzene **Paradi**		Chlorination of benzene in presence of Fe (see Chapter 11, p. 477)	Insecticide, disinfectant, moth repellant, organic syntheses
221. o,o′-Dichlorobenzidine		Reducing o-chloronitrobenzene to o,o′-dichlorohydrazobenzene, followed by a molecular rearrangement	Disazo dyes
222. 2,5-Dichloronitrobenzene		Nitration of p-dichlorobenzene	2,5-dichloroaniline, sulfur dyes
223. Dichlorophthalic acid		Chlorination of phthalic anhydride in presence of oleum and iodine	Xanthone dyes
224. m-Diethylaminophenol		Fusion of diethylaniline-m-sulfonic acid with NaOH	Xanthone dyes

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
225. Diethylaniline		Action of ethyl alcohol on aniline in presence of a dehydrating agent such as HCl, or $2C_2H_5Cl$ on aniline	Triphenylmethane dyes, organic syntheses
226. Diethyl phthalate		Heating ethyl alcohol and phthalic anhydride in the presence of H_2SO_4	Denaturant for alcohol, fixative for perfumery, solvent
227. m-Dihydroxybenzene **Resorcinol**		Fusion of m-benzenedisulfonic acid with NaOH	Dyes, antiseptic, organic syntheses
228. p-Dihydroxybenzene **Hydroquinone**		Reducing quinone with H_2SO_3	Photographic developer, organic syntheses
229. p,p'-Bis(dimethylamino)-benzophenone **Michler's ketone**		Action of phosgene and dimethylaniline	Auramine dye and triphenylmethane dyes
230. m-Dimethylaminophenol		Fusion of dimethylaniline-m-sulfonic acid with NaOH	Xanthone dyes
231. Dimethylaniline		Heating aniline and CH_3OH under pressure in presence of H_2SO_4 or HCl, or action of $2CH_3Cl$ on aniline	Dyes, organic syntheses (see Chapter 32, p. 1253)

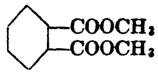
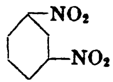
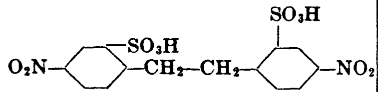
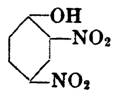
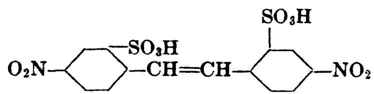
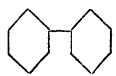
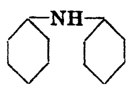
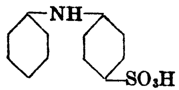
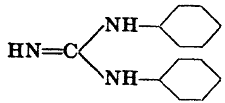
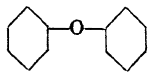
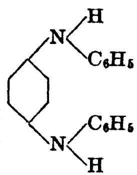
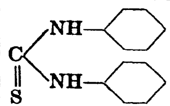
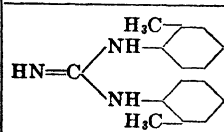
232. Dimethyl phthalate		Condensation of CH_3OH and phthalic anhydride	Plasticizer for Nitrocellulose and cellulose acetate lacquers (see Chapter 31, p. 1203)
233. m-Dinitrobenzene		Nitration of benzene	m-Nitroaniline, m-phenylenediamine
234. p,p′-Dinitrodibenzyl-o,o′-disulfonic acid		Oxidation of p-nitrotoluenesulfonic acid with NaOCl	Stilbene dyes
235. 2,4-Dinitrophenol		Hydrolysis of chlorodinitrobenzene	Sulfur dyes
236. p,p′-Dinitrostilbene-o,o′-disulfonic acid		Oxidation of sodium p-nitrotoluenesulfonate with NaOCl	Stilbene dyes
237. 2,4-Dinitrotoluene D.N.T.		Nitration of toluene	Tolylenediamine
238. Diphenyl Xenene		Pyrogenetic decomposition (dehydrogenation) of benzene	Diphenyl derivatives, heat transfer agent
239. Diphenylamine		Heating aniline and aniline hydrochloride under pressure (see Chapter 33, p. 1274)	Azo dyes, stabilizer for smokeless powder, sulfur dyes, poison gas reagent (see Chapters 32, p. 1250, 33, p. 1274)

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
240. Diphenylaminesulfonic acid		Sulfonation of diphenylamine	Triphenylmethane dyes
241. Diphenylguanidine		Thiocarbanilide + NH_4OH + (HOK + PbO as catalysts) → Diphenylguanidine + H_2S	Rubber accelerator (see Chapter 39, p. 1465)
242. Diphenyl oxide **Phenyl ether**		By-product in manufacture of phenol from chlorobenzene, condensation of sodium phenolate and chlorobenzene	Perfumery, heat transfer agent
243. Diphenyl-p-phenylenediamine		Heating a mixture of aniline, p-aminophenol, diphenylamine and HCl	Antioxidant in rubber
244. Diphenylthiourea **Thiocarbanilide**		Passing the vapor of CS_2 into aniline heated to 115°	Rubber accelerator, organic syntheses
245. o-Ditolylguanidine		Thiocarb-o-toluide is heated with NH_4OH in presence of catalysts (PbO)	Rubber accelerator

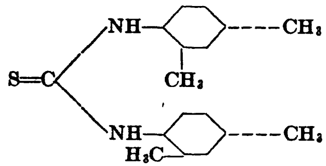
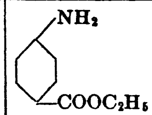
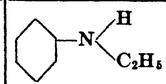
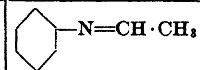
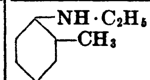
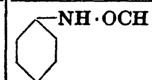
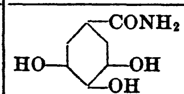
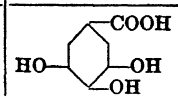
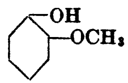
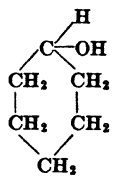
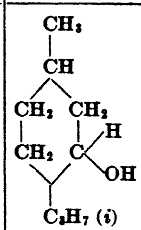
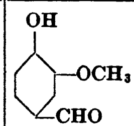
246. o-Ditolylthiourea p-Ditolylthiourea **Thiocarbtoluide**		Passing the vapor of CS_2 into hot o-toluidine or p-toluidine	Rubber accelerator
247. Ethyl-p-aminobenzoate **Anesthesine, Benzocaine**		Esterification of p-aminobenzoic acid	Anesthetic
248. Ethylaniline		Heating aniline and C_2H_5OH or C_2H_5Cl in autoclave	Methylethylaniline, benzylethylaniline
249. Ethylideneaniline		Condensation of acetaldehyde and aniline	Rubber accelerator
250. N-ethyl-o-toluidine		Heating o-toiluidine and ethyl alcohol under pressure	Triphenylmethane dyes
251. Formanilide		Heating formic acid and aniline	Rubber accelerator
252. **Gallamide**		Action of ammonium sulfite on tannin	Oxazine dyes
253. **Gallic acid**		Hydrolysis of tannins, nut galls, etc., by enzymes or acids	Dyeing, ink, photography

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
254. Guaiacol		Constituent of beech-wood tar or prepared by diazotizing o-anisdine and subsequently boiling the solution with dilute H_2SO_4	Intestinal antiseptic in medicine
255. Hexahydroaniline **Cyclohexylamine**	$(CH_2)_5{=}CH \cdot NH_2$	Catalytic reduction of aniline	Solvent, emulsifying agent, insecticide, organic syntheses
256. Hexahydrophenol **Hexalin**		Catalytic reduction of phenol	Solvents for oils, fats, greases. Used in soaps for the textile industry
257. 3-Hydroxymenthane **Menthol**		Separated from oil of peppermint	Medicine, perfumery, confectionery
258. p-Hydroxy-m-methoxybenzaldehyde **Vanillin**		From natural source, or by oxidation of isoeugenol, or by synthesis from guaiacol	Flavors, perfumery

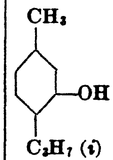
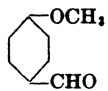
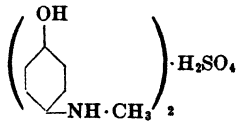
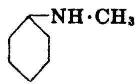
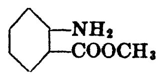
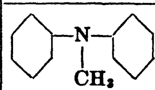
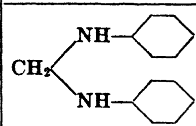
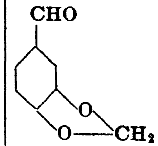
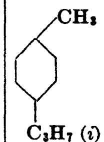
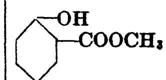
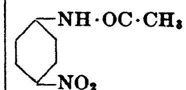
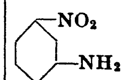
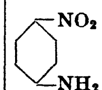
259. 3-Hydroxy-1-methyl-4-isopropylbenzene **Thymol**		Separated from oil of thyme and other essential oils or by fusion of cymenesulfonic acid	Medicine, preservative, perfumery
260. p-Methoxybenzaldehyde **Anisaldehyde, Aubepine**		Oxidation of anethole	Perfumery, flavors
261. N-methyl-p-aminophenol sulfate **Metol**		Methylation of p-aminophenol or by treating p-aminophenol with formaldehyde and reducing the product formed with Al amalgam	Photographic developer
262. Methylaniline		Heating aniline and methanol with HCl under pressure or condensing aniline and formaldehyde and subsequently reducing the product with Zn dust and NaOH	Ethylmethylaniline and benzylmethylaniline
263. Methyl anthranilate		Esterification of anthranilic acid with methanol	Perfumery, flavors
264. N-methyldiphenylamine		Heating diphenylamine with methanol in the presence of HCl	Triphenylmethane dyes
265. Methylenedianilide		Condensation of formaldehyde and aniline	Rubber accelerator

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
266. 3,4-Methylenedioxybenzaldehyde **Heliotropin or piperonal**		Oxidation of safrole	Perfumery, cosmetics, soaps
267. p-Methylisopropylbenzene **Cymene**		From natural source or heating camphor with P_2O_5	Solvent, organic syntheses
268. Methyl salicylate **Synthetic oil of wintergreen**		Heating salicylic acid and methanol in the presence of H_2SO_4	Flavor, perfumery, medicine
269. p-Nitroacetanilide		Nitration of acetanilide	p-Nitroaniline, acetyl-p-phenylenediamine
270. m-Nitroaniline		Reduction of m-dinitrobenzene with Na_2S	Dyes
271. p-Nitroaniline		Nitration of acetanilide and hydrolysis of the acetyl group	Azo and sulfur dyes (see Chapter 28, p. 1117)

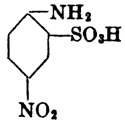
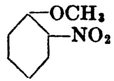
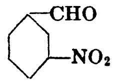
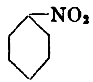
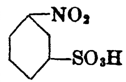
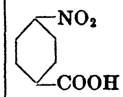
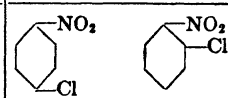
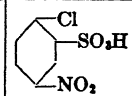
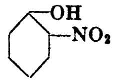
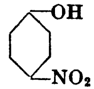
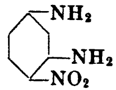
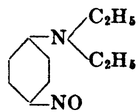
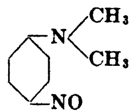
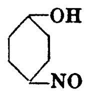
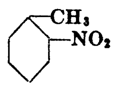
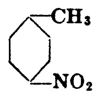
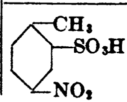
272. p-Nitroaniline-o-sulfonic acid		Heating p-nitrochlorobenzene-o-sulfonic acid with alcoholic ammonia in an autoclave	Azo dyes
273. **o-Nitroanisole**		Methylation of o-nitrophenol	Dianisidine
274. m-Nitrobenzaldehyde		Nitration of benzaldehyde	Triphenylmethane dyes, organic syntheses
275. Nitrobenzene **Oil of Mirbane**		Nitration of benzene	Aniline, organic syntheses, perfumery
276. m-Nitrobenzenesulfonic acid		Nitration of benzenesulfonic acid	Metanilic acid
277. p-Nitrobenzoic acid		Oxidation of p-nitrotoluene	p-Aminobenzoic acid, organic syntheses
278. p-Nitrochlorobenzene o-Nitrochlorobenzene		Nitration of chlorobenzene	Organic syntheses
279. p-Nitrochlorobenzene-o-sulfonic acid		Sulfonation of p-nitrochlorobenzene with fuming H_2SO_4	p-nitroaniline-o-sulfonic acid

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
280. o-Nitrophenol p-Nitrophenol	 	Nitration of phenol; o- volatile with steam	Picric acid, sulfur dyes, aminophenols
281. 4-Nitro-m-phenylenediamine		Heating 4-nitroaniline-3-sulfonic acid with NH_4OH in autoclave	Azo dyes
282. p-Nitrosodiethylaniline		Action of HONO on diethylaniline hydrochloride	Azine dyes
283. p-Nitrosodimethylaniline		Action of HONO on dimethylaniline hydrochloride	Dyes, its hydrochloride used as a rubber accelerator
284. p-Nitrosophenol		Action of HONO on phenol	Sulfur and indophenol dyes
285. o-Nitrotoluene p-Nitrotoluene M.N.T.	 	Nitration of toluene	Dyes, T.N.T.
286. p-Nitrotoluene-o-sulfonic acid		Sulfonation of p-nitrotoluene with oleum	Stilbene and azo dyes

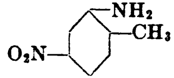
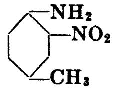
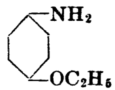
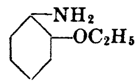
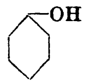
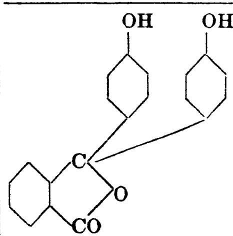
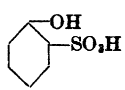
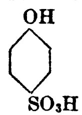
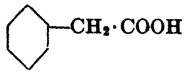
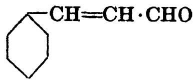
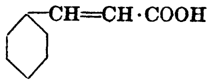
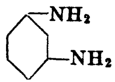
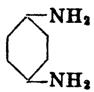
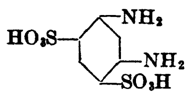
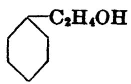
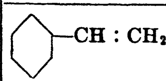
287. 5-Nitro-o-toluidine		Nitration of o-toluidine	Nitro and azo dyes
288. 2-Nitro-p-toluidine		Nitration of acetyl-p-toluidine and subsequent hydrolysis of acetyl group	Azo dyes (see Chapter 28, p. 1117)
289. Nitro-m-xylene		Nitration of m-xylene	Xylidine
290. **p-Phenetidine** **o-Phenetidine**	 	Ethylation of the corresponding acetaminophenol and removal of acetyl group	Xanthone dyes and organic syntheses
291. Phenol **Carbolic acid**		Coal tar distillation or fusion of sodium benzenesulfonate with NaOH or hydrolysis of C_6H_5Cl with NaOH under pressure and catalyst (see Chapters 11, p. 476, 16, p. 662)	Organic syntheses, antiseptic, synthetic resins, salicylic acid, picric acid, etc. (see Chapters 32, 31)
292. Phenolphthalein		Condensation of phthalic anhydride and phenol in presence of conc. H_2SO_4	Laxatives, indicator
293. Phenolsulfonic acids o-, and p-	 	Sulfonation of phenol	Medicine, organic syntheses, picric acid

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
294. **Phenylacetic acid**		Hydrolysis of benzyl cyanide	Its esters in flavors and perfumes
295. β-Phenylacrylaldehyde **Cinnamaldehyde**		Condensation of benzaldehyde with acetaldehyde or from natural source	Organic syntheses, perfumery, flavors
296. β-Phenylacrylic acid **Cinnamic acid**		Heating benzaldehyde with sodium acetate in the presence of acetic anhydride (Perkin's reaction)	Organic syntheses, esters are used in perfumery and flavors
297. m-Phenylenediamine		Reduction of m-dinitrobenzene	Azo dyes
298. p-Phenylenediamine		Reduction of p-aminoazobenzene or p-nitroacetanilide and hydrolysis of the acetyl group	Dyes, rubber accelerator, organic syntheses
299. m-Phenylenediaminedisulfonic acid		Sulfonation of m-phenylenediamine hydrochloride with oleum	Azo dyes
300. Phenylethyl alcohol		Reduction of ethyl phenyl acetate with Na and alcohol; reduction of phenylacetaldehyde	Perfumery
301. Phenylethylene **Styrene**		Pyrolytic dehydrogenation of ethyl benzene in presence of steam or by removal of HCl from chloroethylbenzene (see Chapter 31, p. 1218)	Styrene resins

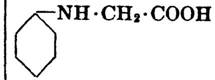
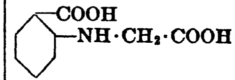
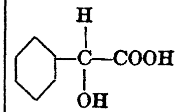
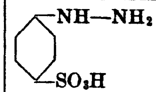
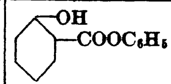
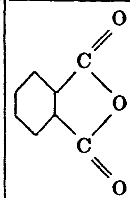
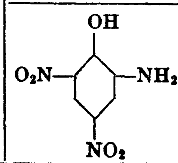
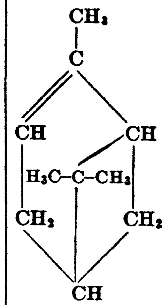
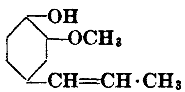
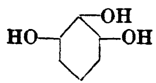
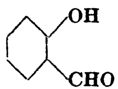
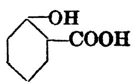
302. N-Phenylglycine		Action of chloroacetic acid on aniline	Indigo group dyes
303. **N-Phenylglycine-o-carboxylic acid**		Action of chloroacetic acid on anthranilic acid	Indigo group dyes
304. Phenyl glycolic acid **Mandelic acid and its salts**		Addition of HCN to benzaldehyde and the subsequent hydrolysis of the CN group	Bactericidal agent
305. Phenylhydrazine-p-sulfonic acid		Reduction of diazotized sulfanilic acid or sulfonation of phenylhydrazine	Pyrazolone dyes
306. **Phenyl salicylate** **Salol**		Esterification of salicylic acid with phenol	Medicine
307. **Phthalic anhydride**		Passing naphthalene vapor and air over a catalyst (V_2O_5)	Organic syntheses, anthraquinone, dyes, perfumery products, resins (see Chapters 30 and 31)
308. **Picramic acid**		Reduction of picric acid with NaHS or Na_2S	Azo dyes

TABLE 9—BENZENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
309. **Pinene**		Fractionation of oil of turpentine	Artificial camphor, solvent, thinner
310. **p-Propenyl-o-methoxyphenol Isoeugenol**		Fusion of eugenol with KOH	Vanillin, perfumery
311. **Pyrogallol Pyrogallic acid**		Heat gallic acid and H_2O in an autoclave	Photographic developer, dyes, organic syntheses, germicide in medicine, oxygen absorbent in alkaline solution
312. **Salicylaldehyde**		Action of $CHCl_3$ on sodium phenolate in presence of NaOH (Reimer-Tiemann reaction)	Perfumery, coumarin
313. **Salicylic acid** and its salts		Action of CO_2 on dry sodium phenolate under pressure and heat (see Chapter 34, p. 1306)	Dyes, medicinals, antiseptics, *etc.* Its salts and esters are used in medicine as antirheumatic; perfumery, food preservative

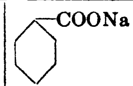
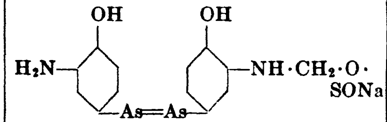
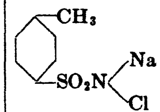
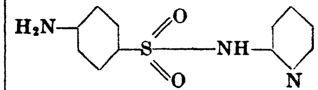
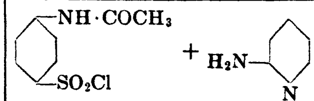
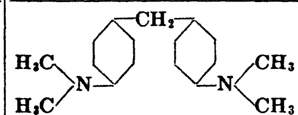
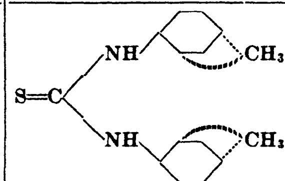
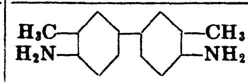
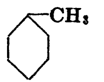
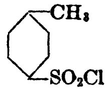
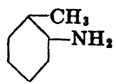
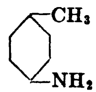
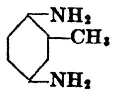
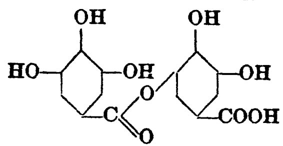
314. Sodium benzoate		Neutralization of benzoic acid with NaOH	Food preservative
315. Sodium-3,3′-diamino-4,4′-dihydroxyarsenobenzene-N-methylene-sulfinate **Neosalvarsan** **Neoarsphenamine**		Action of sodium formaldehyde sulfoxylate ($HOCH_2 \cdot OSONa$) on salvarsan	Medicine
316. Sodium-p-toluenesulfon-N-chloramide **Chloramine-T**		Action of NaOCl upon p-toluenesulfonamide	Disinfectant, antiseptic
317. 2-Sulfanilylaminopyridine **Sulfapyridine**			Antipneumococcic action
318. p,p′-Tetramethyldiaminodiphenylmethane **Methane base**		Action of formaldehyde on dimethylaniline in presence of conc. HCl	Auramine and acridine dyes
319. Thiocarbtoluide		Passing the vapor of CS_2 into a mixture of hot o- or p-toluidines	Rubber accelerator
320. **o-Tolidine**		Reduction of o-nitrotoluene to hydrazotoluene with Zn dust and HCl and subsequent molecular rearrangement	Disazo dyes

TABLE 9—BENZENE DERIVATIVES—*Concluded*

Name	*Formula*	*Preparation*	*Uses*
321. **Toluene** **Toluol**		Fractional distillation of "light oil" fraction from destructive distillation of coal. Cyclization of petroleum (see Chapters 16, p. 660, 14, p. 574)	Solvent, fuel, organic syntheses
322. p-Toluenesulfonyl chloride		Action of PCl_5 on p-toluenesulfonic acid	Azo dyes, Chloramine-T, organic condensing agent
323. o-Toluidine p-Toluidine	 	Reduction of the corresponding nitrotoluene with Fe and HCl	Azo, triphenylmethane and azine dyes
324. m-Tolylenediamine		Reduction of dinitrotoluene with Fe and HCl	Azo, azine, sulfur dyes
325. p-Tolylenediamine		Reduction of aminoazotoluene with Zn dust and HCl	Azo and azine dyes
326. Tricresyl phosphate	$(CH_3 \cdot C_6H_4)_3PO_4$	Heating $POCl_3$ and cresol	Manufacture of pyroxylin plastics Synthetic rubber plasticizer (see Chapter 39, p. 1465)
327. **Tannic acid**		Extraction from natural tannin-containing materials	Ink, tanning, alcohol denaturant, mordant in dyeing and printing textiles, astringent in medicine

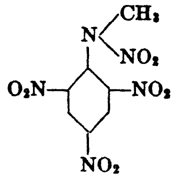
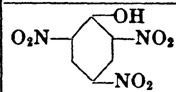
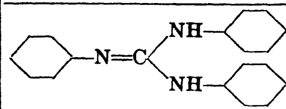
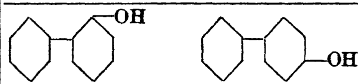
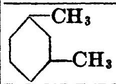
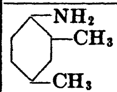
328. **Tetryl**		Nitration of methyl- or dimethylaniline	Detonator for high explosives (see Chapter 32, p. 1253)
329. Trichlorobenzenes	Mixture of isomers (1,2,4- and 1,2,3-)	Chlorination of benzene	Solvent, dielectric, heat transfer medium
330. 2,4,6-Trinitrophenol **Picric acid**		Action of mixed acid on phenolsulfonic acids	Explosives, medicine, picramic acid (see Chapter 32)
331. Triphenylguanidine		Heating thiocarbanilide and aniline in alcoholic solution with PbO (catalyst)	Rubber accelerator
332. Triphenyl phosphate	$(C_6H_5)_3PO_4$	Phenol and $POCl_3$ are boiled in presence of $ZnCl_2$	Camphor substitute in celluloid, plasticizer and softener for lacquers (see Chapter 31, p. 1202)
333. o-Xenol p-xenol		By-product in the manufacture of phenol from chlorobenzene (Dow process), whereby the resulting chlorodiphenyls are also hydrolyzed	Germicide, fungicide, organic syntheses
334. **m-Xylene Xylol**		Fractional distillation of "light oil" fraction from the destructive distillation of coal	Solvent, fuel, xylidine, organic syntheses, dyes
335. Xylenols	Mixture of isomeric $C_6H_3 \cdot OH \cdot (CH_3)_2$	Fractional distillation of coal tar	Disinfectants, resins
336. 2,4-Xylidine		Separating it from commercial xylidine as the acetate	Azo dyes
337. Xylidine (commercial—5 isomers)	$C_6H_3(NH_2)(CH_3)(CH_3)$	Nitration of xylene and subsequent reduction with Fe and HCl	Azo dyes

TABLE 10—NAPHTHALENE DERIVATIVES

The following chart * shows the position of entering substituents in the naphthalene ring
If a hydrogen atom in naphthalene is replaced

by	Cl		Br		OH		OR		NO_2		NH_2		NHR		SO_3H		CN		COOH	
in the position	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
the new group	enters in the position																			
Cl	4		4		2 ?	1								1			5	5 or 8	5	
Br	4 5 or 8	? 5 or 8	4 5	8		1			5 or 8				4	1	5		5		5	
NO_2	4	8	4	8	2	1	2 4	1 6 or 7 8	5 8		5 8	5 8	2 4	1	4 5 8	4 5 8	5 ?		5 8	5 8 ?
SO_3H under 100°	4 5	6 8	4 ?	6 8	2 4	6 8			5 6 7		4	5 8			5 6	5	5 ?		α β β	α
SO_3H above 100°	5	6			2	6 7					5 6	6 7				5 6 7				
NO					2 4	1														
COOH					2	1 3														

* Cain and Thorpe: "Synthetic Dyestuffs and Intermediate Products."

TABLE 10—NAPHTHALENE DERIVATIVES—*Continued*

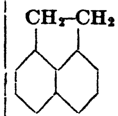
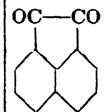
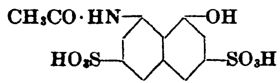
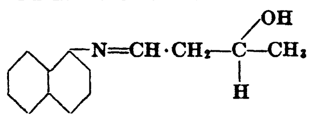
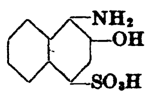
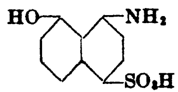
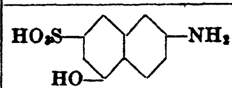
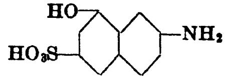
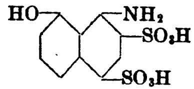
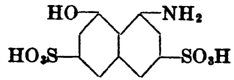
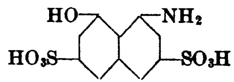
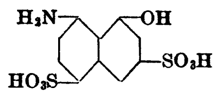
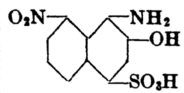
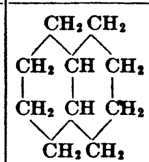
Name	*Formula*	*Preparation*	*Uses*
338. **Acenaphthene**		From the heavy oil and anthracene oil fraction of coal tar	Acenaphthenequinone
339. **Acenaphthenequinone**		Oxidation of acenaphthene with chromic acid	Ciba colors
340. **8-Acetamino-1-naphthol-3,6-disulfonic acid** **Acetyl H acid**		Acetylation of H acid	Azo dyes
341. **Aldol-α-naphthylamine**		Condensation of α-naphthylamine and aldol	Rubber antioxidant (see Chapter 39, p. 1465)
342. **1-Amino-2-naphthol-4-sulfonic acid** **1,2,4 acid**		Reduction and sulfonation of 1-nitroso-β-naphthol	Azo dyes
343. **1-Amino-8-naphthol-4-sulfonic acid** **S acid**		Fusion of 1-naphthylamine-4,8-disulfonic acid with NaOH at 220°	Azo dyes
344. **2-Amino-5-naphthol-7-sulfonic acid** **J acid**		Heating the Na salt of 2-naphthylamine-5,7—disulfonic acid with conc. NaOH in an autoclave	Disazo dyes

TABLE 10—NAPHTHALENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
345. 2-Amino-8-naphthol-6-sulfonic acid **Gamma or G acid**		Heating the Na salt of 2-naphthylamine-6,8-disulfonic acid with conc. NaOH in an autoclave	Disazo dyes
346. 1-Amino-8-naphthol-2,4-disulfonic acid **Chicago acid**		Fusion of sodium 1,8-naphthasultam-2,4-disulfonate with NaOH	Azo dyes
347. 1-Amino-8-naphthol-3,6-disulfonic acid **H acid**		Fusion of 1-naphthylamine-3,6,8-trisulfonic acid with NaOH	Azo dyes and acetyl H acid
348. 2-Amino-8-naphthol-3,6-disulfonic acid **2 R acid**		Fusion of 2-naphthylamine-3,6,8-trisulfonic acid with NaOH	Azo dyes
349. 8-Amino-1-naphthol-3,5-disulfonic acid **K acid**		Fusion of 1-naphthylamine-4,6,8-trisulfonic acid with NaOH	Azo dyes
350. 1-Amino-8-nitro-2-naphthol-4-sulfonic acid **Nitro-1,2,4 acid**		Nitration of 1-amino-2-naphthol-4-sulfonic acid	Azo dyes
351. Decahydronaphthalene **Decalin**		Catalytic reduction of naphthalene	Motor fuel and solvent

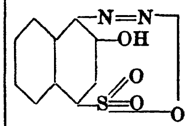
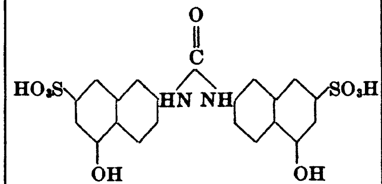
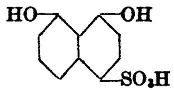
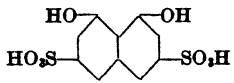
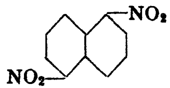
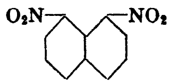
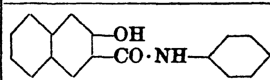
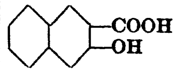
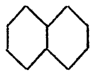
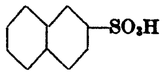
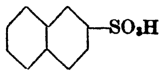
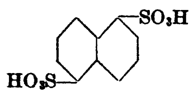
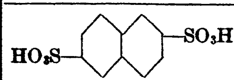
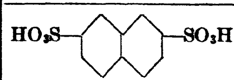
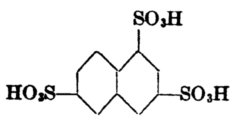
352. 1-Diazo-2-naphthol-4-sulfonic acid		Diazotization of 1-amino-2-naphthol-4-sulfonic acid	Azo dyes
353. 5,5-Dihydroxy-7,7-disulfo-2,2-dinaphthylurea **J acid urea**		Condenstion of J acid with phosgene	Dyes
354. 1,8-Dihydroxynaphthalene-4-sulfonic acid **Dioxy S acid**		Fusion of 1-naphthol-4,8-disulfonic acid with NaOH	Azo dyes
355. 1,8-Dihydroxynaphthalene-3,6-disulfonic acid **Chromotropic acid**		Fusion of sodium salt of 1-naphthol-3,6,8-trisulfonic acid with NaOH or heating H acid with NaOH solution under pressure	Azo dyes
356. 1,5-Dinitronaphthalene		Nitration of α-nitronaphthalene	Sulfur dyes
357. 1,8-Dinitronaphthalene		Nitration of α-nitronaphthalene	Sulfur dyes
358. 2-Hydroxy-3-naphthoic anilide **Naphthol AS**		Condensation of aniline with 2-hydroxy-3-naphthoic acid	Azo dyes

TABLE 10—NAPHTHALENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
359. **3-Hydroxy-2-naphthoic acid**		Action of CO_2 on dry sodium-2-naphtholate under pressure at 200–250°	Azo dyes
360. **Naphthalene**		From coal tar (see Chapter 16, p. 663)	Phthalic anhydride, moth repellant, organic syntheses, dyes
361. **α-Naphthalenesulfonic acid**		Sulfonation of naphthalene with H_2SO_4 at 80°	α-Naphthol
362. **β-Naphthalenesulfonic acid**		Sulfonation of naphthalene with H_2SO_4 at 180°	β Naphthol
363. **Naphthalene-1,5-disulfonic acid** **Armstrong's delta acid**		Sulfonation of naphthalene with fuming H_2SO_4	1,3,5-naphthalenetrisulfonic acid, 1-naphthol-5-sulfonic acid
364. **Naphthalene-2,6-disulfonic acid** **Ebert and Merz' beta acid**		Sulfonation of sodium β-naphthalenesulfonate	Dyes
365. **Naphthalene-2,7-disulfonic acid** **Ebert and Merz' alpha acid**		Sulfonation of sodium β-naphthálenesulfonate	Dyes
366. **Naphthalene-1,3,6-trisulfonic acid** **Trisulfonic acid**		Sulfonation of sodium-β-naphthalenesulfonate with fuming H_2SO_4	1-naphthol-3,6-disulfonic acid 1-naphthylamine-3,6,8-trisulfonic acid

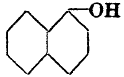
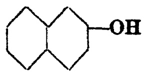
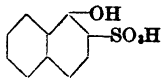
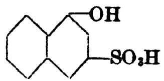
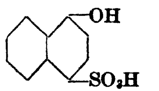
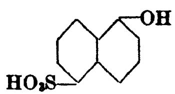
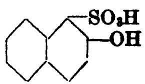
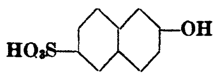
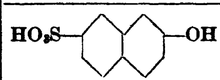
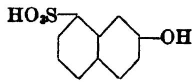
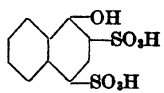
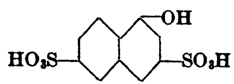
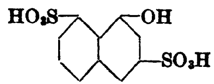
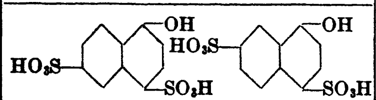
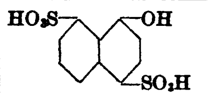
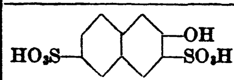
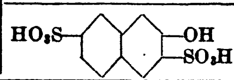
367. **α-Naphthol**		Fusion of α-naphthalenesulfonic acid with NaOH	Dyes, organic syntheses
368. **β-Naphthol**		Fusion of β-naphthalenesulfonic acid with NaOH	Dyes, organic syntheses, antiseptic, parasiticide (see Chapters 28, p. 1124, 34, p. 1310)
369. 1-Naphthol-2-sulfonic acid **Schäffer's or Baum's acid**		Heating α-naphthol with conc. H_2SO_4 at 90°	Dyes
370. 1-Naphthol-3-sulfonic acid **Armstrong and Wynne's acid**		Boiling the solution of the diazo compound of 1-naphthylamine-3-sulfonic acid	Azo dye
371. 1-Naphthol-4-sulfonic acid **Nevile-Winther's acid**		Boiling diazotized naphthionic acid with dilute H_2SO_4	Azo dyes
372. 1-Naphthol-5-sulfonic acid **L or Cleve's acid**		Fusion of 1,5-naphthalenedisulfonic acid with NaOH	Azo dyes
373. 2-Naphthol-1-sulfonic acid		Sulfonation of β-naphthol	2-Naphthylamine-1-sulfonic acid
374. 2-Naphthol-6-sulfonic acid **Schäffer's acid**		Sulfonation of β-naphthol at 100°	Monoazo dyes
375. 2-Naphthol-7-sulfonic acid **F acid** **Bayer's acid** **Cassella's acid**		Fusion of sodium salt of naphthalene-2,7-disulfonic acid with NaOH at 200°	Monoazo dyes

TABLE 10—NAPHTHALENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
376. 2-Naphthol-8-sulfonic acid **Crocein acid** **Bayer's acid**		Sulfonation of β-naphthol at low temperatures	Azo dyes
377. 1-Naphthol-2,4-disulfonic acid		Sulfonation of α-naphthol with conc. H_2SO_4	Martius yellow dye
378. 1-Naphthol-3,6-disulfonic acid **R. G. acid** **G. R. acid**		Diazotization of 1-naphthylamine-3,6-disulfonic acid and subsequent boiling with H_2O	Azo dyes
379. 1-Naphthol-3,8-disulfonic acid **Epsilon or Andresen's acid**		Diazotization of 1-naphthylamine-3,8-disulfonic acid and boiling until evolution of nitrogen ceases	Azo dyes
380. 1-Naphthol-4,6-disulfonic acid 1-Naphthol-4,7-disulfonic acid **Dahl's acid**		Boiling of the corresponding diazo compounds of amines with H_2O	Azo dyes
381. 1-Naphthol-4,8-disulfonic acid		Diazotization of 1-naphthylamine-4,8-disulfonic acid and subsequent boiling with H_2O	Azo dyes
382. 2-Naphthol-3,6-disulfonic acid **R acid**		Sulfonation of β-naphthol with conc. H_2SO_4 at 100°	Azo dyes
383. 2-Naphthol-3,7-disulfonic acid **F acid**		Heating β-naphtholsulfonic acid with conc. H_2SO_4 at 120°	Azo dyes

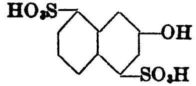
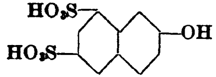
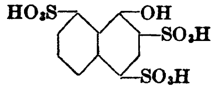
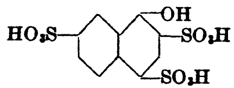
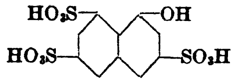
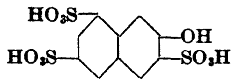
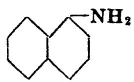
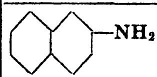
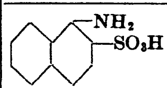
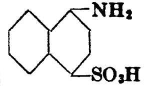
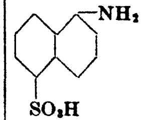
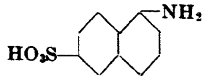
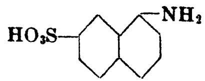
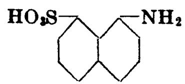
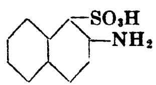
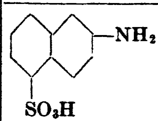
384. 2-Naphthol-4,8-disulfonic acid **C acid**		Boiling the diazo compound of the corresponding β-naphthylamine disulfonic acid with H_2O	Azo dyes
385. 2-Naphthol-6,8-disulfonic acid **G acid**		Sulfonation of β-naphthol with conc. H_2SO_4 at 60°	Azo dyes
386. 1-Naphthol-2,4,8-trisulfonic acid		Further sulfonation of α-naphthol-sulfonic acid or -disulfonic acid with fuming H_2SO_4	Dinitronaphtholsulfonic acid
387. 1-Naphthol-2,4,7-trisulfonic acid		Action of fuming H_2SO_4 on α-naphthol	Naphthol yellow S dye
388. 1-Naphthol-3,6,8-trisulfonic acid **Oxy Koch's acid**		Boiling the diazo salt of the corresponding aminotrisulfonic acid with H_2O	Azo dyes
389. 2-Naphthol-3,6,8-trisulfonic acid		Heating β-naphthol with fuming H_2SO_4 at 140–160°	Disazo dyes
390. α-Naphthylamine		Reduction of α-nitroaphthalene with Fe and HCl	Organic syntheses, dyes
391. β-Naphthylamine		Heating β-naphthol with ammonium sulfite and ammonia under pressure	Dyes, organic syntheses
392. 1-Naphthylamine-2-sulfonic acid		Heating sodium naphthionate and naphthalene	Dyes

TABLE 10—NAPHTHALENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
393. 1-Naphthylamine-4-sulfonic acid **Naphthionic acid**		Heating α-naphthylamine with H_2SO_4	Azo dyes
394. 1-Naphthylamine-5-sulfonic acid **Laurent's acid** **L acid**		Reduction of 1-nitro-5-naphthalene-sulfonic acid	Azo dyes
395. 1-Naphthylamine-6-sulfonic acid **Cleve's β-acid**		Reduction of the corresponding nitro-naphthalenesulfonic acid	Disazo dyes
396. 1-Naphthylamine-7-sulfonic acid **Cleve's Delta acid**		Reduction of the corresponding nitro-naphthalenesulfonic acid	Disazo dyes
397. 1-Naphthylamine-8-sulfonic acid **Schöllkopf's acid**		Reduction of corresponding nitro-naphthalenesulfonic acid	Azo dyes
398. 2-Naphthylamine-1-sulfonic acid **Tobias acid**		Heating sodium-2-naphthol-1-sulfonate with NH_4HSO_3 and NH_3 in an autoclave	Monoazo dyes (see Chapter 28, p. 1117)
399. 2-Naphthylamine-5-sulfonic acid **Dahl's acid**		Sulfonation of β-naphthylamine at low temperatures	Azo dyes

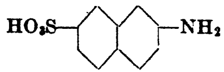
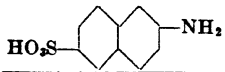
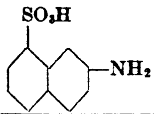
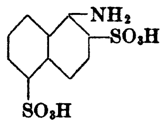
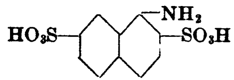
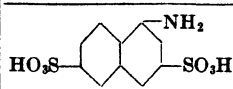
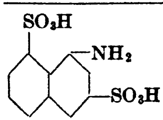
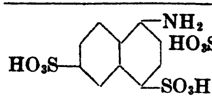
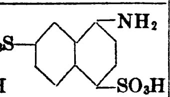
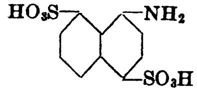
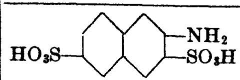
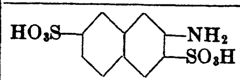
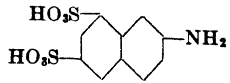
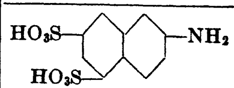
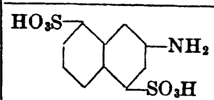
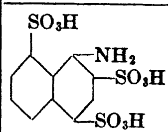
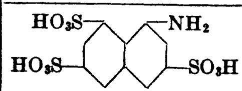
400. 2-Naphthylamine-7-sulfonic acid **Amido-F-acid** **Bayer's acid** **F acid** **Cassella's acid**		Heating β-naphtholsulfonic acid with NH_4OH in an autoclave	Azo dyes
401. 2-Naphthylamine-6-sulfonic acid **Broenner's acid**		Heating the sodium salt of Schäffer's acid with ammonia under pressure	Azo dyes
402. 2-Naphthylamine-8-sulfonic acid **Badische acid**		Heating β-naphthylamine with conc. H_2SO_4 at 100°	Azo dyes
403. 1-Naphthylamine-2,5-disulfonic acid **Landshoff and Meyer acid**		Sulfonation of 1-naphthylamine-2-sulfonic acid with fuming H_2SO_4	Azo dyes
404. 1-Naphthylamine-2,7-disulfonic acid **Kalle's acid**		Heating 1-naphthylamine-2,4,7-trisulfonic acid with H_2O under pressure	Azo dyes
405. 1-Naphthylamine-3,6-disulfonic acid **Freund's acid**		Reduction of 1-nitro-3,6-naphthalenedisulfonic acid	Disazo dyes
406. 1-Naphthylamine-3,8-disulfonic acid **Epsilon acid**		Reduction of the corresponding nitronaphthalenedisulfonic acid	Azo dyes
407. 1-Naphthylamine-4,6-disulfonic acid 1-Naphthylamine-4,7-disulfonic acid **Dahl's acid II** **Dahl's acid III**	 II  III	Sulfonation of naphthionic acid	Azo dyes

TABLE 10—NAPHTHALENE DERIVATIVES—*Continued*

Name	*Formula*	*Preparation*	*Uses*
408. 1-Naphthylamine-4,8-disulfonic acid **Delta acid**		Heating naphthionic acid with fuming H_2SO_4	Azo dyes
409. 2-Naphthylamine-3,6-disulfonic acid **Amido R acid**		Heating R acid with ammonia and ammonium bisulfite under pressure	Azo dyes
410. 2-Naphthylamine-3,7-disulfonic acid **Disulfoacid F**		Heating β-naphtholdisulfonic acid with NH_4OH under pressure	Azo dyes
411. 2-Naphthylamine-6,8-disulfonic acid **Amido G acid**		Heating the sodium salt of G acid with ammonia and $NaHSO_3$ under pressure	Azo dyes
412. 2-Naphthylamine-5,7-disulfonic acid		Sulfonation of β-naphthylaminesulfonic acid	J acid
413. 2-Naphthylamine-4,8-disulfonic acid **Disulfoacid C**		Reduction of 2-nitro-4,8-naphthalenedisulfonic acid	Azo dyes
414. 1-Naphthylamine-2,4,8-trisulfonic acid **Naphsultamdisulfonic acid S**		Heating 1-naphthylamine-8-sulfonic acid with fuming H_2SO_4	Azo dyes
415. 1-Naphthylamine-3,6,8-naphthalenetrisulfonic acid **Koch's acid** **Amido H acid**		Reduction of 1-nitronaphthalene-3,6,8-trisulfonic acid	H acid, azo dyes

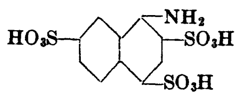
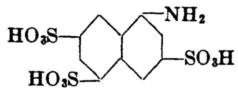
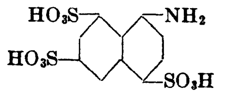
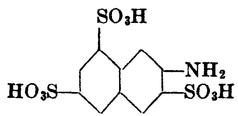
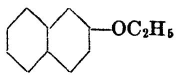
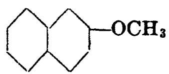
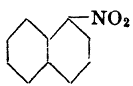
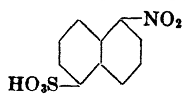
416. 1-Naphthylamine-2,4,7-trisulfonic acid		Heating naphthionic acid with fuming H_2SO_4	Azo dyes
417. 1-Naphthylamine-3,5,7-trisulfonic acid		Reduction of corresponding nitronaphthalenetrisulfonic acid	Azo dyes
418. 1-Naphthylamine-4,6,8-trisulfonic acid		Nitration of naphthalene-1,3,5-trisulfonic acid and subsequent reduction	K acid
419. 2-Naphthylamine-3,6,8-trisulfonic acid		Heating β-naphthol-3,6,8-trisulfonic acid with NH_4OH under pressure	Azo dyes
420. β-Naphthyl ethyl ether **Nerolin**		Action of diethyl sulfate on β-naphthol	Perfumery and flavoring
421. β-Naphthyl methyl ether **Yara-Yara**		Action of dimethyl sulfate on β-naphthol	Perfumery, flavoring
422. α-Nitronaphthalene		Nitration of naphthalene	α-Naphthylamine, dyes
423. 1-Nitro-5-naphthalenesulfonic acid **α- or Laurent's acid**		Sulfonation of α-nitronaphthalene with fuming H_2SO_4	1-Naphthylamine-5-sulfonic acid

TABLE 10—NAPHTHALENE DERIVATIVES—*Concluded*

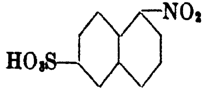
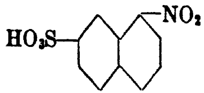
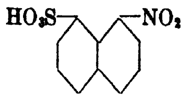
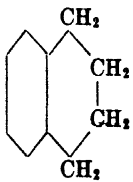
Name	*Formula*	*Preparation*	*Uses*
424. 1-Nitro-6-naphthalenesulfonic acid **Cleve's β-acid**		Nitration of β-naphthalenesulfonic acid	1-Naphthylamine-6-sulfonic acid
425. 1-Nitro-7-naphthalenesulfonic acid **Cleve's delta acid**		Nitration of β-naphthalenesulfonic acid	1-Naphthylamine-7-sulfonic acid
426. 1-Nitro-8-naphthalenesulfonic acid		Nitration of α-naphthalenesulfonic acid	1-Naphthylamine-8-sulfonic acid
427. Tetrahydronaphthalene **Tetralin**		Catalytic reduction of naphthalene	Solvents for oils, fats and greases, in soaps used for textile processes, motor fuel

TABLE 11—ANTHRACENE DERIVATIVES

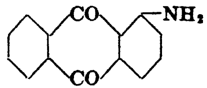
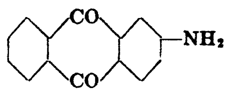
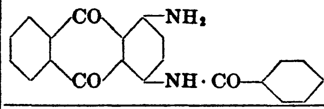
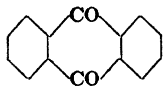
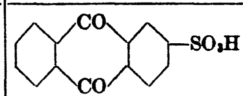
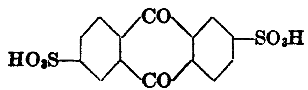
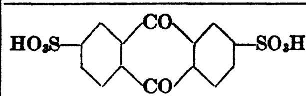
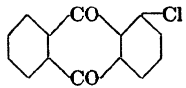
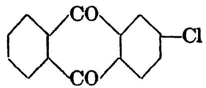
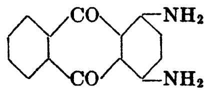
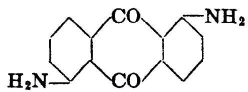
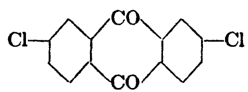
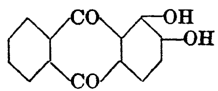
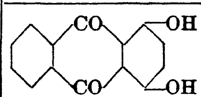
Name	Formula	Preparation	Uses
428. 1-Aminoanthraquinone		Action of ammonia on the sodium salt of 1-anthraquinonesulfonic acid under pressure	Anthraquinone dyes
429. 2-Aminoanthraquinone		Action of ammonia on sodium-2-anthraquinonesulfonate under pressure	Anthraquinone dyes
430. 1-Amino-4-benzoylaminoanthraquinone		Heating 1,4 - diaminoanthraquinone with benzoyl chloride	Anthraquinone dyes
431. Anthracene		From anthracene oil fraction of coal tar (see Chapter 16, p. 664)	Anthraquinone and derivatives
432. Anthraquinone		Action of anthracene and chromic acid or from dehydration of o-benzoylbenzoic acid, or by the catalytic air oxidation of anthracene	Anthraquinone dyes
433. Anthraquinone-2-sulfonic acid Na salt known as "Silver salt"		Sulfonation of anthraquinone with fuming H_2SO_4 at 160°	Anthraquinone dyes
434. Anthraquinone-2,6-disulfonic acid *α*-anthraquinonedisulfonic acid		Heating anthraquinone with fuming H_2SO_4	Anthraquinone dyes
435. Anthraquinone-2,7-disulfonic acid *β*-anthraquinonedisulfonic acid		Heating anthraquinone with fuming H_2SO_4	Anthraquinone dyes

TABLE 11—ANTHRACENE DERIVATIVES—*Concluded*

Name	*Formula*	*Preparation*	*Uses*
436. 1-Chloroanthraquinone		Chlorination of potassium anthraquinone-1-sulfonate	Anthraquinone dye
437. 2-Chloroanthraquinone		Chlorination of sodium anthraquinone-2-sulfonate	Anthraquinone dye
438. 1,4-Diaminoanthraquinone		Reduction of 1-nitro-4-aminoanthraquinone with Na_2S	Anthraquinone dyes
439. 1,5-Diaminoanthraquinone		Reduction of 1,5-dinitroanthraquinone	Anthraquinone dyes
440. 2,7-Dichloroanthraquinone		Action of $NaClO_3$ and HCl on anthraquinone-2,7,-disulfonic acid	Anthraquinone dyes
441. 1,2-Dihydroxyanthraquinone **Alizarin**		Fusion of β-anthraquinonesulfonic acid with NaOH and $KClO_3$ and subsequent acidification	Substituted alizarins and dyes
442. 1,4-Dihydroxyanthraquinone **Quinizarin**		Condensation of *p*-chlorophenol with phthalic anhydride in H_2SO_4 solution in presence of boric acid	Anthraquinone dyes

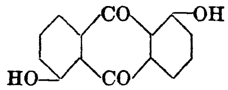
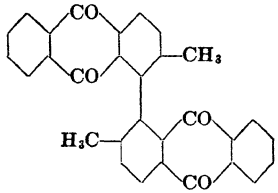
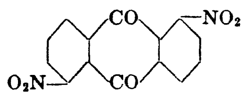
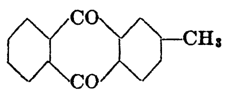
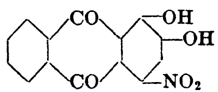
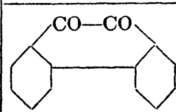
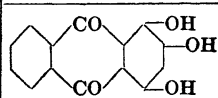
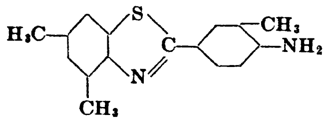
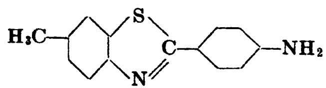
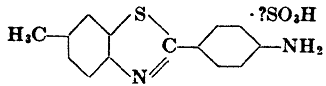
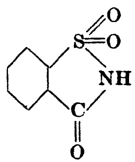
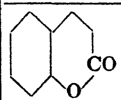
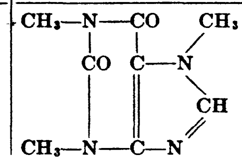
443. 1,5-Dihydroxyanthraquinone **Anthrarufin**		Action of $Ca(OH)_2$ on anthraquinone-1,5-disulfonic acid	Anthraquinone dyes
444. 2,2-Dimethyl-1,1-bianthraquinone		Diazotizing 1-amino-2-methylanthraquinone and subsequently treating with acetic acid and Cu powder	Anthraquinone dyes
445. 1,5-Dinitroanthraquinone		Nitration of anthraquinone	Anthraquinone dyes
446. 2-Methylanthraquinone		Condensation of phthalic anhydride and toluene in presence of $AlCl_3$ and subsequently heating with H_2SO_4	Anthraquinone dye
447. 4-Nitroalizarin		Nitration of esters of alizarin	Anthraquinone dyes
448. Phenanthraquinone		Oxidation of phenathrene with chromic acid	Flavinduline dye
449. Purpurin		Oxidation of alizarin with MnO_2 and H_2SO_4	Anthraquinone dyes

TABLE 12—HETEROCYCLIC COMPOUNDS

Name	*Formula*	*Preparation*	*Uses*
450. 1-(*p*-Amino-*m*-methylphenyl)-3,5-dimethyl benzothiazole **Dehydro-thio-*m*-xylidine**		Heating *m*-xylidine with sulfur	Azo and thiobenzenyl dyes
451. 1-(*p*-Aminophenyl)-5-methyl-benzothiazole **Dehydro-thio-*p*-toluidine**		Heating *p*-toluidine with sulfur	Azo and thiobenzenyl dyes
452. 1-(4-Amino-?-sulfophenyl)-5-methylbenzothiazole **Dehydro-thio-p-toluidine-sulfonic acid**		Sulfonation of the primuline melt (from *p*-toluidine and sulfur)	Stilbene, azo and thiobenzenyl dyes
453. *o*-Benzoic sulfimide **Saccharin**		Oxidation of *o*-toluenesulfonamide and the subsequent removal of H_2O	Sweetening agent
454. Benz-α-pyrone **Coumarin**		Heating salicylaldehyde with sodium acetate and acetic anhydride	Flavors and perfumery
455. **Caffeine**		Methylation of theobromine	Medicine, soft drinks

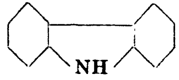
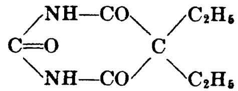
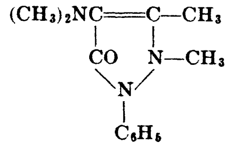
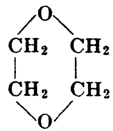
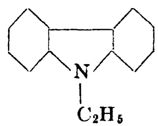
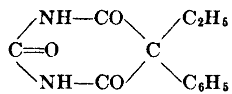
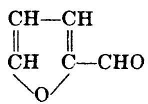
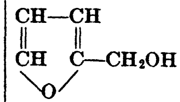
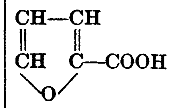
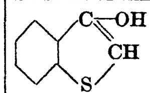
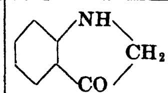
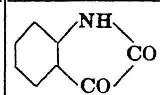
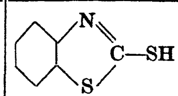
456. Dibenzopyrrole **Carbazole**		Extraction from anthracene oil fraction of coal tar	Hydron blue dye, N-ethylcarbazole
457. **Diethyl malonyl urea** **Veronal** **Barbital**		Condensation of urea with diethyl malonic ester under pressure	Hypnotic and analgesic
458. 4-Dimethylamino-1-phenyl-2,3-dimethyl pyrazolone **Pyramidon**		Antipyrine is converted into its nitroso derivative and subsequently to its amino compounds. Methylation with methyl chloride produces pyramidon	Antipyretic and analgesic
459. **1,4-Dioxan**		Polymerization of ethylene oxide	Solvent for cellulose acetate, dyes, fats, ethyl cellulose, vegetable and mineral oils
460. **N-Ethylcarbazole**		Action of diethyl sulfate on potassium carbazole	Hydron blue dyes
461. Ethyl phenyl malonyl urea **Luminal** **Phenobarbital**		Condensation of urea with ethyl phenyl malonic ester	Hypnotic and analgesic in medicine
462. **Furfural**		Hydrolysis of pentosans contained in natural-occurring substances such as corn-cobs, straw, etc.	Synthetic resins and plastics, organic syntheses, solvent, rubber accelerator, insecticide (see Chapter 31, p. 1465)

TABLE 12—HETEROCYCLIC COMPOUNDS—*Continued*

Name	*Formula*	*Preparation*	*Uses*
463. **Furfuramide**	$(C_5H_4O)_3N_2$	Treatment of furfural with ammonia	Antioxidant in rubber, fungicide
464. **Furfuryl alcohol**		Furfural treated with NaOH (see Furoic acid)	Resin solvent, organic syntheses, dispersant for textile dyes
465. **Furoic acid**		Furfural treated with NaOH yields furfuryl alcohol and the sodium salt of furoic acid	Solvent for cellulose nitrate, fungicide, bactericide, preparation of its esters
466. **2-Hydroxythionaphthene Thioindoxyl**		Heating phenyl thioglycolic-*o*-carboxylic acid with NaOH solution and subsequent heating of product with acid thereby eliminating CO_2	Indigoid dyes
467. **Indoxyl**		Fusion of phenylglycine with $NaNH_2$	Indigo and Ciba colors
468. **Isatin**		Oxidation of indoxyl	Indigo dyes
469. **Mercaptobenzo-thiazole Captax**		Heating thiocarbanilide and sulfur in an autoclave	Accelerator

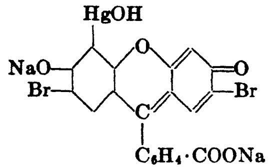
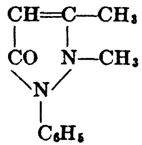
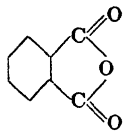
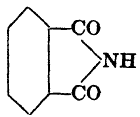
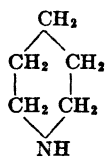
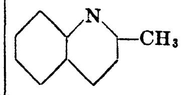
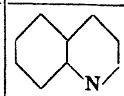
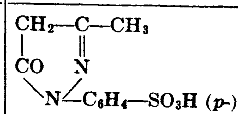
470. **Mercurochrome**		Boiling the sodium salt dibromofluorescein with mercuric acetate	Germicide
471. **1-Phenyl-2,3-dimethyl-5-pyrazolone Antipyrine**		Phenylmethylpyrazolone is methylated with CH_3Cl in an autoclave	Analgesic and antipyretic
472. **Phthalic anhydride**		Passing naphthalene vapor and air over a catalyst	Organic syntheses, anthraquinone, dyes, etc. Synthetic resins (see Chapter 31, p. 1213)
473. **Phthalimide**		Passing ammonia gas into molten phthalic anhydride	Anthranilic acid
474. **Piperidine**		Reduction of pyridine	Organic syntheses
475. **Piperidine pentamethylene dithiocarbamate**	$C_5H_{10}N—CS—SNH_2C_5H_{10}$	Reaction of piperidine with CS_2	Rubber accelerator

TABLE 12—HETEROCYCLIC COMPOUNDS—*Concluded*

Name	*Formula*	*Preparation*	*Uses*
476. Pyridine		Distillation of "light oil" fraction of coal tar (see Chapter 16)	Denaturant for alcohol, solvent, organic syntheses
477. Quinaldine		Condensation of aniline and paraldehyde in presence of conc. HCl	Quinoline dyes
478. Quinoline		Coal tar or heating a mixture of aniline, nitrobenzene, glycerol and H_2SO_4 (Skraup's reaction)	Quinoline dye, rubber accelerator, organic syntheses
479. 1-(*p*-Sulfophenyl)-3-methyl-5-pyrazolone		Heating phenylhydrazine-*p*-sulfonic with acetoacetic ester	Pyrazolone dyes
480. Abietic acid	$C_{19}H_{28}O_2$	Purified from rosin (see Chapter 17, p. 692)	Preparation of esters, paints and varnishes (see Chapter 31, p. 1205)

READING LIST

Barnett, E. B., "Coal Tar Dyes and Intermediates," D. Van Nostrand Co., Inc., New York (1919).
Bernthsen, A., "A Textbook of Organic Chemistry," D. Van Nostrand Co., Inc., New York (1931).
Cain, J. C., and Thorpe, J. F., "Synthetic Dyestuffs and Intermediate Products for Dyes," C. Griffin and Co., Ltd., London (1933).
"Census of Dyes and Other Synthetic Organic Chemicals," Government Printing Office, Washington, D. C.
Egloff, G., "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York (1937).
Ellis, C., "The Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., New York (1937).
Groggins, P. H., "Aniline and Its Derivatives," D. Van Nostrand Co., Inc., New York (1924).
Groggins, P. H., "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., New York (1938).
Martin, G., "Industrial and Manufacturing Chemistry: A Practical Treatise," D. Appleton and Co., New York (1921).
Read, W. T., "Industrial Chemistry," John Wiley and Sons, Inc., New York (1938).
Richter, V., "Organic Chemistry," P. Blakiston's Son and Co., Philadelphia (1938-).
Riegel, E. R., "Industrial Chemistry," Reinhold Publishing Corp., New York (1937).
Rowe, F. M., "Colour Index," Society of Dyers and Colorists, England (1924).
Sadtler, S. P., and Matos, L. J., "Handbook of Industrial Organic Chemistry," J. B. Lippincott Co., Philadelphia (1923).
Shreve, R. N., "Dyes Classified by Intermediates," The Chemical Catalog Co., Inc., New York (1922).
Thorpe, T. E., "Outlines of Industrial Chemistry," The Macmillan Co., London (1918).
Thorpe, T. E., "A Dictionary of Applied Chemistry," Longmans, Green and Co., New York (1937-1939).
Ullmann, F., "Enzyklopadie der Technischen Chemie," Urban and Schwartzenberg, Berlin (1914-1923).
Whitmore, F. C., "Organic Chemistry," D. Van Nostrand Co., Inc., New York (1937).

CHAPTER 28

MANUFACTURE OF INTERMEDIATES AND DYES

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Dyes interest us frequently because of their influence on the improvement in appearance and salability of a great many other products. By and large we *could* dispense with dyes but we would thereby revert to an almost primitive state in many of our activities and with many of the products that we use. In some very important cases, dyes could not be dispensed with as they perform most essential functions. Examples of this are the employment of dyes for stains in microscopy leading to the identification of pathogenic organisms, the antiseptic application of such medicinal dyes as Acriflavine, Methylene Blue and Iodeikon; the use of such dyes as Methyl Violet and Crystal Violet in typewriter ribbons and carbon papers; the employment of various dyes in writing and printing inks; the transforming of light energy by dyes as the basis of panchromatic photography and special processes such as infra-red photography; and finally the making of colored photographs, colored prints and all the various dyed or pigmented reproductions.

ECONOMIC ASPECTS

In 1914 it was calculated that the industries making products valued at $2,631,390,000 were directly dependent on dyestuffs.[1] The corresponding summation for 1931 was $4,772,088,000 and for 1939 $6,624,125,000. The industries included are: dyeing and finishing of textiles, such as cotton, silk, wool and rayon; the dyeing of hats, rugs, mats and leather; the making of pigments, paints, varnishes and inks; the tinting of paper, perfumery and cosmetics; the coloring of feathers and furs, and many other substances. By picturing to ourselves the kind of a world we would live in with the dyes absent, we can get a clearer concept as to what this class of compounds means to us in the ordinary contacts of life.

Growth of the Industry—Prior to 1914 the small but important dye manufacturers made less than 10% of the dyes needed for the American industries. So, when the war of 1914-18 cut off importations there was almost a panic among the various dye-consuming industries. However, American chemists and chemical engineers, supported by business men rallying around the small nucleus of dye manufacturers already in America supplemented by a number of new endeavors, soon greatly increased the production of American-made dyes and gradually overcame the deficiency until, in a few years even after the resumption

[1] Stine, C. M. A., Ind. Eng. Chem., *25*, 489 (1933).

of international trade, America was making more than 90% of the dyes she consumed. This is also the present-day situation. Furthermore, while imports of some patented or small volume dyes are less than 10% of total consumption, the American manufacturer is exporting a larger tonnage and a larger value of certain dyes like indigo that he has learned to manufacture on such a large scale and so economically that he competes in the world markets.

So we may well say that the value of dyes and intermediates in our modern technical civilization is greatly in excess of the dollars and cents values such as are presented in the summary of dyes and intermediates and related products in Table 1.

TABLE 1—INTERMEDIATES, DYES, AND CERTAIN OF OTHER CLASSES OF COAL-TAR CHEMICALS: COMPARISON OF UNITED STATES PRODUCTION AND SALES, AVERAGE 1925-30, ANNUAL 1936-40

(Production and sales in thousands of pounds, value in thousands of dollars)*

Product	*Average 1925-30*	*1936*	*1937*	*1938*	*1939*	*1940*
Intermediates:						
Production	267,492	509,706	575,893	401,943	607,175	805,807
Sales	109,133	223,119	242,194	171,514	269,084	315,967
Sales value	22,408	31,806	35,639	26,090	38,489	46,428
Finished coal-tar prods.:						
Production	138,078	336,348	373,063	276,387	437,867	522,850
Sales	133,964	287,276	315,742	245,340	353,604	402,324
Sales value	65,027	120,765	128,736	104,372	146,156	171,427
Dyes:						
Production	94,003	119,523	122,245	81,759	120,191	127,834
Sales	92,207	117,573	118,046	87,803	114,494	122,677
Sales value	39,428	63,686	64,613	53,096	70,224	76,432
Medicinals:						
Production	4,508	12,034	14,800	11,097	15,188	18,208
Sales	4,106	10,079	11,989	8,885	12,932	15,004
Sales value	7,464	9,763	11,496	9,509	13,711	17,511
Flavors and perfume materials:						
Production	3,966	3,481	4,356	3,837	5,349	5,490
Sales	3,919	3,437	3,907	3,664	4,938	5,067
Sales value	2,901	3,220	3,983	3,368	4,447	4,759
Resins:						
Production	24,442	117,302	142,025	106,923	179,338	222,943
Sales	22,135	86,214	109,201	84,764	128,420	153,521
Sales value	7,756	17,056	20,582	15,811	23,028	33,378

* U. S. Tariff Commission, Synthetic Organic Chemicals, U. S. Production and Sales, Report No. 140, 1939.
1940 figures taken from Preliminary Report, June 1941.

Very closely connected with the manufacture of intermediates and dyes is that of a number of other allied chemical industries, for by using the same intermediates, a given series of reactions makes dyes, another series makes medicinal products or perfumes or flavoring materials and particularly in recent years the various plastic products. This is the reason that the U. S. Tariff Commission yearly reports the production of these so closely connected industries with that of intermediates and dyes, as depicted in this table.

The picture of accomplishments represented by Table 1* was only attained after a very great expenditure for research and development on the fundamental chemistry of the reactions leading to intermediates and then to dyes, as well as on the equipment necessary to carry out these reactions on a commercial scale. Particularly in this latter field did the genius of the American chemical engineer exhibit itself in the daring required to carry out the intricate nitrations, sulfonations and oxidations and the like,[2] on a larger scale than elsewhere in the world prior to the American entrance into the manufacture of intermediates and dyes. Even now, the American manufacturers are spending between four and five cents out of every sales dollar for further improvements in procedure, plant and application. Such a proportion amounts to two or three million dollars each year. While this expenditure has not resulted in many new dyes, it has led to new and

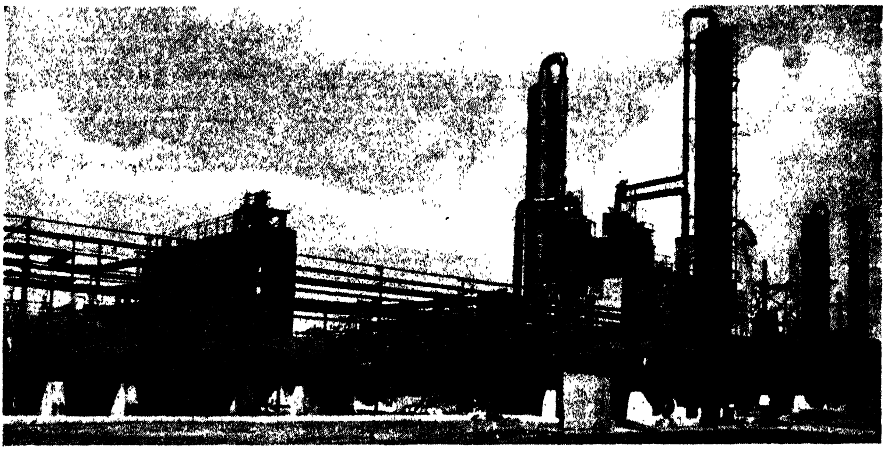


FIG. 1. Coal-tar Distillation Plant. At right, towers for rectifying of naphthalene, phenol, and anthracene. (Courtesy Calco Chemical Co.)

improved processes and equipment for the manufacture of many intermediates, with a consequent considerable reduction in cost of the finished dyes and related products. For instance, the controlled air oxidation of naphthalene to phthalic anhydride has not only lessened the cost of the dyes dependent upon phthalic anhydride, such as Eosin, but has led to new and cheaper processes for making anthraquinone dyes, as well as plasticizers, solvents and resins based upon phthalic anhydride. Finally, competition between the various dye manufacturers has caused this saving to be passed on to the ultimate consumer, so that now we may say that the American public is the beneficiary of the American dye industry wherein they are getting dyes of the same or superior purity and properties such as fastness, as they did when these were imported,—and at a less cost!

RAW MATERIALS

The sequence of dye manufacture is from the basic coal-tar hydrocarbons, such as benzene, toluene, xylene, naphthalene, anthracene and carbazole which are changed by virtue of chemical reactions into five hundred or more intermediate

[2] For a discussion of these various processes, see Chapter 3.

products. These intermediate products are then subjected to about a dozen further chemical reactions whereby they are built up into the complexes we recognize as dyes. Frequently the named basic coal-tar hydrocarbons are called *crudes* because in the initial start of the dye industry, 85 years ago, such products

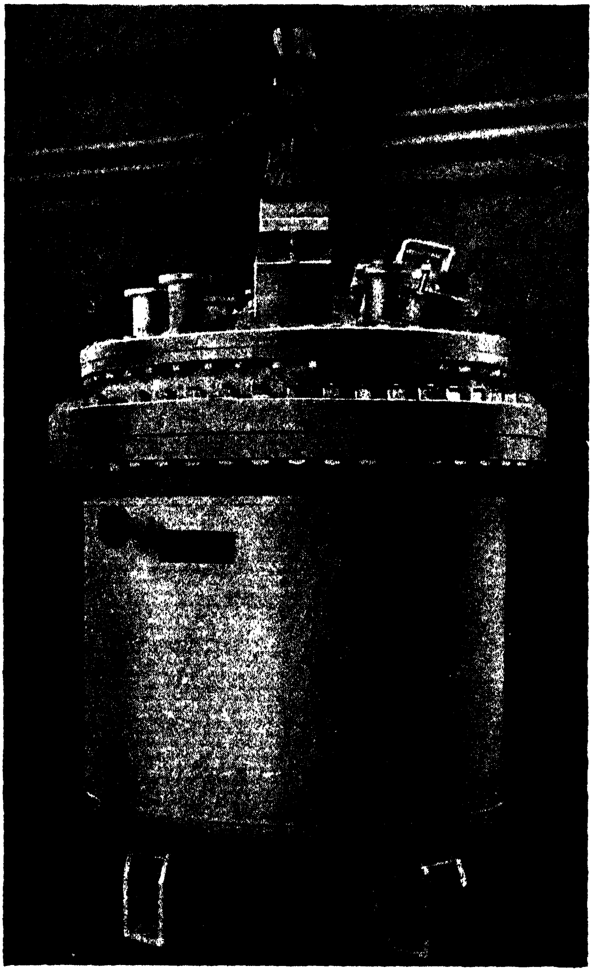


FIG. 2. Cast Iron Steam-jacketed Sulfonator. 600 gal. capacity. Welded steel jacket for 125 lbs. steam at 450 deg. F. (Courtesy J. P. Devine Co.)

were not pure; indeed they were mixtures. Due to the present skill of the coal-tar distiller these basic hydrocarbons are now exceedingly pure materials for the low price at which they sell and it is suggested that the term *crudes* as applied to these be abandoned.

To commercialize the various unit processes necessary to fabricate either the intermediates or the dyes, there is required a very considerable tonnage of other chemicals such as acids, alkalies of different strengths, as well as halogens and different salts. Indeed for some of the more complicated dyes as much as 75 to 100 pounds of miscellaneous inorganic chemicals are necessary to make one pound of the finished dye.

INTERMEDIATES

The intermediate products between the basic raw materials and the finished dyes are the backbone of any dye industry and indeed they are a strong support for a number of other industries as well. It was only after there had been worked out the conditions and equipment necessary for the manufacture of these inter-

FIG. 3. Reaction Kettles. Pilot Plant for Intermediates. (Courtesy Monsanto Chemical Co.)

mediates here that the foundations were laid for a domestic dye industry. While a number of serious efforts had been made to manufacture intermediates and dyes here in America, at the start of 1914 the only intermediates[3] produced in quantity were nitrobenzene, aniline, nitrotoluene, toluidine and nitronaphthalene. A great deal of money was spent upon solving the chemical and engineering problems necessary to make these economically. The triumphs in this field have, however, been noteworthy, in that now in America more than 500 intermediates are made on a commercial scale and enter into the manufacture of dyes and related products.

At first glance, this all seems like a complicated picture, but if we bear in mind that only a dozen or so commercialized chemical reactions or unit processes act either alone or in sequence on the basic raw materials to convert them into the intermediates, we can bring some kind of order into this picture. For

[3] Weiss, J. M., Chem. Industries, *46*, 687-92 (1940).

example, when benzene is nitrated, nitrobenzene results which upon reduction gives aniline, which upon sulfonation furnishes sulfanilic acid. Now the nitrobenzene, or the aniline, or the sulfanilic acid are employed as one of the stepping

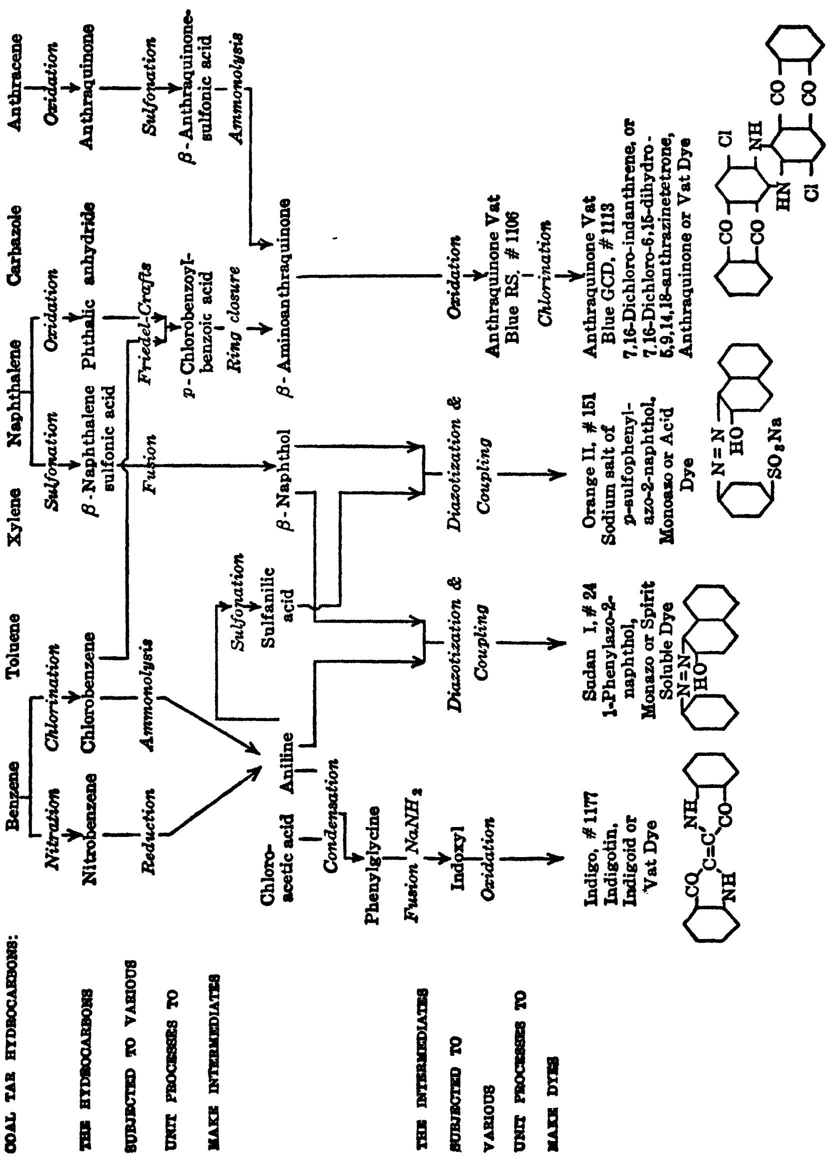


FIG. 4. Sequence of Dye Manufacture from Coal Tar Hydrocarbons.

stones to the finished dye. Similarly, naphthalene can be mono-, di-, or trisulfonated and, under varying conditions, to give different isomers. If we make first naphthalene-1,3,6-trisulfonic acid, this can be nitrated and reduced to furnish 1-naphthylamine-3,6,8-trisulfonic acid (Koch acid). This itself can be fused to form 1-amino-8-naphthol-3,6-disulfonic acid (H acid). It is really by multiplicity of these unit processes, either individually or in sequence, that we can make the chemical change necessary to give the desired intermediate product. The amazing part in all this is that the chemists and chemical engineers are able to carry out these processes to give, as a rule, good yields of exceedingly pure intermediate products, and at a low cost.

Outline of Steps of Manufacture—To better present this picture and to lead into the next step, namely, the making of the dyes themselves, and to begin to show their relationship to the intermediates, Figure 4 is presented, wherein the course is charted leading from the basic coal-tar hydrocarbons through the intermediates to the finished dyes. The six basic coal-tar hydrocarbons, by a sequence of the chemical changes using various acids, alkalies and other chemicals, furnish the 500 intermediates and these, subjected to a relatively few chemical changes, furnish the thousand dyes which are used commercially. Many other thousands of dyes have been made and discarded in the laboratories as not having properties competitive with the thousand-odd ones which have met commercial acceptance. The allied industries, as depicted in Table 1, obtain different products by a different set of chemical changes. For instance, phenol and formaldehyde, by their polymerization, lead up to the bakelite or phenol-formaldehyde resins which are sold in such quantities and which were the stimulating incentive for the investigation and commercialization of a good many other resins and plastics.

To bring some order among these 500 intermediates, Table 2 has been prepared which classifies the most important of the intermediates under the principal unit process involved in its manufacture. This table, containing only a small portion of the intermediates [4] reported, will emphatically show the breadth and variety of the reactions used to make the intermediate products needed. A short description following each intermediate will serve to indicate the usual chemical procedure involved in its manufacture, epitomizing the unit process involved. Of course in such a table the byproducts are omitted. It should be noted in considering any of these reactions that by starting with pure raw materials and by purifying as the reactions proceed, the desired product is furnished with a surprisingly low degree of impurities.

TABLE 2—SOME IMPORTANT INTERMEDIATES * CLASSIFIED BY UNIT PROCESSES †

Nitration

Chloro-2,4-dinitrobenzene, from chlorobenzene through *o*- and *p*-Chloronitrobenzenes, by strong mixed acid.

o- and *p*-Chloronitrobenzene, from chlorobenzene by mixed acid. Separate by distillation and crystallization.

Dinitrobenzene, from benzene through nitrobenzene by strong mixed acid.

p-Nitroacetanilide and *p*-Nitroaniline, from acetanilide by cold mixed acid nitration. Hydrolysis furnishes *p*-nitroaniline.

Nitrobenzene, from benzene by mixed acid.

Nitro-2,5-dichlorobenzene, from *p*-dichlorobenzene by mixed acid.

α-Nitronaphthalene, from naphthalene by mixed acid.

o- and *p*-Nitrophenol, from phenol by nitric or mixed acid. Separate by steam distillation. (*Cf.* Hydrolysis.)

* Formulae and further descriptions of these and other intermediates will be found in Chapter 27.

† For a description of the principles of the various unit processes see Chapter 3.

[4] Table VII, Coal Tar Intermediates, U. S. Production and Sales, 1939, Report No. 140, U. S. Tariff Commission, Washington, 1940.

TABLE 2—SOME IMPORTANT INTERMEDIATES CLASSIFIED BY UNIT PROCESSES—*continued*

Nitration

o- and *p*-Nitrotoluene, from toluene by mixed acid at moderate temperature to lessen oxidation. Separate by distillation and crystallization.

m-Nitro-*p*-toluidine, from *p*-toluidine by mixed acid at low temperature.

Amination by Reduction

Acetyl-*p*-phenylenediamine, from *p*-nitroacetanilide by iron and acetic acid under 60° C.

α-Aminoanthraquinone, from *α*-nitroanthraquinone by Na_2S solution.

p-Aminophenol, from nitrosophenol by aqueous Na_2S.

o-Aminophenol-*p*-sulfonic acid, from *o*-nitrophenol-*p*-sulfonic acid by Na_2S following sulfonation, nitration and hydrolysis of chlorobenzene.

Aniline, from nitrobenzene by iron and a little dilute HCl.

Chlorotoluidine-sulfonic acid, from *o*-chlorotoluene-*p*-sulfonic acid by nitration and subsequent iron reduction.

Diaminostilbene-disulfonic acid, from dinitrostilbene-disulfonate by alkaline zinc reduction.

Diaminoanthraquinone, from corresponding dinitro- or aminonitroanthraquinone by reduction, or from corresponding dichloro-, disulfo-, or dihydroxyanthraquinone by ammonolysis.

2,5-Dichloroaniline and sulfonic acid, from nitro-2,5-dichlorobenzene by iron and a little aqueous HCl. Sulfonation.

Hydrazoanisole and rearrangement to dianisidine, from *o*-nitroanisole by alkaline zinc reduction in alcoholic solution, followed by acid rearrangement.

Hydrazobenzene and rearrangement to benzidine, from nitrobenzene by alkaline reduction by Fe or Zn, followed by acid rearrangement.

Hydrazotoluene and rearrangement to tolidine, from *o*-nitrotoluene by alkaline reduction by Zn followed by acid rearrangement.

Metanilic acid, from nitrobenzene-*m*-sulfonic acid, following oleum sulfonation of nitrobenzene.

α-Naphthylamine, from *α*-nitronaphthalene by iron and a little dilute HCl.

m-Nitroaniline, from dinitrobenzene by hot aqueous sodium polysulfide.

m-Phenylenediamine, from dinitrobenzene by iron and a little dilute HCl.

p-Phenylenediamine, from *p*-nitroaniline by iron and a little dilute HCl, boiling at the end.

Picramic acid, from picric acid by hot sodium polysulfide solution.

Toluidines, from nitrotoluenes by iron and a little dilute HCl.

m-Tolylenediamine, from *m*-dinitrotoluene by iron and a little dilute HCl.

Xylidines, from nitroxylenes by iron and a little dilute HCl.

Amination by Ammonolysis

β-Aminoanthraquinone, from *β*-chloroanthraquinone by excess of 28% aqueous ammonia at 200° C. in a stirred autoclave, or from *β*-anthraquinonesulfonate by excess ammonia water.

Aniline, from chlorobenzene by excess 28% aqueous ammonia at 200° C. and 900 lbs. pressure, in presence of Cu_2O.

β-Naphthylamine, from beta-naphthol by excess of 28% ammonia catalyzed by ammonium sulfite, at 150° C. in a stirred autoclave.

2-Naphthylamine-1-sulfonic acid (Tobias acid), from 2-naphthol-1-sulfonic acid by excess ammonia water and ammonium sulfite at 150° C. in an autoclave.

2-Naphthylamine-6-sulfonic acid (Bronner's acid), from sodium salt of 2-naphthol-6-sulfonic acid (Schaeffer's acid) by 28% NH_3 at 180° C. in an autoclave.

2-Naphthylamine-6,8-disulfonic acid (amino-G acid), from 2-naphthol-6,8-disulfonate by heating with ammonia and sodium bisulfite in an autoclave.

p-Nitroaniline, from *p*-chloronitrobenzene by excess of 28% aqueous ammonia at 170° C. and 500 lbs. pressure.

Phthalimide, from molten phthalic anhydride by gaseous NH_3 at 240° C.

TABLE 2—SOME IMPORTANT INTERMEDIATES CLASSIFIED BY UNIT PROCESSES—*continued*

Halogenation

Chloracetic acid, from glacial acetic acid by passing in chlorine at 100° C. in presence of red phosphorus.

Chlorobenzene, from benzene by action of Cl_2 in presence of iron at 50-60° C.

p-Dichlorobenzene, from benzene or chlorobenzene by action of Cl_2 in presence of iron at 50-60° C.

2,6-Dichlorobenzaldehyde, from *o*-nitrotoluene by ortho ring chlorination by Cl_2 followed by reduction, diazotization and the Sandmeyer reaction, giving 2,6-dichlorotoluene, which upon side chain chlorination furnishes 2,6-dichlorobenzyl chloride, which hydrolyzes to 2,6-dichlorobenzaldehyde.

Sulfonation

1-Amino-2-naphthol-4-sulfonic acid, from 1-nitroso-2-naphthol by joint reducing and sulfonating action of sodium bisulfite.

Benzenesulfonic acid, by passing hot benzene vapor through sulfuric acid until all sulfuric acid reacted.

β-Naphthalenesulfonic acid, from naphthalene and 66° sulfuric acid at 160° C. The α-isomer simultaneously formed is hydrolyzed to naphthalene and removed by passing in steam.

Naphthionic acid, from α-naphthylamine and 66° sulfuric acid at 170-180° C.

2-Naphthol-6-sulfonic acid (Schaeffer's acid), from β-naphthol by 98% sulfuric acid at 100° C.

2-Naphthol-3,6-disulfonic acid (R acid), from β-naphthol by excess sulfuric acid at low temperatures and separation from G acid.

2-Naphthol-6,8-disulfonic acid (G acid), from β-naphthol by excess sulfuric acid at elevated temperature and separation from R acid.

1-Naphthylamine-5-sulfonic acid (Laurent's acid), from α-naphthylamine by oleum.

2-Naphthylamine-5,7-disulfonic acid, from β-naphthylamine by oleum sulfonation.

2-Naphthylamine-6,8-disulfonic acid (Amino-G acid), from β-naphthylamine by oleum sulfonation. *Cf. preceding and also Ammonolysis.*

1-Naphthylamine-3,6,8-trisulfonic acid (Koch acid), from naphthalene by trisulfonation with oleum, followed by nitration and iron reduction.

p-Nitrotoluene-*o*-sulfonic acid, from *p*-nitrotoluene by oleum.

Oxidation

Anthranilic acid, from phthalimide by alkaline hypochlorite.

Anthraquinone, from anthracene by chromic acid.

1,4-Dihydroxyanthraquinone (quinizarin), from anthraquinone by sulfuric acid oxidation in presence of boric acid.

Dinitrostilbene-disulfonic acid, from *p*-nitrotoluene by sulfonation and alkaline NaOCl oxidation.

Phthalic anhydride, from naphthalene by air oxidation at 425° C. in presence of vanadium pentoxide.

Alkylation

Benzylethylaniline (and sulfonic acid), from ethylaniline and benzyl chloride.

Diethylaniline, from aniline, ethyl alcohol and little HCl in an autoclave, or from aniline and diethyl sulfate.

Dimethylaniline, from aniline, methanol and little sulfuric acid at 200° C. in an autoclave.

o-Nitroanisole, from *o*-chloronitrobenzene by methanol and caustic soda.

Hydrolysis

1-Amino-8-naphthol-3,6-disulfonic acid (H acid), from 1-naphthylamine-3,6,8-trisulfonic acid by caustic soda fusion in an autoclave.

TABLE 2—SOME IMPORTANT INTERMEDIATES CLASSIFIED BY UNIT PROCESSES—*continued*

Hydrolysis

2-Amino-5-naphthol-7-sulfonic acid (J acid), from 2-naphthylamine-5,7-disulfonic acid by caustic soda fusion in an autoclave.

2-Amino-8-naphthol-6-sulfonic acid (Gamma acid), from 2-naphthylamine-6,8-disulfonic acid by caustic soda fusion in an autoclave.

1,5-Dihydroxyanthraquinone (anthrarufin), from anthraquinone-1,5-disulfonic acid by milk of lime.

1,8-Dihydroxynaphthalene-3,6-disulfonic acid (chromotropic acid), from 1-naphthol-3,6,8-trisulfonic acid by caustic soda fusion at 200° C.

2,4-Dinitrophenol, from chloro-2,4-dinitrobenzene by boiling with soda ash solution.

β-Naphthol, from purified β-naphthalenesulfonate (naphthalene and hot sulfuric acid) by caustic soda fusion.

α-Naphthol, from purified α-naphthalenesulfonate (naphthalene and cold sulfuric acid) by caustic soda fusion.

1-Naphthol-4-sulfonic acid (Nevile-Winther's acid), from sodium naphthionate.

p-Nitroaniline, from *p*-nitroacetanilide, by boiling with caustic soda solution.

o- or *p*-Nitrophenol, from *o*- or *p*-chloronitrobenzene by hot dilute NaOH solution.

Phenol from benzenesulfonate by caustic soda fusion at 320° C.

Phenol from chlorobenzene by caustic soda solution at 300° C., 5000 lbs. pressure.

Friedel & Crafts

Benzanthrone, from naphthalene, benzoyl chloride and $AlCl_3$, to α-benzoylnaphthalene to benzanthrone.

Benzoylbenzoic acid, from phthalic anhydride, benzene and aluminum chloride.

p-Chlorobenzoylbenzoic acid, from phthalic anhydride, chlorobenzene and aluminum chloride.

Acylation

Acetanilide, from aniline by heating with glacial acetic acid.

Acetyl-*p*-toluidine, from *p*-toluidine by heating with glacial acetic acid.

Carboxylation

β-Hydroxynaphthoic acid, from sodium β-naphtholate and CO_2 under pressure 200° C.

Salicylic acid, from sodium phenate and CO_2 under pressure and at 140° C.

Condensation

β-Hydroxynaphthoic acid anilide, from β-hydroxynaphthoic acid and aniline.

Phenylglycine, from aniline and chloroacetic acid.

Phenyl-1-naphthylamine-8-sulfonic acid, from 1-naphthylamine-8-sulfonic acid, aniline, and aniline hydrochloride by heating in an autoclave.

Tetramethyldiaminobenzophenone (Michler's ketone) from dimethylaniline (2 mols) and phosgene.

Tetramethyldiaminodiphenylmethane, from dimethylaniline (2 mols) and formaldehyde in presence of hydrochloric acid.

Miscellaneous

Aminoazotoluene (and sulfonate), from *o*-toluidine to diazoaminotoluene, and molecular rearrangement.

Anthraquinone (ring closure) from *o*-benzoylbenzoic acid by sulfuric acid.

Benzoic acid, from phthalic acid by decarboxylation.

2-Chloroanthraquinone (ring closure), from *p*-chlorobenzoylbenzoic acid by sulfuric acid.

To illustrate the procedures employed in manufacturing intermediates, two typical flow sheets are depicted in Figures 5 and 6 which cover aniline and

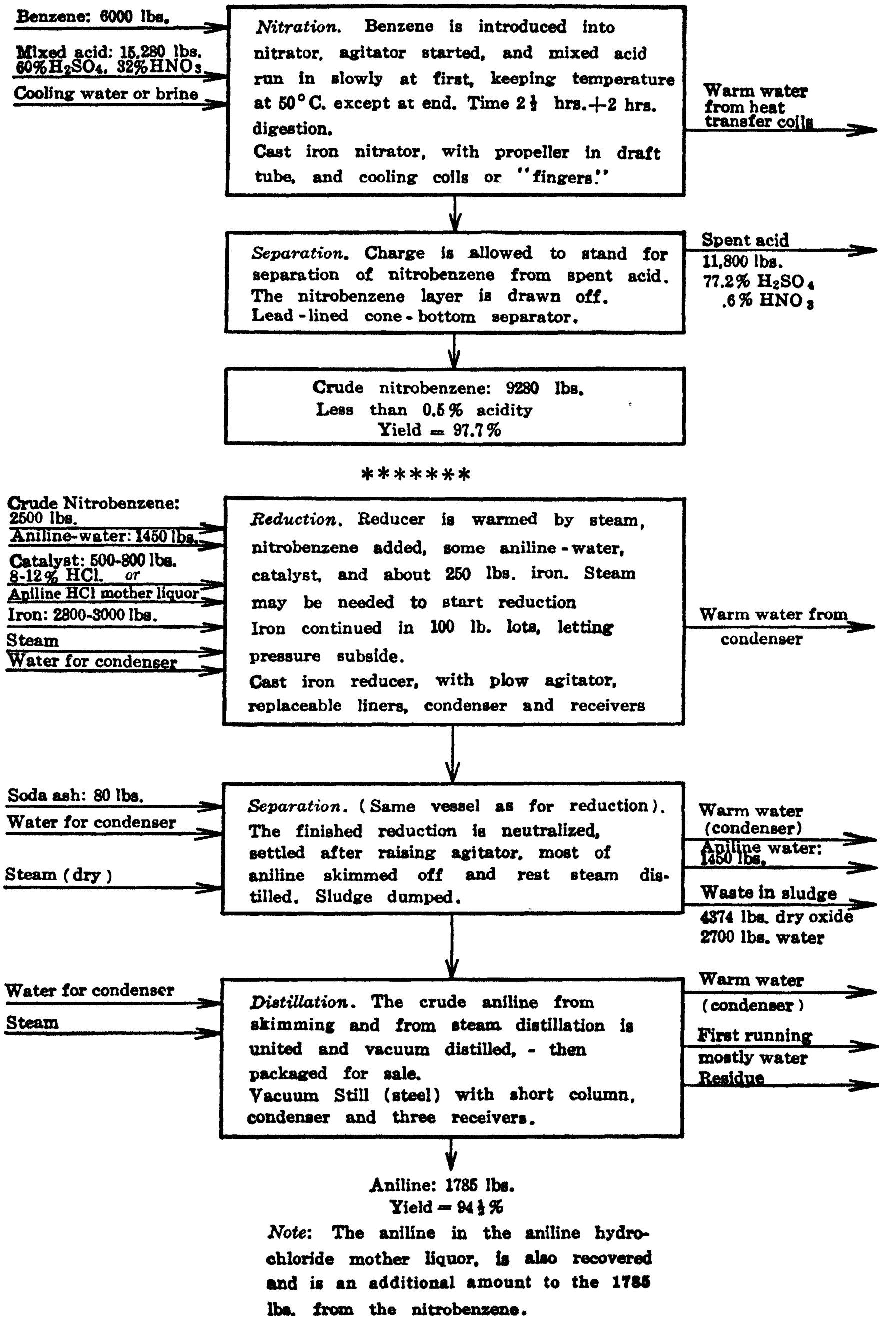


Fig. 5. Flow Sheet of Manufacture of Aniline from Benzene.

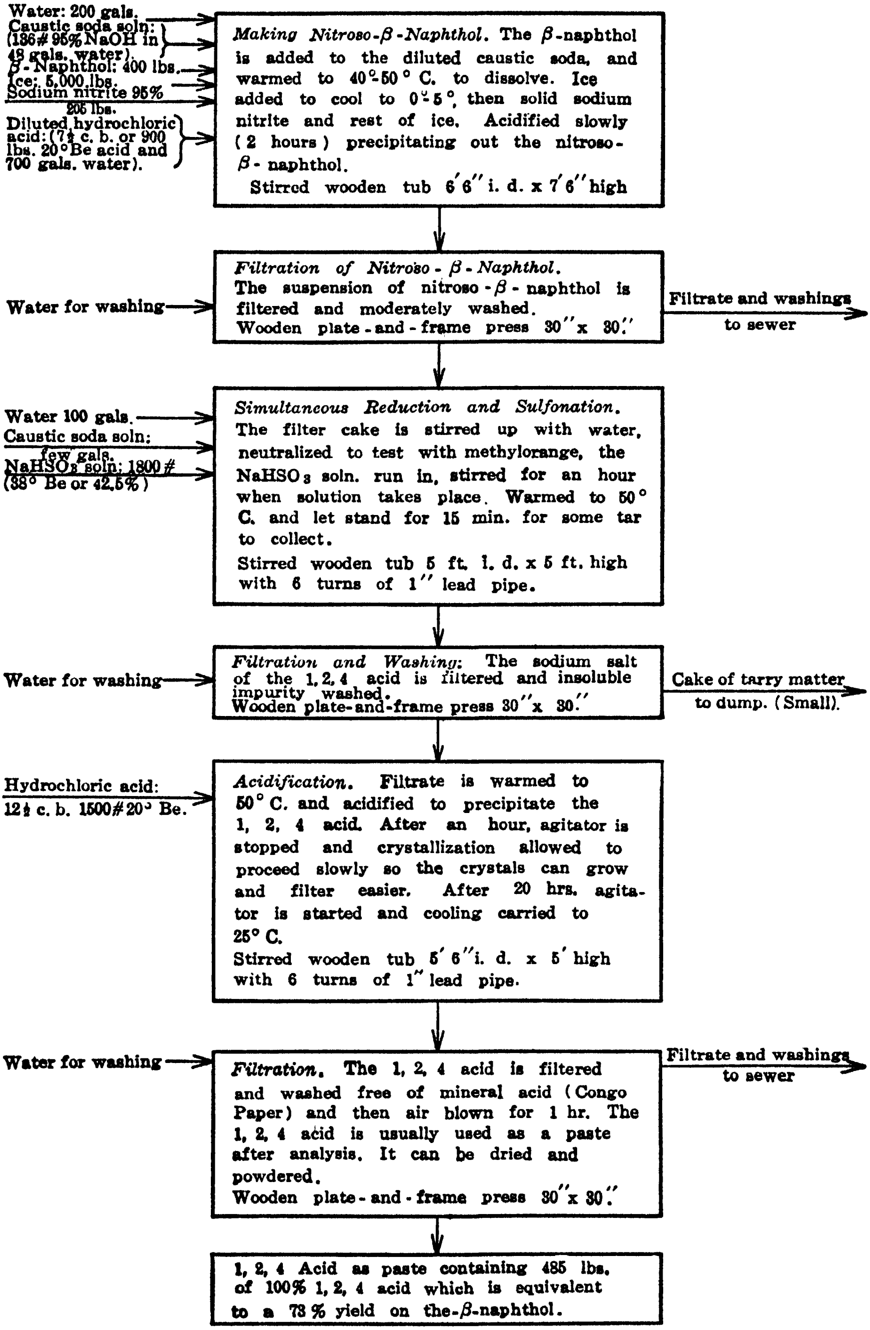


FIG. 6. Flow Sheet of Manufacture of 1-Amino-2-naphthol-4-sulfonic Acid.

1-amino-2-naphthol-4-sulfonic acid respectively. The quantities of these intermediates manufactured amounts to over 20,000 tons annually for aniline and over 500 tons for the 1-amino-2-naphthol-4-sulfonic acid. Available statistics of production and of sale are reported yearly by the United States Tariff Commis-

FIG. 7. Nitrator House for Dyestuff Intermediates at Deepwater Point, N. J., plant of the E. I. Du Pont de Nemours Co. Note outside safety quick-exit spiral. There are no windows, ventilation being by artificial means. On the other side are safety explosion hatches for every floor. (Courtesy E. I. Du Pont de Nemours Co.)

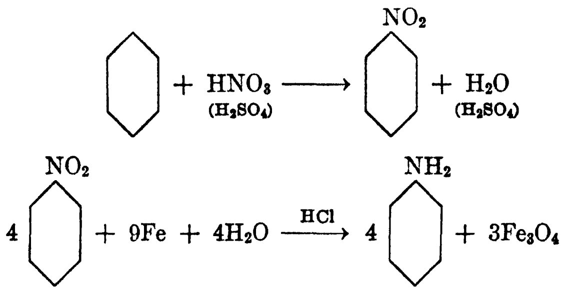
sion (*loc. cit.*) for these and all the other principal intermediates made in the United States.

MANUFACTURE OF ANILINE

In the manufacture of aniline [5] there are two procedures that are technically employed, involving respectively the following sequences: (1) Benzene subjected

[5] For a detailed description of the chemistry and engineering involved in the properties, reactions and making of aniline, consult the book, P. H. Groggins, "Aniline and Its Derivatives," D. Van Nostrand Co., New York, 1924. *Cf.* Chapter on Amination in book edited by P. H. Groggins, "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., New York, 1938.

to nitration gives nitrobenzene and this subjected to iron reduction furnishes aniline. (2) Benzene subjected to chlorination gives chlorobenzene and this subjected to ammonolysis under pressure furnishes aniline. These two procedures are competitive and quite probably each operates more cheaply in its respective manufacturing location than the other process would. Figure 5 depicts the unit process and the unit operations necessary to carry out the making of aniline through nitrobenzene. It is the historical one that has been used throughout the years. The Americans improved the equipment applied to this series of reactions, largely by better design for the necessary heat transfer in removing heats of reaction and for the stirring required for efficient and safe operation. In some of the large nitrators employed in America as much as one thousand gallons of benzene are introduced in each charge. The reactions carried out are often summarized as follows:



Particularly in the reduction, the reactions are much more complicated and we can probably formulate these changes with the sequences listed hereunder:

$$
\begin{aligned}
Fe + 2H_2O &\xrightarrow{FeCl_2} Fe(OH)_2 + H_2 \\
C_6H_5NO_2 + 3Fe + 4H_2O &\xrightarrow{FeCl_2} C_6H_5NH_2 + 3Fe(OH)_2 \\
C_6H_5NH_2 + H_2O &\longrightarrow C_6H_5NH_3OH \rightarrow C_6H_5NH_3^+ + OH^{-*} \\
FeCl_2 &\longrightarrow Fe^+ + 2Cl^- \\
2C_6H_5NH_3^+ + 2OH^- + Fe^+ + 2Cl^- &\longrightarrow 2C_6H_5NH_3Cl\dagger + Fe(OH)_2 \\
C_6H_5NH_3Cl &\longrightarrow C_6H_5NH_3^+ + Cl^- \\
2C_6H_5NH_3^+ + 2Cl^- + 2Fe(OH)_2 + 2Fe &\longrightarrow 2C_6H_5NH_2 + FeCl_2 + Fe_3O_4 + 3H_2
\end{aligned}
$$

* This reaction is similar to the solution of ammonia in water: $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$.

† Frequently aniline hydrochloride is the only catalyst employed.

The above reactions indicate that the iron ends up as the ferroso-ferric oxide—and this is generally the case, but if less iron is used, the analysis indicates a greater proportion of ferrous iron present, probably as ferrous hydroxide. In any case the iron used for reduction should be cast iron turnings (or powdered iron) free from oil and non-ferrous metals.

Quite frequently when we carry out reactions on a large scale and have more opportunity to investigate, we discover that a simple textbook reaction is the summation of a number of chemical steps. Indeed in this reduction of nitrobenzene by iron on the large scale, there is a stage when some hydrogen is evolved and another when the iron swells, due to the iron hydroxide formation. In considering the iron reduction of nitrobenzene it should be noted that the hydrochloric acid, or ferrous chloride, added is only as a catalyst. It is often economical to add this in the form of aniline hydrochloride mother liquors obtained from the manufacture of aniline salt (aniline hydrochloride).

MANUFACTURE OF AMINO-NAPHTHOL-SULFONIC ACIDS

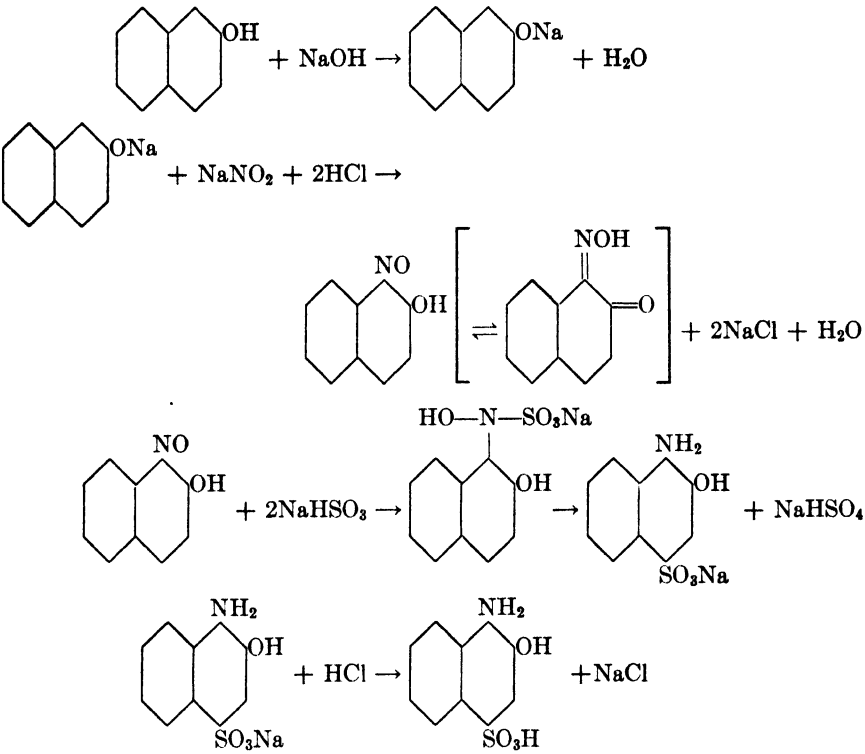
Many amino-naphthol-sulfonic acids are integral parts of certain very important azo dyes.[6] Some of these acids are fairly simple and others are much more complicated in their chemical structure. The following list gives a few of the most important members of this class of intermediates:

1,2,4 Acid or 1-amino-2-naphthol-4-sulfonic acid
J Acid or 2-amino-5-naphthol-7-sulfonic acid
Gamma Acid or 2-amino-8-naphthol-6-sulfonic acid
H Acid or 1-amino-8-naphthol-3:6-disulfonic acid

Many of these amino-naphthol-sulfonic acids are made by complicated reactions involving the simultaneous formation of isomers [7] which must be separated. However, to illustrate the unit processes and unit operations involved in making a typical acid of this class, Figure 6 is inserted, wherein beta-naphthol is converted into 1,2,4 acid by a series of steps which in this particular acid are relatively simple and easily carried out and which may be formulated as follows:

[6] For the lists of dyes derived from these amino-naphthol-sulfonic acids see R. Norris Shreve, "Dyes Classified by Intermediates," Chemical Catalog Co., New York, 1922, wherein under each intermediate is given the dyes derived therefrom. The use of these amino-naphthol-sulfonic acids has been confined almost exclusively to the dye field. This book also gives the various trivial names of the different intermediates.

[7] Groggins, P. H., "Unit Processes in Organic Synthesis," pages 240-246, etc., McGraw-Hill Co., New York, 1938.



These reactions furnish the 1,2,4 acid as a fairly cheap compound, selling for around 60 cents per pound. The following skeleton tabulation will indicate something about the cost of making this aminonaphtholsulfonic acid by the procedure shown in Figure 6.

Manufacturing Cost:	Per 100# of 1,2,4 Acid (100% basis)		
β-Naphthol	82.5 lbs.[8]		
Hydrochloric Acid 20° Bé	494. "		
Caustic Soda	35. "		
Sodium Nitrite	42. "		
Sodium Bisulfite Soln. 38° Bé	371. "		
Productive Labor		$3.00	$10.20
Non-productive Labor		.70	
Power and Steam		2.00	
Maintenance		2.00	
Supplies		1.00	
Overhead		1.50	

To these must be added depreciation, interest, taxes, and pro rata sales expense.

1,2,4 Acid enters as an essential intermediate into the manufacture of some very fine blue and blue-black chrome dyes on wool, known as Eriochrome Blue

[8] The extension of the chemical cost is not given here as prices vary from time to time. However, by taking the current prices from the Oil, Paint & Drug Reporter, these items can be extended and added to the labor, power and steam, etc.

Blacks or Salicine Blacks or simply as Chrome Blue-Black B and U (Color Index #201 and #202). In the last few years more than one million pounds of this 1,2,4 acid have entered annually into dye manufacture. It is interesting to note that in the manufacture the equipment listed in Figure 6 is very simple in nature, consisting mostly of wooden vats and wooden filter presses. Where pipes and connections are necessary these are made of lead pipe, using Duriron cocks.

In the manufacture of intermediates the chemical reactions furnish isomeric bodies whose disposal is a major problem. For instance, in the nitration of toluene both ortho- and para-nitrotoluene result, as is likewise true of the sulfonation of naphthols. Fortunately for the dye industry, the explosive TNT consumes any excess nitration products of toluene, but this was not always true in the past when large stocks first of one nitro-isomer and then of the other did accumulate. Even now certain isomers of naphthalene derivatives are hard to dispose of profitably.

DYES

The manufacture of dyes, on first inspection of their formulas, would impress one as a very complicated procedure. Indeed there are certain aspects of this fabrication that involve a number of intricate steps. However, the thousand commercially used dyes are made out of the five hundred-odd intermediates by a dozen or so unit processes. By understanding the conditions and the equipment necessary to carry out the pertinent unit process, and by applying these to various intermediates, much clarification is obtained in the understanding not only of the manufacture, but also of the structure of the dyes.

Classification of Dyes—On the other hand, dyes are not grouped by the unit process as frequently as is done with the intermediates. From the manufacturing viewpoint, dyes are classified by their chemical structure which, however, would closely parallel a unit process classification. The extensive dye tables,[9] as well as the U. S. Tariff Commission,[10] employ this chemical classification which is based essentially upon dividing these dyes according to the main structural chemical group or the chromophore imparting color. Likewise Table 3 presents selected dyes arranged in chemical classes.

The Color Bodies—In line with the normally accepted cause of color[11] there is required to be in the molecule of a useful dye a certain amount of unsaturation in the form of aromatic rings which are postulated to exist in the quinoid structure and which contain, or have attached to themselves, a color-giver or chromophore group. We call the aromatic body containing a chromophore the chromogen. These chromogens possess color, but in some cases they need to have other groups attached to the molecule in order to facilitate the dyeing or the adherence of the color body to a fabric. These assisting bodies are known as auxochromes; therefore to have a dye, one or more auxochromes must as a rule be

[9] Rowe, F. M., "Colour Index and Supplement," Soc. of Dyers & Colourists, Bradford, England (1924) (1928); Schultz, Gustav, "Farbstofftabellen," 7th ed., Leipzig, Akd. Verlag, 2 vols. (1925) and 2 supplements (1931).

[10] U. S. Tariff Commission, Synthetic Organic Chemicals, U. S. Production and Sales, Report No. 140 (1939).

[11] Watson, E. R., "Color and Its Relation to Chemical Constitution," Longmans, Green & Co., New York, 1918. Günther Schiemann, "Die Chemie der natürlichen und künstlichen organischen Farbstoffe," Leopold Voss, Leipzig (1936).

TABLE 3—IMPORTANT DYES ARRANGED BY CHEMICAL* CLASSIFICATION

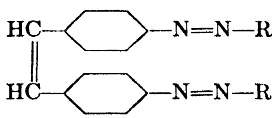
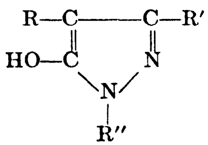
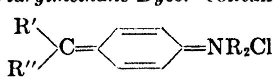
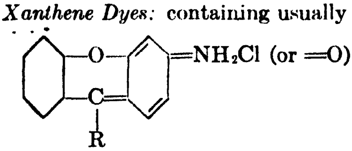
Colour Index No.	*Name and Class of Dye*	*Intermediates from which Dye is Made*	*Dye Application Class*
	Nitroso Dye: containing =N·OH or —N=O		
5	Naphthol Green	2-Naphthol-6-sulfonic acid (Schaeffer's acid)	A
	Nitro Dye: containing =NO·OH or $—NO_2$		
10	Naphthol Yellow S	1-Naphthol-2,7-disulfonic acid	A
	Monazo Dyes: containing R—N=N—R′		
20	Chrysoidine Y	Aniline *m*-Phenylenediamine	B
24	Sudan I	Aniline β-Naphthol	SS
138	Metanil Yellow	Metanilic acid Diphenylamine	A
142	Methyl Orange	Sulfanilic acid Dimethylaniline	A†
151	Orange II	Sulfanilic acid β-Naphthol	A
202	Chrome Blue Black U	1-Amino-2-naphthol-4-sulfonic acid β-Naphthol	A M
	Disazo Dyes: containing R—N=N—X—N=N—R′		
246	Acid Black 10B (Naphthol Blue Black)	*p*-Nitroaniline H acid	A
332	Bismarck Brown 2R	*m*-Tolylenediamine (3 mols)	B
401	Developed Black BHN	Benzidine 2-Amino-8-naphthol-6-sulfonic acid (alk.) 1-Amino-8-naphthol-3,6-disulfonic acid (alk.)	D
406	Direct Blue 2B	Benzidine 1-Amino-8-naphthol-3,6-disulfonic acid (alk.) (2 mols)	D
518	Direct Pure Blue 6B	Dianisidine 1-Amino-8-naphthol-2,4-disulfonic acid (alk.) (2 mols)	D

* For the structural formulas of the dyes and intermediates mentioned in this table, see the tables of Chapter 27.

† Indicator.

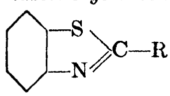
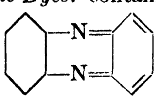
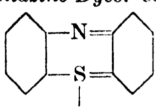
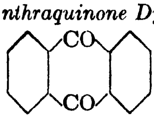
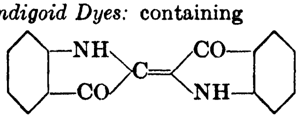
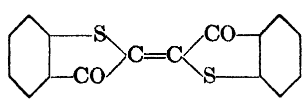
NOTE. In this table A stands for Acid dye, B for Basic dye, D for Direct dye, M for Mordant dye, S for Sulfur dye, SS for Spirit Soluble dye and V for Vat dye.

TABLE 3—IMPORTANT DYES ARRANGED BY CHEMICAL CLASSIFICATION—*continued*

Colour Index No.	*Name and Class of Dye*	*Intermediates from which Dye is Made*	*Dye Application Class*
	Trisazo Dyes: containing R—N=N—X—N=N—Y—N=N—R′		
593	Direct Green B	Benzidine Phenol 1-Amino-8-naphthol-3,6-disulfonic acid *p*-Nitroanisidine	D
	Stilbene Dyes: containing 		
620	Direct Yellow R	*p*-Nitrotoluene-*o*-sulfonic acid (4 mols)	D
	Pyrazolone Dyes: containing 		
640	Tartrazine	Phenylhydrazine-*p*-sulfonic acid (2 mols) Dioxytartaric acid	A
	Ketonimine Dyes: containing $NH{=}C\langle{}^{R}_{R}$		
655	Auramine	Dimethylaniline (2 mols) Phosgene	B
	Triarylmethane Dyes: containing 		
657	Malachite Green	Dimethylaniline (2 mols) Benzaldehyde	B
680	Methyl Violet and Base	Dimethylaniline (3 mols)	B
	Xanthene Dyes: containing usually 		
764	Phenol Phthalein	Phthalic anhydride and Phenol (2 mols)	*
768	Eosin	Phthalic anhydride Resorcinol (2 mols)	A

* Indicator.

TABLE 3—IMPORTANT DYES ARRANGED BY CHEMICAL CLASSIFICATION—*continued*

Colour Index No.	*Name and Class of Dye*	*Intermediates from which Dye is Made*	*Dye Application Class*
	Thiazole Dyes: containing 		
814	Direct Fast Yellow	*p*-Toluidine (4 mols) Sulfur	D
	Azine Dyes: containing 		
864–5	Nigrosine	Aniline Nitrobenzene	A*
	Thiazine Dyes: containing 		
922	Methylene Blue	Dimethylaniline (2 mols) Sodium thiosulfate	B
	Sulfur Dyes: containing S		
978	Sulfur Black	2,4-Dinitrophenol Sulfur	S
	Anthraquinone Dyes: containing 		
1054	Acid Alizarin Blue B	Anthrarufin	A
1095	Anthraquinone Vat Yellow GC (12½%)	2-Methylanthraquinone (2 mols)	V
1113	Anthraquinone Vat Blue GCD	2-Aminoanthraquinone (2 mols)	V
	Indigoid Dyes: containing  or 		
1177	Indigo, synthetic	Aniline (2 mols) Chloracetic acid (2 mols), etc.	V
1217	Vat Orange R (10%)	6-Ethoxythioindoxyl (2 mols)	V

* Used largely as leather dyes either spirit soluble or water soluble after sulfonation

attached to the chromogen. The auxochromes, or assisting bodies, are such groups as $—NH_2$, $—NR_2$ and —OH. Allied to these are the solubilizing groups, $—SO_3Na$ and —COONa. While these are of much importance and greatly influence the application of dyes or manner in which the dyes go into a fiber, the color-givers

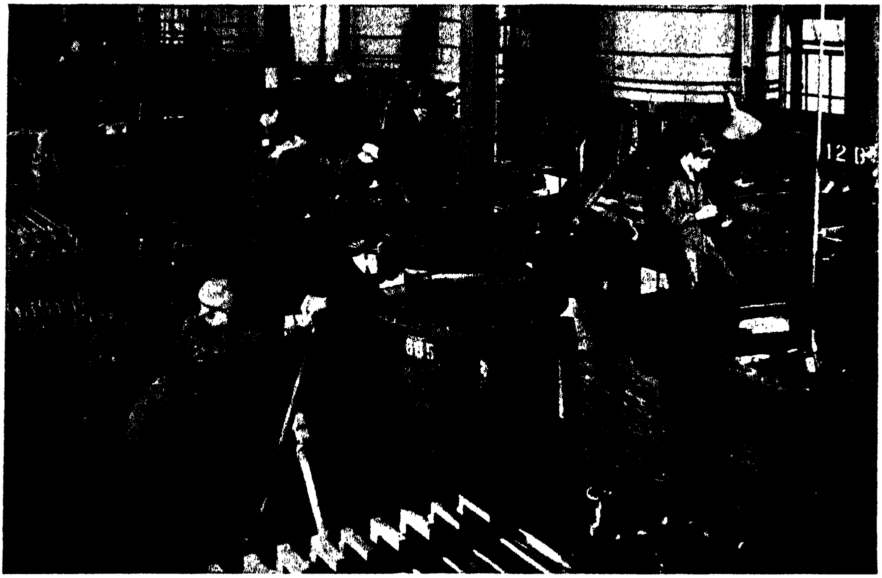


FIG. 8. Typical Factory for Finishing Azo Dyes. (Courtesy Calco Chemical Co.)

or chromophores have more weight in determining the chemical classification. Important chromophores are:

1. The nitroso group: —N═O (or ═N—OH).
2. The nitro group: $—NO_2$ (or ═NO · OH).
3. The azo group: —N═N—.
4. The ethylene group: $>$ C═C $<$.
5. The carbonyl group: $>$ C═O.
6. The carbon-nitrogen groups: $>$ C═NH, —CH═N—.
7. The sulfur groups: $>$ C═S, $>$C—S—S—C$<$.

These chromophores either singly, or frequently with deepening of color, repeatedly enter into the characteristic chemical structure of dyes. This chemical classification is very convenient from the point of view of the fabricator, since it parallels so closely the unit process classification and permits the grouping of dyes made by like chemical changes. Thus one finds large buildings devoted almost exclusively to the manufacture of azo dyes (containing the azo chromophore —N═N—) wherein the unit processes of diazotization and coupling are carried out, involving a great number of intermediates reacting, however, in quite similar equipment, frequently successively in the same equipment under like conditions. This permits the application of like principles and like equipment to making a considerable number of dyes with a consequent saving in the training of men and in the capital invested in equipment. A similar state of affairs exists in the making of dyes classified by the triarylmethane (triphenylmethane) grouping or the anthraquinone grouping. These contain like chromophores.

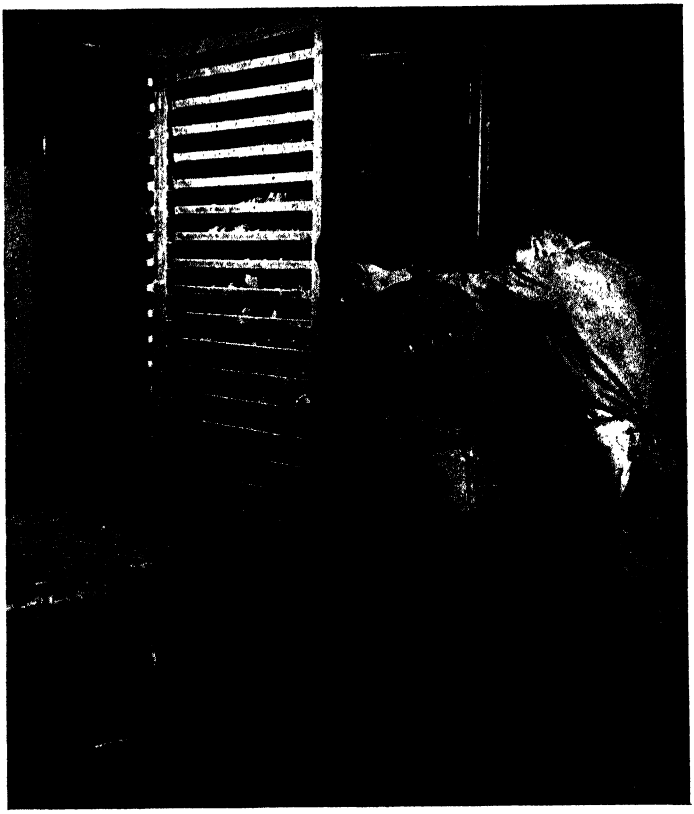


FIG. 9. Loaded Rack of Azo Colors Being Run into Air Dryer at the Dye Works of E. I. Du Pont de Nemours Co., Deepwater Point, N. J. (Courtesy E. I. Du Pont de Nemours Co.)

Comparison of Classifications—There is no use manufacturing a product that cannot be sold. Chromophore or chemical classification is not suitable from a sales viewpoint; therefore in the application of dyes to cotton or silk or wool or for staining furniture there is another classification which brings together the various dyes, no matter from what chemicals manufactured or no matter from what chromophore derived, under a given *application* classification. This application arrangement is frequently more influenced by the auxochrome or solubilizing group present than by the chromophore. Such use classes are exemplified by *acid dyes* containing one or more $—SO_3Na$ groups and dyeing wool from an acid bath, or by *basic dyes* containing $—NH_2$, or $—N(CH_3)_2$ groups and coloring cotton by the help of tannic acid, or mordant dyes having a $—OH$ radical and dyeing wool through the help of a mordant or an assistant such as chromium salts. Many of these application classes do occur under some of the chemical or chromophore classes, such as among the members of the *Azo Dyes*, or the *Triarylmethane Dyes* or the *Anthraquinone Dyes*. However, the application of dyes is an art in itself and the application classification is treated separately in Chapter 29.

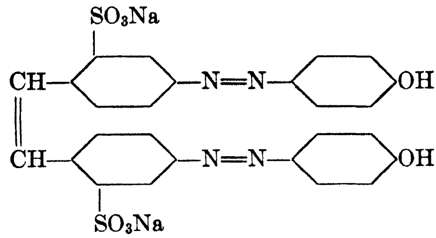
Table 3 follows the usual arrangement by chemical grouping of the tabulations of Rowe and Schultz.[9] The respective intermediates whose chemical union by the appropriate unit process gives the dye in question are listed. By looking at the dyes as made up out of these intermediates in this manner, it is thought that much simplification will result. A book [6] dealing with the dyes on the basis of intermediates is available for a closer study of this reasonable and manufacturing viewpoint.

TABLE 4—IMPORTANT DYES DERIVED FROM PHENOL *

Colour Index No.	*Ordinary Name and Class of Dyes*	*Other Intermediates Used*	*Dye Application Class*
	DISAZO DYES		
364	Paper Yellow	Diaminostilbene-disulfonic acid Phenol (2 mols)	D
365	Chrysophenine G	Diaminostilbene-disulfonic acid Phenol (2 mols) Ethylation	D
382	Direct Scarlet B	Benzidine 2-Naphthol-6,8-disulfonic acid Ethylation	D
	TRISAZO DYES		
583	Direct Green ET	Benzidine 1-Amino-8-naphthol-3,6-disulfonic acid (H acid) Aniline	D
593	Direct Green B	Benzidine 1-Amino-8-naphthol-3,6-disulfonic acid (H acid) *p*-Nitroaniline	D
	TRIARYLMETHANE DYES		
680	Methyl Violet	Dimethylaniline (3 mols)	B
	SULFUR DYES		
978	Sulfur Black	(Dinitration) Sulfur	S

* Shreve, "Dyes Classified by Intermediates," *loc. cit.*, lists 23 dyes from phenol but some of these are manufactured in America in only small tonnages.

Various Dyes from a Single Intermediate—It should be mentioned here that a given intermediate such as aniline, or β-naphthol, dimethylaniline or phenol is employed as a building-stone in the fabrication of dyes containing a variety of chemical chromophores. Specifically, phenol is used to make the many dyes exhibited in Table 4. The unit processes of diazotization of the tabulated amine and coupling with the hydroxy body results in such azo dyes as are listed in the above table; for example:

Paper Yellow 

This dye, Paper Yellow, does not possess good alkali resistance or fastness because of the free OH groups. This is remedied by ethylation, furnishing the

Fig. 10. Equipment in Which an Intermediate for Azo Colors is Being Distilled, at the Dye Works of E. I. Du Pont de Nemours Co., Deepwater Point, N. J. (Courtesy E. I. Du Pont de Nemours Co.)

much faster (to alkaline washing, etc.) Chrysophenine G. Phenol serves also with formaldehyde as the basis of the phenol-formaldehyde or Bakelite resins, as well as a medicinal product and as the basis for further synthesis into photographic chemicals and perfumes. Truly the intermediates bring the dyes into a close relationship with most of our organic technology.

MANUFACTURE OF TYPICAL DYES

To further illustrate the making of dyes, Figures 11 and 12 are presented. Figure 11 is a flow sheet of an azo plant making Orange II. Such a plant consists of a series of stirred wooden tubs, often of large size, wherein various amines

Water: 780 gals.
Soda Ash: 106 lbs.
Sulfanilic Acid: 365 lbs.
Steam

Sulfanilic Acid Solution and Purification. To the warmed solution of the soda ash in 2/3 of the water, the sulfanilic acid is slowly added, heated and boiled until no odor of aniline (impurity in sulfanilic acid) is apparent. Rest of water is added, allowed to stand over night and filtered from small amount of "carbon."
Stirred wooden tub, 5 ft. 6 in. i. d. x 5 ft. 6 in. high, with steam coils.
Cloth bag filter over diazo tub.

↓

Hydrochloric Acid: 20° Be: 1150 lbs.
Ice: 1500 lbs.
Sodium Nitrite: 96 %: 142 lbs.
Water: 80 gals.

Diazotization. The filtered sulfanilic solution is acidulated, cooled to 0° C. and the previously prepared nitrite solution run in quickly to effect diazotization before separated sulfanilic acid crystals grow in size.
Stirred wooden diazo tub, 6 ft. 6 in. i. d. x 5 ft. 6 in. high.

↓

Water: 780 gals.
Caustic Soda 95 %: 90 lbs.
Beta-naphthol: 290 lbs.
Soda Ash: 100 lbs.

Naphthol Solution. To the warmed caustic soda solution in the water the beta-naphthol is added and stirred to complete solution when soda ash is entered. After settling 12 hrs, run clear solution to coupling tub and strain residue through cloth bag.
Stirred wooden tub. 5 ft. 6 in. i. d. x 5 ft. 6 in. high.

↓

Ice: 1000 lbs.

Coupling. The naphthol solution is cooled to 10° C. and the diazo solution run in over 2 hours with constant stirring. The dye separates well but should be stirred for 12 hours.
Stirred wooden coupling tub, 8 ft. i. d. x 6 ft. high.

↓

Filtration. The orange dye is filtered and washed and air blown to remove some of the moisture.
Wooden plate and frame filter press, 30 in. x 30 in.

→ Dye mother liquor to sewer

↓

Drying and Standardization. The dye is dried in a hot air tray dryer, ground in a ball mill and tested for strength. It is then again milled but with sufficient dried sodium sulfate to furnish usually 80% pure dye.

↓

Orange II. 585 lbs.
95% yield of 80 % dye

FIG. 11. Flow Sheet for Making Orange II.

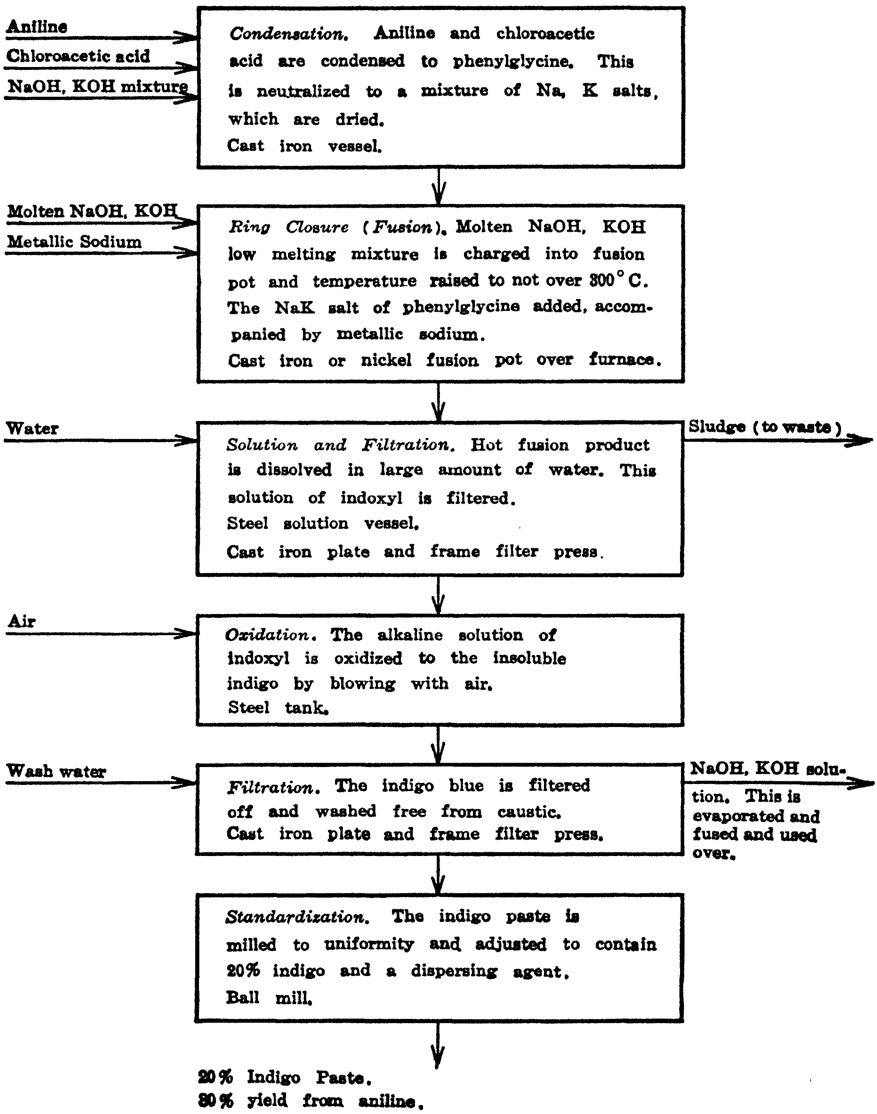
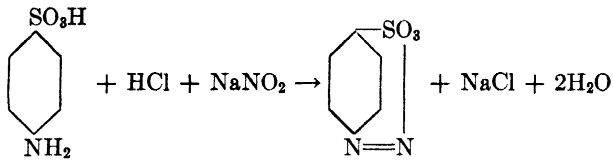
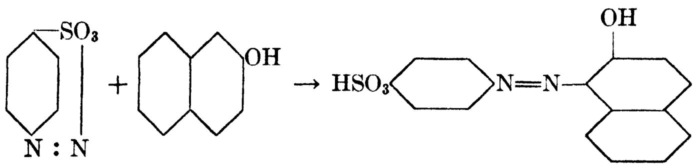


FIG. 12. Flow Sheet for Making Indigo.

(see Table 3 under Azo Dyes) are diazotized[12] with sodium nitrite and hydrochloric acid, mostly in the cold (ice), and then coupled with phenols or naphthols or other amines or their derivatives, resulting in such azo dye reactions[13] as:



Sulfanilic Acid — Diazotized Sulfanilic Acid

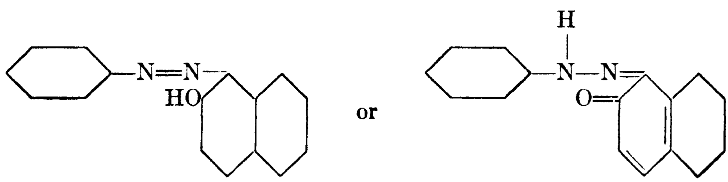


Precipitates as sodium salt

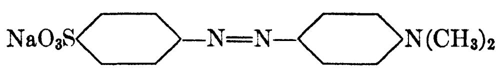
Diazotized Sulfanilic Acid — β-Naphthol — Orange II

Other typical azo dyes may be represented by these formulas:

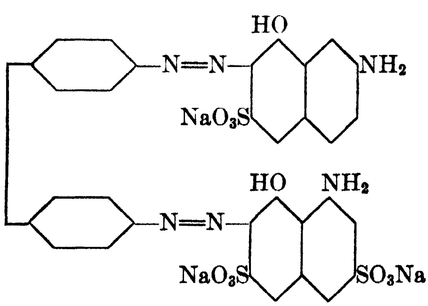
(1) Sudan I. No. 24



(2) Methyl Orange. No. 142



(3) Developed Black BHN. No. 401

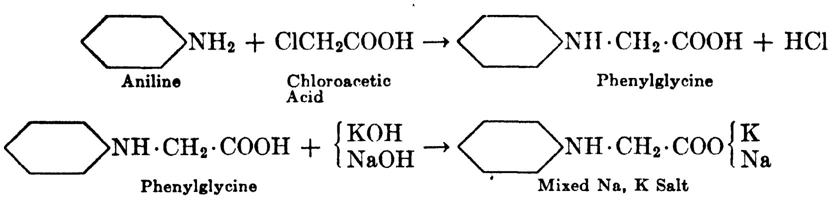


[12] Woodward, H. C., Chapter III in Groggins "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., New York, 1938.
[13] Further details as to the making of Orange II will be found in O'Brien, "Factory Practice in Manufacture of Azo Dyes," pp. 105-109, Chemical Publishing Co., Easton, Pa. (1924).

The simple monazo dye, Sudan I, has little or no affinity for fibers and is used as an oil soluble orange to color alcohol or waxes. Methyl Orange[14] changes its color with variation in pH and is the well-known indicator; it is too fugitive to light to be used as a textile dye. Developed Black BHN is a splendid dye for direct dyeing of cotton, this important dyeing characteristic being largely caused by the benzidine grouping and helped by the two aminonaphtholsulfonic acids. The Developed Black, possessing free amino groups, can have these diazotized after dyeing the cotton; this diazo body can be coupled with additional intermediates, as for example, beta-naphthol, which changes the color from blue to navy blue of a bright shade.

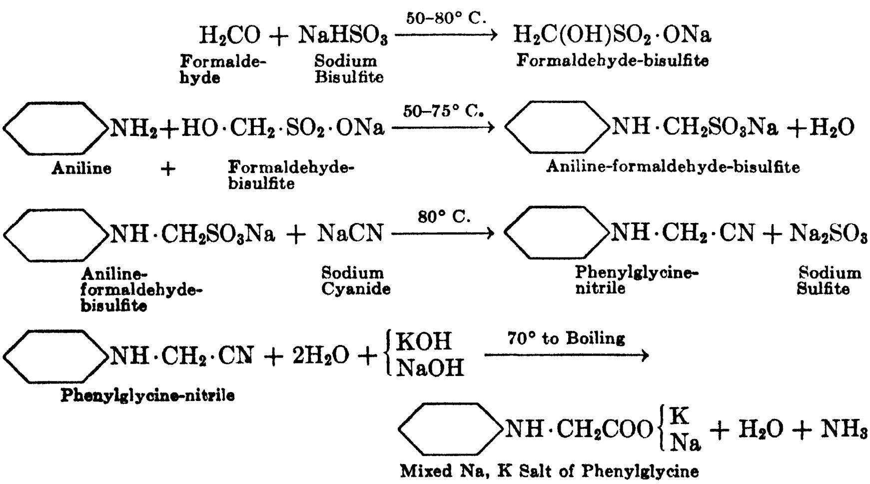
Manufacture of Indigo—Indigo is that dye upon whose commercial synthesis the most effort was placed and the most money spent. Previously Indigo had entered commerce as a product of the growing of the plant in India. It is thus an example of the making in chemical factories of products once commercially extracted from plants grown upon our soils. Figure 12 gives a flow sheet of one of the modern simplified processes from aniline oil. However, the initial industrial procedures were much more complicated and started from naphthalene. The cheaper modern procedures are based on aniline and lead up to phenylglycine through two avenues of approach as these reactions show:

Phenylglycine by chloroacetic acid



The above method is outlined in Figure 12. An alternate method is as follows:

Phenylglycine by formaldehyde and sodium cyanide



[14] Peters, C. A., and Redmon, B. C., J. Chem. Ed., *17*, No. 11, 525 (1940).

The mixed sodium potassium salt of phenylglycine is made, since it has a lower melting point than either salt. For the manufacture of Indigo, this

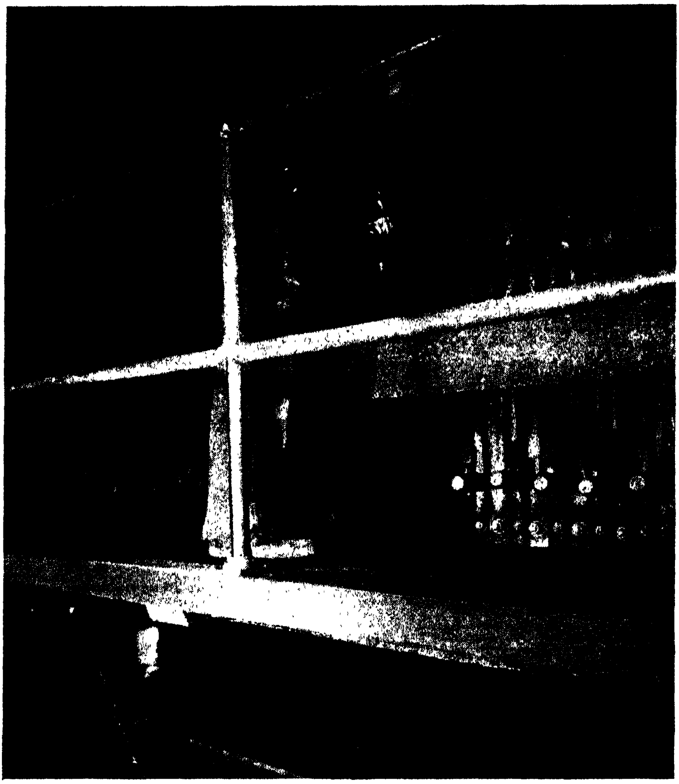
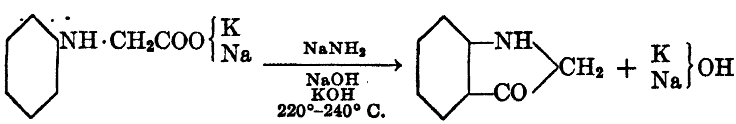


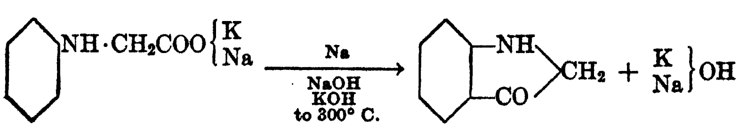
FIG. 13. Indigo Paste Being Removed from Plate and Frame Filter Press at the E. I. Du Pont de Nemours Co. Dye Works at Deepwater Point, N. J. (Courtesy E. I. Du Pont de Nemours Co.)

product is converted by ring closure to indoxyl by either of two fusion dehydrations in presence of excess NaOH—KOH:

Using sodium amide:



Using metallic sodium:



While apparently the sodium amide or the metallic sodium do not enter into the reaction, these two reagents and the mixed NaOH and KOH maintain the

FIG. 14. Truckload of Crude Phthalic Anhydride, an Important Dye Intermediate, Ready for Processing at the Deepwater Point, N. J., plant of the E. I. Du Pont de Nemours Co. (Courtesy E. I. Du Pont de Nemours Co.)

necessary fluxing and anhydrous condition for the dehydrating ring closure to proceed with good yields. The alkaline solution of indoxyl upon being blown with air forms the insoluble blue indigo:

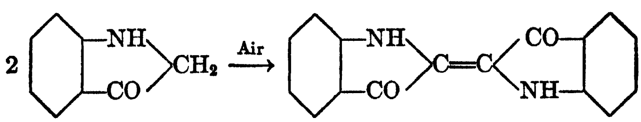


Figure 12 represents an outline flow sheet for making indigo through chloroacetic acid. Further details are available in the literature.[15]

The Phthalocyanines—The intensity of research on dyes during the first fifty years after Perkins' initial discovery was so high that the easily ascertained

[15] Groggins, P. H., "Aniline and Its Derivatives," p. 207 *et seq.*, D. Van Nostrand Co., New York, 1924. Thorpe & Ingold, "Vat Colours," p. 47 *et seq.*, Longmans, Green & Co., London, 1923.

classes were revealed and developed. As a consequence, over the last thirty years, very few fundamentally new products have been made. But in many instances, new processes for old dyes and intermediates, or improved processes, or new members of old classes, were worked out.

However, the phthalocyanines[16] do represent a new arrangement of chemical atoms[17] that have most excellent properties in the dye field. Indeed we may say that here is a *new class* among synthetic dyes with members particularly

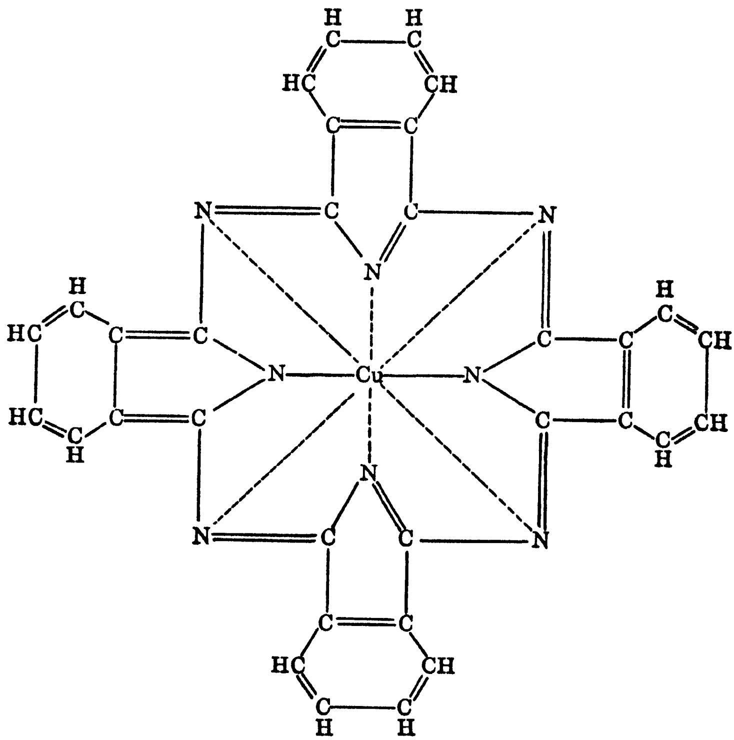


FIG. 15. The Copper Phthalocyanine Structure.

applicable to blue and green pigments. They were discovered by accident as an impurity in the manufacture of phthalimide.

The copper phthalocyanine structure is shown in Figure 15. Here we have four isoindole units linked by four nitrogen atoms and one copper atom to furnish a complicated ring structure which, however, may be viewed as somewhat similar to the basic ring system of chlorophyll.[16] This ring system and its derivatives show remarkable stability to heat and light and chemical agents. Because of this stability and of their insolubility in water, these phthalocyanines are of particular applicability to the pigment and paint fields.

[16] Dahlen, M. A., Ind. Eng. Chem., *31*, 839 (1939). This article describes the discovery, development and relationships of the phthalocyanines, and gives a list of references and patents, and particularly describes the excellent work of R. P. Linstead.

[17] We might call this a *new* chromophore.

Three of these pigments have become of considerable importance commercially: The metal-free phthalocyanine is sold as Monastral Fast Blue GS powder (du Pont). The copper derivative is merchandized as practically pure Monastral Fast Blue BSN powder. Other modifications are on the market with dispersing agents and the like. The highly chlorinated copper phthalocyanine is sold as

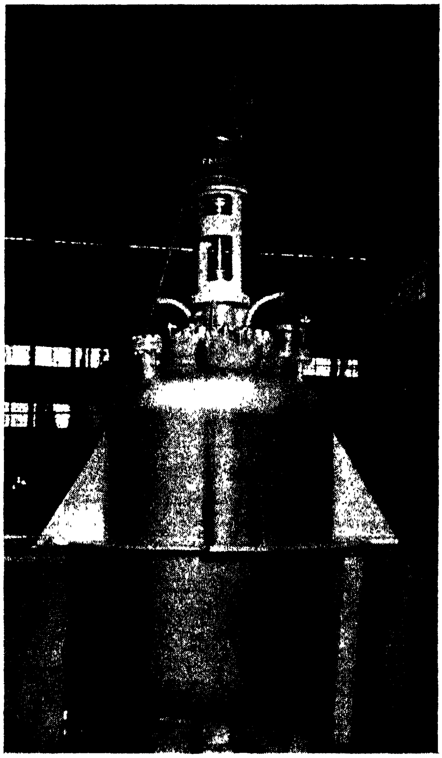
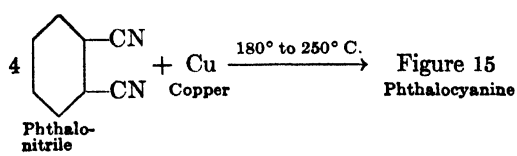


FIG. 16. 900 Gal. Direct-fired Autoclave 4′ 8″ x 5′ 7″ High in Straight Shell Complete with Motor-driven Turbine Agitator and Internal Cooling Coil. Designed for 950 lbs. working pressure and constructed of F. B. quality steel. (Courtesy Blaw-Knox Co.)

Monastral Fast Green GS powder and allied forms. It has about fourteen chlorine atoms per phthalocyanine unit.

These dyes are only of the blue and green shades but they supply a long-felt want for pigments of their excellent properties. They serve as pigments in printing inks, artists' colors, paints, lacquers, enamels, coated textiles, paper, linoleum, and rubber.

Their manufacture may be represented by the following equation:



However, other methods are available, such as heating the phthalonitrile with cuprous chloride, or probably better by reacting phthalic anhydride and urea in presence of cupric chloride. The crude reaction product must be dissolved in concentrated sulfuric acid and reprecipitated by dilution with water to obtain the physical and chemical form suitable for dyes.

MISCELLANEOUS DYE NOTES

The chemistry of the manufacture of azo dyes to be prepared on the fiber has been given much attention.[18] While Para Red, as manufactured on the fiber by coupling diazotized aniline with beta-naphthol, is not used to the extent it once was, the principle at the base of this dye is growing in importance each year. With a dye that is so insoluble that it cannot well be applied by ordinary dyeing, the actual making of it on the fiber by the interaction of soluble constituents furnishes products of desired fastness and stability. These are all being grouped under the heading *Azoics.*

The general reaction in these dyes may be formulated as follows:

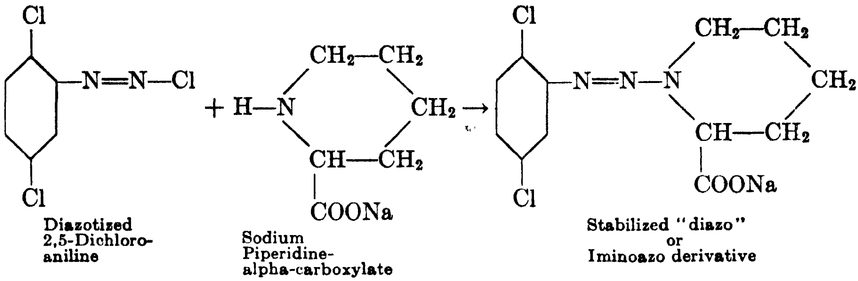
$$RNH_2 + NaNO_2 + 2HCl \rightarrow RN{=}NCl + NaCl + 2H_2O$$

$$RN{=}NCl + HR'OH \rightarrow RN{=}NR'OH + HCl$$

This procedure required the making of the unstable diazotized solution when and as needed. However, enterprising manufacturers have put on the market stabilized diazonium salts under the general class name of *stabilized azoics.*[19] The general principle involved has been to make a weak compound between the diazonium derivative of the amine on the one hand and the stabilizing chemical on the other which would be stable in neutral or alkaline conditions. These stabilized "diazos" keep well and can be applied in the presence of the coupling constituent with no reaction until acidification. These are sold under the name *Diagens* or *Rapidogens* and a typical reaction involving manufacture and application is given as follows:

[18] Dorman, K. L., Am. Dyestuff Reporter, *28,* 79 (1939).
[19] Lubs, H. A., Am. Dyestuff Reporter, *26,* 101 (1937).

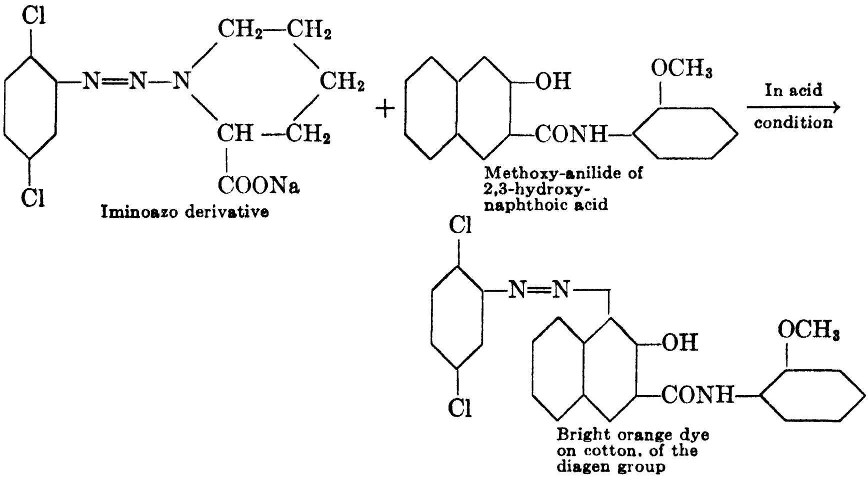
Diagen or rapidogen dyes (stabilized azoics)



Diazotized 2,5-Dichloro-aniline

Sodium Piperidine-alpha-carboxylate

Stabilized "diazo" or Iminoazo derivative



Iminoazo derivative

Methoxy-anilide of 2,3-hydroxy-naphthoic acid

In acid condition

Bright orange dye on cotton, of the diagen group

We continually hear of the importance of vegetable dyes. But most members of this class have now disappeared from commerce or are being made synthetically in chemical laboratories, except for logwood [20] and its derivatives. Large amounts of logwood (or hematine) are used to give black and blue-black dyes on wool and silk and to a less extent on cotton, using mordants.

While a great many inorganic salts are colored, and while a number of them are used directly to make certain of our very best pigments, not many can be employed for the dyeing of fabrics. An exception to this is the use of iron salts to form a khaki shade on cotton. Here the cotton is soaked in a solution of ferrous sulfate, treated with an alkali to precipitate the ferrous hydroxide which is then oxidized with a bleaching powder solution to the ferric state.

READING LIST

The following list, mostly of books, embraces the most pertinent references to Dyes and Intermediates. As this is an old industry, books published a number of years ago are still of much value. To supplement and to bring up-to-date the compilation under the subject of patents, reference should be made to Chemical Abstracts.

[20] See Chapter 20

INTERMEDIATES

Barnett, E. deB., "Anthracene and Anthraquinone," D. Van Nostrand Co., New York (1921).

Cain, J. C., "Manufacture of Intermediate Products for Dyes," Macmillan & Co., New York (1919).

Davidson, A., "Intermediates for Dyestuffs," Ernest Benn, Ltd., London (1926).

Groggins, P. H., "Aniline and Its Derivatives," D. Van Nostrand Co., New York (1924).

Groggins, P. H., "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., New York (1938).

Reverdin, F. and Fulda, H., "Tabellarische Uebersicht der Naphthalinderivate," Basel (1894).

Schwalbe, C., "Benzol-tabellen," Berlin (1903).

Shreve, R. N., "Dyes Classified by Intermediates," Chem. Catalog Co., New York (1922).

Wichelhaus, H., "Sulfurieren, Alkalischmelze der Sulfosäuren," Leipzig (1911).

DYES

Bucherer, H. Th., "Lehrbuch der Farbenchemie," Leipzig (1914).

Cain, J. C., "Chemistry and Technology of the Diazo Compounds," Edw. Arnold, London (1920).

Cain, J. C., "The Manufacture of Dyes," Edw. Arnold, London (1922).

Fierz-David, H. E., "The Fundamental Processes of Dye Chemistry," D. Van Nostrand Co., New York (1921).

Fierz-David and Blangey, "Grundlegende Operationen der Farbenchemie," fourth edition, J. Springer, Vienna (1938).

Georgievics and Grandmougen, "Textbook on Dye Chemistry," Scott, Greenwood and Son, London (1920).

Green, A. G., "Landmarks in Evolution of the Dye Industry," Jubilee Issue of Soc. Dyers & Colourists (1934).

Hantsch, A. and Reddelien, G., "Die Diazoverbindungen," Julius Springer, Berlin (1921).

Heumann, K., "Die Anilinfarben und ehre Fabrikation," F. Vieweg & Sohn, Braunschweig (1906).

Hewitt, J. T., "Synthetic Coloring Matters: Dyestuffs Derived from Pyridine, Quinoline, Acridine and Xanthene," Longmans, Green & Co., London (1922).

Hewitt, J. T., "Synthetic Coloring Matters: Azine and Oxazine Dye-stuffs," Longmans, Green & Co., New York (1918).

Lange, O., "Die Schwefelfarbstoffe ihre Herstellung und Verwendung," Spamer, Leipzig (1925).

Mayer, F., "Chemie der Organischen Farbstoffe," Julius Springer, Berlin (1934).

Morton, J., "History of Development of Fast Dyeing and Dyes," T. & A. Constable, Ltd., Edinburgh (1929).

Nietzki, R., "Chemistry of Organic Dyestuffs," Gurney & Jackson, London (1931).

O'Brien, W. B., "Factory Practice in the Manufacture of Azo Dyes," Chem. Pub. Co., Easton, Pa. (1924).

Pauli, R., "Die Synthese der Azofarbstoffe," Johann Barth, Leipzig (1904).

Robinson, R., "Synthetic Coloring Matters: Triphenylmethane Dyes," Longmans, Green & Co., New York (1918).

Rowe, F. M., "Colour Index and Supplement," Society of Dyers & Colourists, Bradford, Yorkshire (1924).

Rowe, F. M., Two lectures on the development of the chemistry of commercial synthetic dyes (1856-1938), Inst. of Chemistry, London (1938).

Saunders, K. H., "Aromatic Diazo Compounds and Their Technical Applications," Longmans, Green & Co., New York (1936).

Schultz, G., "Farbstofftabellen," seventh edition, Akd. Verlag, Leipzig (1931).

Thorpe, J. F., "Dictionary of Applied Chemistry," Longmans, Green & Co., London (1937 on).

Thorpe, J. F. and Ingold, "Synthetic Coloring Matters: Vat Colors," Longmans, Green & Co., New York (1923).

Thorpe and Linstead (rewriting of Cain & Thorpe), "The Synthetic Dyestuffs and Their Intermediate Products," C. Griffin & Co., London (1932).

Truttwin, H., "Enzyklopädie der Kupenfarbstoffe," J. Springer, Berlin (1920).

Ullmann, Dr. F., "Enzyklopädie der Technischen Chemie," Urban & Schwarzenberg, Berlin (1929).

PATENTS

Doyle, A. M., "Digest of Patents, Coal Tar Dyes and Allied Compounds," Chemical Pub. Co., Easton, Pa. (1925).

Fierz-David and Dorn, M., "Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige," J. Springer, Berlin (1927).

Friedlander, P., "Fortschritte die Teerfarbenfabrikation," J. Springer, Berlin (1910).

Lange, O., "Die Zwischenprodukte der Teerfarbenfabrikation," Otto Spamer, Leipzig (1920).

Winther, A., "Zusammenstellung der Patente auf dem Gebiete der Organischen Chemie," Alfred Topelmann, Giessen (1908).

MISCELLANEOUS

Austin, W. E., "Principles and Practice of Fur Dressing and Fur Dyeing," D. Van Nostrand Co., New York (1922).

Gardner, W. M., "The British Coal Tar Industry," Williams & Norgate, London (1915).

Georgievics, G., "Die Beziehungen zwischer Farbe und Konstitution bei Farbstoffe," Schultess & Co., Zurich (1920).

Green, A. G., "Analysis of Dyestuffs and Their Identification in Dyed and Colored Materials," Griffin & Co., London (1920).

Knecht, Rawson & Lowenthal, "Manual of Dyeing," eighth edition, Griffin & Co., London (1925).

Watson, E. R., "Colour and Its Relation to Chemical Constitution," Longmans, Green & Co., London (1918).

Whittaker, C. M., "Testing of Dyestuffs in the Laboratory," Heywood & Co., Ltd., London (1920).

Whittaker and Wilcox, "Dyeing with Coal Tar Dyestuffs," third edition, Bailliere, Tindall & Cox, London (1938).

CHAPTER 29

APPLICATION OF DYESTUFFS

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Professor of Chemistry, and Head of the Department of Textile Chemistry and Dyeing at the Lowell Institute, Lowell, Mass.

Textile Coloring—Textile coloring may be defined as the process or combination of processes used to fix a color or colors uniformly, and more or less permanently, upon textile material. It includes both dyeing and printing.

Dyeing—The term dyeing is sometimes given almost as broad an interpretation as textile coloring, but to be specific, it should include only those processes in which the entire body of the material being colored is immersed in the coloring bath, a greater or less period of the time required for the coloring.

Textile Printing—Textile printing is a process by means of which the coloring matters applied may be confined, by use of a roller printing machine, blocks or screens, to certain portions of the material, thus producing a definite colored design. The necessary dyestuffs and chemicals are made into a paste, with starch, dextrine, and various gums, and applied to the cloth usually by means of engraved copper rollers, one for each color, the cloth being finally subjected to special aging and drying processes. By this method it is possible to produce prints containing ten or more different colors.

By combined dyeing and printing many different and pleasing effects may be produced.

Staining—Staining is the term often applied to the process of coloring such materials as wood, bone, and ivory, and the coloring matter in this case is ordinarily applied with a brush.

The terms staining and dyeing are both applied to the coloring of leather, straw, paper, and feathers, their respective use depending somewhat upon the process used, but in most cases the term dyeing is more accurate. Staining is usually a more superficial process than dyeing.

COMPOUNDS USED BY THE TEXTILE COLORIST

The chemical compounds used by the textile colorist may be divided into two classes:

(1) Those which possess no coloring power, but which are instrumental in the fixation or development of coloring matters upon the fiber.
(2) Those which are true coloring matters.

Compounds Instrumental in the Fixation of Coloring Matters upon the Fiber, Although Possessing No Coloring Power Themselves—The compounds included under this heading are frequently spoken of as *fixing agents*, but when used in this broad and indefinite sense, the term frequently leads to confusion rather than to enlightenment. In order to eliminate this confusion as far as possible, we will classify the most important compounds coming under this class as follows:

(1) Mordants: (*a*) Metallic. (*b*) Non-metallic. (*c*) Acid.
(2) Mordanting assistants.
(3) Chemical fixing agents.
(4) Mechanical fixing agents.
(5) Developing agents.
(6) Dyeing assistants.

Mordants—The mordanting process is the operation whereby various mordants are precipitated and so deposited upon textile material that they may be subsequently united with mordant dyestuffs *in situ* to form insoluble color lakes. Through the combined mordanting and dyeing processes these color lakes become fixed upon the textile material, thus imparting to it a permanent color. Occasionally, in special cases, the dyestuffs may be applied at the same time or even previous to the mordant.

Mordants in general may be defined as substances capable of uniting with certain dyestuffs to form insoluble colored compounds which, under the proper conditions, may be more or less permanently fixed upon textile material. They may be subdivided as *metallic, non-metallic,* and *acid mordants.*

Metallic Mordants. Metallic mordants are substances, usually metallic oxides, hydroxides or extremely basic salts which are capable of uniting with certain dyestuffs, known as mordant dyestuffs, to form insoluble colored compounds which for the most part are known as *color lakes.*

Non-metallic Mordants. The only non-metallic mordant of importance, and this of only minor importance, is sulfur. Sulfur is sometimes used as a mordant when applying certain basic colors, e.g., malachite green upon wool.

Acid Mordants. Tannic acid and various substances rich in this acid, such as sumac, gall nuts, and various bark extracts, and less frequently various fatty acids, such as oleic and stearic acids, and Turkey-red oil, are the only acid mordants of importance. Of these acid mordants tannic acid and its related compounds are the only ones commonly used, and these chiefly in the application of the basic colors to cotton material. The acid mordants are of minor importance as compared with the metallic mordants.

Mordanting Principles. As often applied, the term "mordant" indicates the soluble metallic salt used to produce the mordant, but in the proper sense the mordant is that substance, which in direct combination with the dyestuffs, forms the color lake. In order to avoid this confusion, we will designate the compound used to produce the mordant as the *mordanting principle.* Thus in one of the most common wool-mordanting processes the soluble potassium or sodium dichromate is the mordanting principle, but the insoluble chromium chromate and chromium hydrate ultimately fixed upon and within the fiber constitute the true mordant.

Mordanting Assistants—Mordanting assistants are compounds such as tartar, lactic acid, oxalic acid, residual products of sulfite pulp waste liquors, and sulfuric acid used in conjunction with the mordanting principles to assist in bringing about a gradual decomposition of the latter, and assist in producing a uniform deposition of the actual mordant upon and within the textile material. They possess reducing properties.

Chemical Fixing Agents—Under the heading of chemical fixing agents we will include:

First. Those substances which are instrumental in the fixation of various mordants upon textile material by uniting chemically with such mordants and holding them upon the fiber until the proper dyestuffs may be given an opportunity to unite with them. Examples: The various antimony compounds used to fix tannic acid upon cotton fiber. Various tannin compounds used to hold iron upon the fiber as the insoluble tannate of iron when the latter is to act as a mordant with logwood or other mordant dyestuffs.

Second. Those substances which cause the actual precipitation of the mordant usually by the double decomposition of the mordanting principle. Example: When cotton material saturated with nitrate of iron is passed through a solution of sodium carbonate, the basic carbonate and hydrate of iron are precipitated upon the fiber, and sufficiently fixed thereon to act as a mordant.

Mechanical Fixing Agents—These are substances (such as albumen and certain resins) capable of holding pigments, permanently, upon the fiber, or certain gums and starches capable of holding dyestuffs and other substances upon the fiber a sufficient length of time to permit of some desirable reaction taking place. Their action is purely mechanical.

Developing Agents—The term developing agents is applied to organic compounds which in combination with some other organic compound already deposited upon the fiber will develop a colored compound, or if united with a dyestuff already upon the fiber will form a new coloring matter possessing a more desirable or a faster color. Examples: Beta-naphthol upon the fiber, when combined with diazotized paranitro aniline (developing agent) will produce para red. Primuline, a yellow dyestuff, when diazotized upon the fiber by treatment with nitrous acid and then combined with beta-naphthol (developing agent) produces a bright red coloring matter.

Dyeing Assistants—Under this heading are commonly included several types of compounds known, respectively, as Leveling, Exhausting, and Penetrating Agents. Wetting and Dispersing Agents might well be included under this same heading.

Leveling agents are compounds added to the dye bath in conjunction with certain dyestuffs to assist in bringing about a level and even deposition of the latter. Glauber's salt used in conjunction with acid dyes upon wool serves as an example.

Exhausting agents are compounds added to the dye bath for the purpose of causing greater absorption of dye by the material which is being dyed, and also to bring about a correspondingly high exhaustion of dyestuff from the dye bath. Sodium sulfate (Glauber's salt) and sodium chloride (common salt) used in connection with direct cotton dyes are typical illustrations.

Penetrating agents are compounds added to the dye bath to facilitate the wetting-out process and incidentally secure a better penetration of the dyes. Mixtures of sulfonated oils, soap and certain organic solvents are typical illustrations. The recently introduced sulfonated higher alcohols [1] and esters for the most part act as penetrating and wetting out agents.

Application of Metallic Mordants—True mordant dyestuffs can only be applied in conjunction with metallic mordants. The mordanting process is therefore of great importance, the mordant playing almost as necessary a part in the application of a mordant color as does the dyestuff itself. Of all the metals, only a few, namely chromium, iron, aluminum, copper and tin unite with mordant dyestuffs to form valuable color lakes. On account of its general applicability chromium is most frequently used. Iron and copper produce the most permanent, while aluminum and tin produce the brightest color lakes.

Mordanting of Wool. Wool has a natural affinity for certain compounds and this facilitates the mordanting process to a marked degree. When in dilute solution mordanting principles, often in a highly dissociated condition, are aided in their decomposition by this natural attraction of wool fiber, and as a result various metallic compounds (usually oxides, hydroxides or basic salts) are slowly deposited upon the fiber. This process takes place most completely in a boiling bath and in the presence of some secondary soluble compound which has already been described as a mordanting assistant.

Chromium compounds are depended upon, almost entirely, in applying mordant dyestuffs upon wool, and potassium or sodium dichromate are the most important mordanting principles for this purpose. The process most frequently used consists in boiling the wool material in a dilute solution of potassium or sodium dichromate in the presence of either tartaric or lactic acid, the latter compounds acting as mordanting assistants. The boiling should be continued for about one to one and one-half hours in order to secure the most complete decomposition of the mordanting principle, and fixation of the mordant upon the fiber.

Mordanting of Silk. Silk, like wool, possesses a marked affinity for metallic oxides, hydroxides, and basic salts, and for this reason may be readily mordanted. The proccess consists in steeping the silk in a concentrated solution of the proper mordanting principle, such as the sulfate, chloride or acetate of iron, chromium, aluminum or tin, usually in a slightly basic condition, and then thoroughly washing with a large volume of water. This process may be repeated several times, depending upon the depth of color to be obtained upon dyeing.

Silk possesses the property of absorbing large quantities of metallic compounds and advantage is taken of this fact in the weighting of silk. Silk weighting and mordanting are therefore frequently closely associated.

Mordanting of Cotton. The mordanting of cotton is more difficult than that of either wool or silk, owing to the entire lack of natural attraction of cotton for metallic salts, hydroxides and oxides. The methods of cotton mordanting are numerous, but may be grouped under four general headings:

(1) Combined padding, aging, and dunging (fixing) process.
(2) Combined printing, aging, and dunging (fixing) process.
(3) Direct chemical precipitation upon the fiber.
(4) Steam printing.

[1] For a discussion of these compounds see Chapter 42.

In the first method, the cloth is evenly saturated (padded) with a solution of some mordanting principle, usually an acetate of chromium, iron, or aluminum. It is then subjected to a hot, moist atmosphere for a number of hours (aging) which brings about a slow decomposition of the acetate with fixation of metallic oxide upon the fiber, and liberation of acetic acid. The fixation of the mordant and neutralization of the free acid present is brought about by the dunging (fixing) process, which consists in thoroughly treating the aged material in a bath made up with such substances as phosphates, silicates, and carbonates of potassium, sodium, ammonium, and calcium. Sodium arsenate is a valuable fixing agent for this purpose but its use has been largely discontinued owing to the poisonous nature of the arsenic.

The second method differs from the first only in that the mordanting principle is printed upon the fabric rather than padded.

The third method consists in the direct chemical precipitation of the mordant upon the fiber. In this method the material is first padded with the mordanting principle and then passed through a bath containing the precipitant.

In steam printing the mordanting principle, mordant dyestuff and acetic acid are mixed together with the proper thickening agents and then printed upon the cloth. Upon steaming, the acetic acid is driven off, the mordanting principle decomposes and forms the mordant which unites with the coloring matter *in situ*.

Owing to the shortage of coal tar colors, during the first World War, the natural dyes, which are for the most part mordant colors, were extensively used. This led to considerable experimentation in the application of metallic mordants to cotton. One of the most important advances along this line was the introduction of D salt.[2] By boiling cotton material in a solution of this salt it is readily mordanted with a chromium mordant.

CLASSIFICATION OF DYESTUFFS

The great variety of materials used for coloring naturally led to considerable confusion in their classification.

The earliest classification of dyestuffs was made by Bancroft, who divided them into two classes, *substantive* and *adjective*. He designated as substantive dyestuffs those capable of producing a fully developed color upon textile material without the necessary assistance of any other combining substance, and as adjective dyestuffs those requiring an intermediate combining substance (*called a mordant*) to satisfactorily fix and fully develop the color. This grouping is still in use, but during recent years, the tendency has been to use the term *direct color* instead of substantive, and *mordant color* instead of adjective. In general the classification holds true; but there are instances where dyestuffs are substantive toward one fiber, but adjective toward another. This is well illustrated by the basic colors which will dye wool directly but require a mordant upon cotton.

[2] D salt is a preparation so-called after its discoverer, W. C. Durfee. It is apparently a colloidal solution of chromium dioxide together with sufficient chromic acid to establish an equilibrium which, although comparatively stable at ordinary temperature, is easily disturbed through boiling in the presence of textile material or when dried upon textile material, with a resulting deposition of a stable chromium mordant.

The *classification which divides the dyestuffs according to their origin* is of broader application. It recognizes three groups and is as follows:

(1) *Natural Organic Dyestuffs.* Including (*a*) *Vegetable;* (*b*) *Animal.*
(2) *Mineral Dyestuffs.*
(3) *Manufactured Organic Dyestuffs,* or *Coal Tar Dyes.*

Though the various subdivisions of this classification, particularly of the manufactured organic dyestuffs, are numerous and varied in the character of the dyes they include, this general classification has the advantage of conciseness, and one class does not overlap another.

The natural organic dyestuffs include such coloring matters as logwood, indigo, fustic, cutch, and cochineal.

The mineral coloring matters include Prussian blue, chrome yellow, iron buff, chrome green and a number of other inorganic pigments.

The manufactured organic dyestuffs are by far the most important and have special systems of classification.[3]

NATURAL ORGANIC DYESTUFFS

Although the natural organic dyestuffs are now of only minor importance they should be discussed in order to give a complete picture of the field.

For convenience the natural organic dyestuffs may be subdivided as follows:

(1) Indigo and related compounds.
(2) Logwood.
(3) Natural dyestuffs producing shades of a red character.
(4) Natural dyestuffs producing shades of a yellow to brown character.

Indigo—Although indigo blue or indigotin occurs in many plants the largest quantity is found in the genus *Indigofera,* the herbaceous plant *Indigofera tinctoria* being the one which was most widely cultivated. The Indigofera thrive only in tropical climates, and for several hundred years the cultivation of the indigo plant was one of the chief industries of Southern Asia, particularly India and Java. The introduction of the synthetic indigo however dealt a severe blow to the natural indigo industry, and the synthetic indigo [4] has almost completely replaced the older vegetable product. During the first World War the supply of synthetic indigo of coal tar origin was practically cut off and for a while the natural indigo industry was revived, but before the war was over American dyestuff manufacturers began to produce it and, during 1923, 28,000,000 lbs. were manufactured in the United States, which covered practically the entire domestic requirements and some for export. America has been self-contained in indigo manufacture ever since.

Indigo blue, or *indigotin* as it is known chemically, does not exist as such in the plant, but is developed through the indirect decomposition of a glucoside known as indican. When the leaves and stems are steeped in water and allowed to ferment, a clear yellow liquid results which contains the indigo as the soluble indigo white. When this liquor is violently agitated, so as to expose all parts to the action of the oxygen of the air, the soluble indigo white is converted into the

[3] See Chapter 28.
[4] For a description of the manufacture of synthetic indigo see Chapter 28.

insoluble indigo blue. This is allowed to settle, pressed into cakes, and when dry is ready for the market.

Chemistry of Indigo Dyeing.[5] Although the discussion of the use of indigo dyes might now come under the section on synthetic products, it is taken up under natural products, because the evolution of the dyeing operation came with the development of the use of the natural materials.

Indigo differs from the majority of dyestuffs in that it is insoluble in all of the reagents which the dyer can employ practically, but nature has fortunately given it a property which renders its application comparatively simple. When reduced in an alkaline bath, it is easily converted into the soluble indigo white as follows:

$$\underset{\text{Indigo blue}}{C_{16}H_{10}N_2O_2} + 2H = \underset{\text{Indigo white}}{C_{16}H_{12}N_2O_2}$$

Upon even the mildest oxidation, indigo white passes back to indigo blue as follows:

$$\underset{\text{Indigo white}}{C_{16}H_{12}N_2O_2} + O = \underset{\text{Indigo blue}}{C_{16}H_{10}N_2O_2} + H_2O$$

Indigo white being readily soluble in alkaline water solution, and this solution being easily absorbed by both animal and vegetable fibers, the process of application becomes comparatively simple. Upon exposure of the saturated fiber to the air, the indigo white is oxidized almost immediately to the insoluble indigo blue, which is rapidly precipitated upon and within the pores of the fiber to as great a depth as the indigo white solution has penetrated. The alkaline bath of indigo white is commonly called an *indigo vat,* and this process of coloring is usually spoken of as *vat dyeing.*

Application of Indigo. Indigo is extensively used for the dyeing of cotton and wool, but seldom for silk.

Three forms of indigo vats are chiefly depended upon at the present time:

(1) Fermentation vats.
(2) Zinc lime vats.
(3) Hydrosulfite vats.

These vats all involve the principle of reducing finely ground indigo to indigo white, and differ only in the methods used to bring about this reduction.

The *fermentation vat* is the oldest, but is still frequently used in wool dyeing, although never used for cotton dyeing. The reduction in this case is brought about by the fermentation of various organic substances such as bran, woad, molasses, and madder in an alkaline solution.

The *zinc lime vat* has been used largely for cotton dyeing, but not for wool dyeing. The reduction in this case is brought about by the action of zinc powder upon water in the presence of an alkali, that alkali being calcium hydroxide. The reaction may be represented by the following equation:

$$Zn + 2H_2O = Zn(OH)_2 + 2H$$

The *hydrosulfite vat* is the most recent of the indigo reduction vats, and has largely replaced the fermentation vat for wool dyeing, and the zinc lime vat for

[5] See also the section on "Reduction Vat Dyes," p. 1155.

cotton dyeing. In this vat the reduction is brought about by means of a sodium hydrosulfite solution, which is commonly prepared just before use by the action of zinc dust upon sodium bisulfite solution. The reactions may be represented by the following equations:

$$2NaHSO_3 + Zn = Na_2S_2O_4 + Zn(OH)_2$$
$$Na_2S_2O_4 + 2H_2O = 2NaHSO_3 + 2H$$

More recently sodium hydrosulfite ($Na_2S_2O_4$) has been put upon the market in a dry and well stabilized form and is extensively used not only as a reducing agent in the application of indigo, but of the other vat dyes. Its use simplifies the process greatly and avoids unnecessary sediment in the dye vat.

The application of indigo to *cotton and wool* differs chiefly in the fact that it is more difficult to penetrate wool than cotton with the indigo white solution and thus a longer period of immersion and a somewhat higher temperature is required. In the dyeing of wool the alkalinity of the bath must be greatly reduced.

Cotton requires an immersion of only a minute at ordinary temperature, unless the material is heavy, while wool requires from twenty minutes to an hour at a temperature of 120° F.

Indigo Extracts. These are prepared by the action of concentrated sulfuric acid upon indigo blue. The resulting compounds are the indigotin sulfo acids, which are freely soluble in water, and may be easily applied to wool in an acid bath. They dye wool a brighter blue than ordinary indigo, but unfortunately the dyeings produced are extremely fugitive to light, whereas vat indigo on wool produces one of the fastest blues known. The use of the former is very much restricted for this reason. The indigo extracts are of no value for cotton dyeing.

Logwood—Logwood is the product of a large and rapidly growing tree known botanically as the *Hæmatoxylin campechianum.* It is a native of Central America and the adjacent islands; Jamaica being one of the chief centers of the logwood industry. Raw logwood, as the name implies, comes in the form of rough logs, which are ground or rasped into small chips. It may be used in this latter form after it has been properly aged, but during recent years it has been more frequently put upon the market in the more concentrated form of an extract. It is the only vegetable dye that now retains any appreciable commercial importance.

Chemistry of Logwood Coloring. Careful examination of freshly cut logwood chips reveals the presence of a yellowish-crystalline compound having the empirical formula $C_{16}H_{14}O_6$, and to which the name *hæmatoxylin* has been assigned.

When exposed to the air, hæmatoxylin, especially in the presence of an alkali, rapidly oxidizes to a reddish-brown substance known as *hæmatein,* having the empirical formula $C_{16}H_{12}O_6$. Hæmatein is the active coloring matter of logwood. Upon further oxidation it passes into a resinous brown substance which is of no value for coloring purposes.

Logwood is in every sense of the word a mordant dyestuff, a metallic mordant being required to fix the dyestuff satisfactorily upon any textile fiber. During the dyeing process the hæmatein of the logwood unites with the mordant to form an insoluble metallic organic compound or color lake, which becomes fixed upon the fiber.

The chief metals entering into these color lakes are chromium, iron, aluminum, and copper. Logwood is commonly classified as a black dyestuff, and is used chiefly for the production of blacks, but more strictly speaking, it is a blue dyestuff, for with both aluminum and chromium, it produces blue dyeings and although with iron the shade produced approaches black, it is customary to add a small amount of some yellow or brown dyestuff to produce a satisfactory black.

Aging of Logwood. In general, logwood, when ready for the dyer, should contain a high percentage of hæmatein, but little unoxidized hæmatoxylin, and none of the resinous brown oxidation product already mentioned.

In order that this ideal condition may be approached as nearly as possible, logwood must be aged.

Logwood chips are commonly aged as follows:

After having been made into a large pile several feet in depth, the chips are well moistened with water, and then worked over with wooden shovels, every portion of the pile being thus brought in contact with the air. This is continued for a period of from three or fours days to two weeks, depending largely upon atmospheric conditions. After some experience, one can tell from the appearance of the chips when the right stage of oxidation is reached. The chips are then stored in such a way as to be exposed as little as possible to the oxidizing influence of the air.

When aged logwood is known to contain much hæmatoxylin, and consequently incompletely aged, the aging may be continued to a certain extent during the dyeing process by adding some oxidizing agent or using an oxidizing mordant, e.g., chromium in the CrO_3 form.

Logwood Liquor. Logwood liquor is a decoction of logwood made by extracting aged logwood chips with water. It usually has a strength of 15° Tw. (Sp.gr. 1.075) and as it does not keep well is only made as required for use.

Logwood Extracts. At the present time, logwood is most frequently put upon the market in the extract form. Logwood extracts are made by evaporating logwood liquor in vacuum pans until it reaches a sp.gr. of 1.25 or 50° Tw., or it may be carried to dryness to produce the solid extracts.

These solid extracts are prepared by patented processes. They vary somewhat in strength and chemical character, and are frequently designated as *hæmatine crystals.*

Application of Logwood. Logwood is still used in *wool dyeing* on account of its cheapness, and because the characteristic bloomy blue-black which it gives is difficult to produce at as low a cost with coal-tar coloring matters. In wool dyeing, logwood is chiefly used in conjunction with a chromium mordant, a small amount of some yellow or brown dyestuff, frequently fustic, being combined with it, to overcome the pronounced bluish cast which would otherwise result.

One dip logwood blacks are prepared by using some mordanting principle in conjunction with logwood, and a sufficient quantity of an acid, usually oxalic, to prevent too rapid precipitation of the color lake. A mixture frequently used for this purpose consists of logwood extract, ferrous sulfate, copper sulfate, and oxalic acid.

The use of logwood upon *cotton* has greatly diminished during recent years, logwood blacks having been largely replaced by aniline black, sulfur blacks, certain direct cotton blacks and to some extent vat dye blacks. When used upon cotton it is most frequently applied in conjunction with an iron mordant, either alone or in combination with a copper mordant.

Logwood is extensively used for the production of blacks upon *silk*. Iron mordants are depended upon almost entirely for this purpose and tin mordants occasionally. The process usually consists in alternately treating the silk with some tannin material and an iron or a tin compound until the silk is thoroughly filled with the metallic tannate. The silk thus mordanted is then dyed in a logwood bath. By using tin compounds in conjunction with acetate of iron it is possible to weight black dyed silk as much as 200 per cent of its original weight.

Miscellaneous Vegetable Dyestuffs—Although logwood and its derivatives are the only natural vegetable dyestuffs which are still used to any extent commercially, a number of the natural materials still find occasional use. A brief discussion of them is also of historical value.

Soluble Red Woods. Brazil wood, peach wood, Japan wood, and Lima wood are the principal soluble red woods. They are all mordant colors, and may be applied to mordanted cotton or wool by boiling in a plain bath of the extracted color.

Insoluble Red Woods. These include barwood, Saunders wood, and camwood. On account of the insolubility of the coloring matters which they contain, the ground or rasped chips of wood must be added directly to the dye bath. They are all mordant colors. The red woods have been replaced by coal tar colors which give more permanent and clearer dyeing at a lower cost. Hypernic extract is prepared from a mixture of red woods.

Madder. Madder root, which was known to the ancients, was for many hundreds of years the most important of the red natural coloring matters, and was used chiefly in the production of Turkey reds. The active coloring principle of madder is alizarine, $C_{14}H_8O_2$, and the discovery in 1868 by Graebe and Liebermann that alizarine could be cheaply made from coal tar derivatives soon led to the abandonment of madder as a coloring matter except in the Oriental countries where it is native.

Cochineal. Cochineal is a red mordant coloring matter obtained from the dried body of an insect which is native to Mexico and Central America. In the past, cochineal was extensively used for the production of scarlets and crimsons on wool in conjunction with tin and aluminum mordants. Like most of the other natural colors, cochineal has been superseded by the coal tar dyestuffs.

Other red natural dyestuffs worthy of mention are kermes, and lac dye, which are similar to cochineal in origin; also orchil and cudbear bluish-red coloring matters, which like litmus are derived from certain rock mosses or lichens.

Natural Dyestuffs of a Yellow to Brown Color—*The yellow natural dyestuffs* include a number of vegetable dyestuffs which vary between yellow and brown. Fustic, quercitron bark, Persian berries, turmeric, weld, and cutch are the most important.

Fustic or Cuba Wood. Fustic or Cuba wood is the most important of the yellow dyewoods and is still used to some extent in wool dyeing, chiefly in combination with logwood. It is a mordant dyestuff, being used with chromium and aluminum mordants. It possesses excellent fastness. It is sold in the form of ground wood, but more frequently as an extract.

Osage Orange. The wood of the osage orange tree, which grows in the southern part of the United States, was extensively used in the manufacture of wagon wheels, and it was discovered that an extract made from the sawdust and waste possesses dyeing properties almost identical with fustic, both as to color produced and fastness.

Quercitron Bark. Quercitron bark is obtained from the bark of a species of oak which grows in the Middle and Southern States. It is a mordant color and gives brighter yellows than fustic.

Persian Berries. Persian berries is the name applied to the berries of the buckthorn.

Turmeric. Turmeric is the ground root of a plant which grows in Asia. It dyes cotton, wool, and silk bright shades of yellow which are extremely fugitive to light and washing.

Cutch or Gambia. Cutch or gambia, a coloring matter rich in tannin, is extracted from the nuts and tender portions of various forms of acacia trees growing chiefly in India.

Mineral Dyestuffs—The mineral dyestuffs as a class are of minor importance in the textile industry. Various mineral pigments are sometimes used in calico printing, but in the actual dyeing process the only mineral dyes of any importance are Prussian blue, chrome yellow, chrome green, iron, buff, and khaki.

Prussian Blue. Prussian blue may be produced upon textile material by one of two methods. The first consists of mordanting the material with iron oxide, and then boiling in a solution of potassium ferrocyanide. The second method makes use of the fact that both the ferro- and ferricyanides of potassium decompose when boiled in an acid solution and from such a boiling solution Prussian blue is absorbed by textile material. The first process is used chiefly with cotton while the second is better adapted to wool dyeing.

Chrome Yellow. Chrome yellow is the chrome lead chromate which may be precipitated upon the fiber by alternate treatments with solutions of some soluble lead salt and a chromate.

Chrome Green. Chrome green is a basic oxide of chromium precipitated upon the fiber by the reaction of some soluble chromium salt with an alkali.

Iron Buff. Iron buff is a ferric hydroxide precipitated upon the fiber by the reaction of some soluble iron salt with an alkali.

Khaki. Khaki [6] is a yellowish drab color produced by the precipitation upon the fiber of a combination of ferric hydroxide and basic chromium hydroxide. Khaki, when properly dyed, produces an extremely fast color. By varying the proportion of ferric oxide and chromic oxide, shades of buff to olive drab may be produced.

MANUFACTURED ORGANIC DYESTUFFS

The natural dyestuffs were depended upon almost wholly until the discovery of a method of synthesizing *mauve* by Perkin in 1856. Mauve was the first of the so-called coal tar dyes, or better manufactured organic dyestuffs. Its discovery was followed by that of many similar dyestuffs, and a new era soon began in the textile coloring industry. Today well over a thousand entirely different dyestuffs of this class are at the disposal of the textile colorist and from them he can select dyes which will answer almost every requirement of shade and fastness.

[6] See also Chapter 28.

Classification of the Manufactured Organic Dyestuffs—The manufactured organic dyestuffs may be classified according to their chemical derivation, their composition, or in respect to the characteristic color-forming groups which they contain.[7, 8] While these classifications prove very satisfactory for the color-manufacturing chemist, they prove of little or no value to the practical textile colorist. Another classification which groups them according to their action toward the various textile fibers, i.e., according to their application, is the most practical for the student of textile coloring, and will be followed in this chapter.[9] It recognizes ten classes of coloring matters:

(1) Basic dyes.
(2) Phthalic anhydride dyes.
(3) Acid dyes. (Sometimes called sour dyes.)
(4) Direct cotton dyes. (Sometimes called salt colors.)
(5) Sulfur dyes.
(6) Mordant dyes.
(7) Mordant acid dyes.
(8) Insoluble azo dyes. Produced directly upon the fiber.
(9) Reducible vat dyes.
(10) Miscellaneous dyes.

Basic Dyes—Chemically the basic dyestuffs belong to the class of compounds known as substituted amines. Like ammonia they are basic in character, and hence the name.

The basic dyes have a direct affinity for wool and silk, but no direct affinity for cotton, and can only be applied to the latter fiber in conjunction with some acid mordant, usually tannic acid.

Application of Basic Dyes to Wool. Although the basic dyes have a direct affinity for wool, they are not extensively used in wool dyeing, for in most cases there are more desirable acid dyes. When applied to wool it is customary to make up the bath with the required quantity of dyestuff, sufficient acetic acid to render the bath distinctly acid, and Glauber's salt equal to 10 per cent of the weight of material being dyed. Enter material in a cold bath, raise temperature slowly to 195° F. and continue dyeing at this temperature until dye is practically exhausted from the bath.

Application of Basic Dyes to Silk. The basic dyes have a direct affinity for silk, and are extensively used for dyeing this fiber when bright rather than fast colors are desired. The dye bath is made up with 25 per cent "boiled off liquor"[10] and the remainder with water to which is added the required quantity of dyestuff and sufficient sulfuric, acetic, or tartaric acids to render the bath slightly acid. The silk material is entered at 100° F., the temperature of the bath then raised to 140° F., the material worked at this temperature for a few minutes, and the bath finally raised to a temperature of 195° F.

[7] Rowe, F. M., Colour Index and Supplement, Soc. of Dyers and Colourists, Bradford, England (1924), (1928).

[8] See Chapter 28.

[9] For the formulae and brief descriptions of methods of making the various dyes mentioned in this chapter, consult the tables of Chapter 27.

[10] Preliminary to dyeing, silk is subjected to the "boiling off" or "degumming process." The liquor resulting from this operation is known as "boiled-off liquor."

With dyestuffs which go on the fiber unevenly it is advisable to lift the silk material from the bath while the temperature is being raised.

Application of the Basic Dyes to Cotton. Although the basic dyes have no direct affinity for cotton, it is for the dyeing and printing of this fiber that they find considerable application. Before dyeing cotton material it must first be impregnated with tannic acid, and this fixed upon the fiber as an insoluble metallic tannate, usually of antimony. When such a tannin mordanted cotton material is dyed in a bath containing a basic color, an insoluble combination of the dyestuff, tannic acid, and antimony results, which becomes fixed upon the fiber. In calico printing, the basic dyes and tannic acid are mixed together in the printing paste, and chemical combination between the two is brought about by a subsequent steaming process. More thorough fixation of color may be obtained by after-treating the printed and steamed cloth with some soluble antimony compound, usually tartar emetic.

A synthetic cotton mordant for basic dyes, named *Katanol O,* has been extensively used. It is soluble in an alkaline water solution and has direct affinity for cotton. Cotton material may be mordanted with *Katanol O* by simply steeping it in a 5 to 10 per cent bath (based on weight of material), to which about 1 per cent of soda ash and a considerable quantity of common or Glauber's salt has been added. The temperature of the mordanting bath is first raised to 160-175° F. and the material allowed to remain in the cooling bath for about two hours. After rinsing, the mordanted material is dyed in a bath, containing the basic dye, which has been acidulated with acetic acid.

Application of Basic Dyes to Rayon. Cellulose acetate rayon has considerable natural affinity for certain basic dyes, and may be dyed directly with such dyes if fastness is no great object, and heavy shades are not desired.

Cellulose nitrate rayon has less affinity for basic dyes than the acetate variety, but more than either the cupro-ammonium or viscose rayons. These are all quite frequently dyed with basic dyes, usually the same as cotton on a tannin tartar emetic or a *Katanol O* mordant.

Characteristic Properties of the Basic Dyes. The basic dyes are characterized by their great brilliancy and high coloring power. Their fastness to light is by no means satisfactory, but their fastness to washing in most cases is reasonably good. Fastness to rubbing is not always satisfactory when applied on a tannin mordant.

The Phthalic Anhydride Dyes—The phthalic anhydride dyes are so called because they are directly related to this compound. They include the eosines and rhodamines, and are extensively used for the production of bright pinks, particularly in silk dyeing, and less frequently in wool dyeing. They are not used to any great extent in cotton dyeing, although sometimes used in cotton printing. The rhodamines are closely related to the basic dyes and may be applied in a similar manner. The eosines resemble the acid dyes and are applied by similar methods.

Application to Wool. The phthalic anhydride dyes are applied to wool in conjunction with alum, potassium bitartrate, and acetic acid.

Application to Silk. These dyes are applied similarly to basic or acid dyes.

Application to Cotton. In calico printing the phthalic anhydride dyes are either applied in a similar manner to basic dyes, or in conjunction with aluminum acetate.

Characteristic Properties. The phthalic anhydride dyes are characterized by their remarkable brilliancy.

Acid Dyes—The acid dyes are so called on account of their acid character, but more particularly because they dye wool so readily in an acid bath. They are of great importance in wool dyeing, about 75 per cent of all wool dyeing being accomplished at the present time by their use. The acid dyes are also extensively used in silk dyeing, but are of no importance in cotton dyeing.

From a chemical point of view the acid dyes may be subdivided according to their composition into three classes: (1) Those which are nitro compounds, i.e., those containing the nitro or NO_2 group. (2) The sulfonated basic dyes, i.e., those made by introducing the sulfonic acid or HSO_3 group into basic dye molecules. (3) Those which are azo dyes, i.e., those containing the azo or —N=N— group. The dyestuffs of the third group are the most numerous and most valuable of the acid dyes.

Application to Wool. The acid dyestuffs, almost without exception, are absorbed readily by wool in an acid bath and the dyeing process is comparatively simple. The dye bath is prepared with the required quantity of dyestuff, Glauber's salt equal to 15 per cent, and sulfuric acid equal to 3 to 5 per cent of the weight of the material being dyed. The percentage referred to here as in all other cases in this chapter is based upon total weight of material being dyed and not on concentration of solution used. Instead of this mixture of Glauber's salt and sulfuric acid, a corresponding amount of sodium bisulfate may be used. The material is entered at a temperature of about 140° F., brought slowly to a boil, and dyed at a boiling temperature for three-quarters of an hour, or longer if much dyestuff remains in the bath. With some acid dyes better results are obtained by substituting acetic acid for sulfuric acid, particularly at the beginning of the dyeing process. When acetic acid is used about 2 per cent of sulfuric acid is usually added toward the end of the dyeing process.

With some acid dyes which have a tendency to give uneven dyeings the bath is started with an addition of ammonium acetate and no acid. This gradually dissociates, the ammonia being slowly liberated and driven off, and the acetic acid retained in the dye bath. By this method the absorption of dye is cut to a minimum at the beginning of the dyeing, and increases so slowly that even dyeing is assured in most instances. After the dyeing has continued for some time and the bath has become decidedly acid, more acetic acid is added, and finally sulfuric, if necessary to exhaust the dye.

Application to Silk. In silk dyeing the proper quantity of dyestuff is added to a bath, made up with "boiled-off liquor" and water, to which has been added sufficient sulfuric acid to render the bath decidedly acid. The dyeing is begun at 100 to 125° F., and the bath slowly raised to 200° F., but no higher.

Application to Cotton. The acid dyestuffs have no affinity for cotton, and although occasionally used for special purposes they need not be considered in this respect.

The number of the acid dyestuffs is so great and their properties so varied that it is difficult to describe definite properties that will apply to all.

Most of the acid colors are easily soluble in water, and, from an acidified water solution, animal fibers rapidly, and in many cases completely, absorb the dyestuff. The vegetable fibers, in general, have no direct affinity for the acid colors; jute, however, as an exception, has a slight affinity for a few special colors.

Direct Cotton Dyes—The direct cotton dyes, as their class name indicates, have a direct affinity for cotton. All vegetable fibers readily absorb the direct cotton colors from their simple water solution, but for practical results it is advisable to make certain other additions to the dye bath. The direct cotton dyes also dye the animal fibers directly, but in most cases acid dyes are preferred. The direct cotton dyes having a direct affinity for both animal and vegetable fibers find extensive application in the dyeing of *union material* composed of cotton and wool, or cotton and silk, and certain rayon combinations.

Application to Cotton. The direct cotton dyes are usually applied to cotton material by boiling for one hour in a dye bath made up with the necessary quantity of dye, and Glauber's salt or common salt to the extent of 10 to 30 per cent of the weight of material being dyed. In some cases it is advisable to add from 1 to 3 per cent of soda ash, the quantity added varying with the amount of dyestuff used. In the dyeing of delicate tints, and with material which is difficult to penetrate, soap is sometimes added to the bath, and sodium phosphate used instead of Glauber's and common salts. It is always advisable to keep the bath as short, i.e., as concentrated, as possible, when applying these dyes to cotton. An after-treatment with copper sulfate or potassium dichromate solution renders certain of the direct cotton dyes somewhat faster to light.

Cotton material dyed with certain direct cotton dyes, particularly blacks, blues, and browns, may sometimes (depending upon their composition) be rendered much faster to washing and increased in intensity of color by the process known as *diazotizing* [11] and *developing*. To accomplish this, the material, which has already been dyed by one of the regular methods, is rinsed in cold water, and diazotized by working fifteen to twenty minutes in a cold bath of dilute sodium nitrite and sulfuric acid. After removal from this bath the material is again rinsed in cold water and worked for fifteen minutes in a bath containing the proper developer. Beta-naphthol dissolved in the necessary quantity of caustic soda solution is frequently used for this purpose. A few direct cotton dyes are rendered faster to washing, if given an after-treatment in a dilute formaldehyde bath. Notable among these are the polyform dyes.

Application to Wool. Wool may be dyed with most of the direct cotton dyes in a neutral bath with or without the addition of Glauber's salt or common salt.

In some cases it is advisable to add a little acetic acid, but the addition of too much acid causes the dyestuff to go upon the fiber unevenly.

Application to Silk. The direct cotton dyes are applied to silk in much the same manner as to wool. The addition of "boiled-off liquor" is an advantage.

Application to Rayon. Direct cotton dyes as a class have little if any affinity for the acetate rayons, and as a rule cannot be used for dyeing this fiber. The cellulose nitrate, cupro-ammonium and viscose rayons (constituting the so-called regenerated celluloses) may all be dyed with direct cotton dyes by methods similar to those used with cotton. The affinity of these dyes for cellulose nitrate rayon is not quite as marked as with the other two varieties.

[11] For a discussion of the chemistry of this process see Chapter 3.

Application to Cotton and Wool Union Material. The direct cotton dyes having a direct affinity for both cotton and wool are extensively used in the dyeing of union goods. By the choice of proper dyestuffs, and regulation of process, chiefly through variation of temperature, almost any color may be produced upon such material in one bath.

Properties of the Direct Cotton Dyes. The direct cotton dyes vary greatly in fastness. In general, they are not fast to washing when applied to cotton although much faster in this respect upon wool. Many of the reds are extremely sensitive to acid. Their fastness to light varies greatly. In some cases it is very satisfactory but for the most part they are only fair in this respect.

The property known as "bleeding" is one of the valuable as well as one of the detrimental characteristics of the direct cotton dyes.

This property is valuable since it tends to produce very level dyeings, and also to correct unevenness. On the other hand it is detrimental, as it prevents the use of the direct cotton dyes for coloring of ginghams and in calico-printing.

The direct cotton dyes are, as a rule, readily soluble in water.

Sulfur Dyes—The sulfur or sulfide dyes, as they are frequently called, are in many respects similar to the direct cotton dyes, but differ so entirely in many other respects that they are grouped by themselves. In recent years they have become an important factor in cotton dyeing, on account of the fastness of the dyeings they produce, and they are now extensively used for the production of reasonably fast blacks, blues, browns, and compound shades upon cotton.

They are called sulfur dyes for three reasons: In the first place, sulfur is a constituent of all of the dyestuffs of this class; sulfur and sodium sulfide are largely used in their manufacture; and finally, sodium sulfide is almost without exception a necessary constituent of the dye bath during their application.

Application of the Sulfur Dyes. The sulfur dyes are only used in the dyeing of vegetable fibers, the strongly alkaline sodium sulfide bath which must be used to hold the color in solution prohibiting their use with animal fibers. Special methods have been proposed for applying sulfur dyes upon wool, but none has as yet come into practical use. In general they are applied in a bath made up as follows: Dyestuff from 1 to 20 per cent of the weight of the material, sodium sulfide one to four times the weight of dyestuff, soda ash 5 to 10 per cent, and Glauber's or common salt 20 to 50 per cent of the weight of material being dyed. The material to be dyed is entered at or just below the boiling point and dyed at this temperature for one hour. It is advisable to keep the textile material below the surface of the liquor as much as possible.

Properties of the Sulfur Dyes. The most valuable property of the sulfur dyes is their fastness to light, washing, and acids. Their fastness to chlorine and bleaching, however, is in most cases not good.

Nearly all of the sulfur dyes are insoluble in water, but dissolve readily in a solution of sodium sulfide. Copper vessels must not be used for their solution or in their dyeing as the sulfide present rapidly acts upon the copper, coating it with the black copper sulfide.

The shades produced by the sulfur dyes are mostly of a dull character, and blacks, browns, dark blues, dark greens, and dull yellows; also various compound shades of these, such as drabs, slates, olives, and grays predominate. Sulfur yellows and greens as a rule do not equal the other sulfur colors in fastness. As yet no bright sulfur reds have been prepared.

Mordant Dyes—The true mordant dyestuffs included under this heading cannot be permanently fixed upon cotton, wool or silk, except in conjunction with some metallic mordant. The nature of these metallic mordants and the methods of their formation upon textile material have already been described. They are usually fixed upon the textile material as insoluble oxides or hydroxides of chromium, aluminum, and iron, and less frequently tin and copper. During the dyeing process, which follows the mordanting, the mordant dyestuffs, which contain either hydroxyl (OH) or carboxyl (COOH) groups in their composition, react with the mordants in much the same manner as acids react with bases, the result being the formation of insoluble metallic organic compounds of salt-like character which are known as *color lakes.* This reaction takes place *in situ* and the color lake is thus fixed upon and within the fiber.

Application to Wool. The material, which has already been mordanted, is thoroughly washed and then dyed in a bath made up with the necessary quantity of dyestuff and acetic acid. The latter is added to counteract any hardness [12] or alkalinity of the water, and should be slightly in excess.

The dye bath should be at ordinary temperature when the material is entered, but the temperature should be slowly raised to a boil, and the dyeing continued at a boiling temperature for one and one-half hours. This prolonged boiling is necessary in order that complete chemical reaction may take place between mordant and dyestuff.

Application to Cotton. Cotton material mordanted by one of the methods already described may be dyed by simply boiling in a bath containing the mordant dyestuff, but it is more often the case that mordant dyestuffs are applied to cotton in conjunction with some mordanting principle by the steam printing process.

Application to Silk. The mordant dyestuffs may be applied to mordanted silk but are seldom used for this fiber unless extreme fastness to soap and washing is desired.

Properties of Mordant Dyestuffs. While most of the coal tar dyes are soluble in water, and sold in a powdered condition, the mordant dyestuffs are the exception, being nearly all insoluble in water and sold as liquid pastes, which usually contain 20 per cent of coloring matter and 80 per cent of water. Alizarine is the most important of the mordant dyestuffs, and many of the other dyestuffs of this class are direct derivatives of alizarine. For this reason the mordant dyestuffs, as a group, are sometimes designated as the "alizarines." The mordant dyestuffs are characterized by their great fastness both to light and washing as well as to all of the common color-destroying agencies.

Mordant-acid Dyes—The dyestuffs of the group known as the mordant-acid dyes are intermediate in general character between the acid dyestuffs and the mordant dyestuffs. They resemble acid dyes in a general way, dyeing wool directly in an acid bath, but at the same time resemble the mordant dyes, in that they may be applied to advantage in conjunction with metallic mordants.

During recent years, the number of mordant-acid dyes has greatly increased, and at the present time they are receiving much attention in wool dyeing, having

[12] For a discussion of water treatment as applied to dyeing, see Chapter 6.

replaced the mordant dyes to a considerable extent. Their popularity lies in the ease with which they may be applied, and the fact that an after-treatment with some mordanting principle converts them into color lakes possessing excellent fastness to light, acids, washing and soaping.

Application of Mordant-acid Dyes. It is only upon wool that the mordant-acid dyes are useful. They are dyed in the same manner as acid dyes, but after the dyeing is completed the material is raised from the bath; from 1 to 3 per cent of potassium dichromate added and the boiling continued for from one to one and one-half hours. With some dyestuffs it is better to after-treat with the potassium dichromate in a separate bath, and in some instances a small quantity of some mordanting assistant, such as tartar or lactic acid, may be added to advantage.

Properties of the Mordant-acid Dyes. The mordant-acid dyes when properly applied approach almost if not quite the fastness of the straight mordant dyes. Difficulty is sometimes experienced in producing the exact shade desired, because the color produced at the end of the dyeing is often greatly changed during the after-treatment. It is not infrequent that a yellow or red will produce a dark blue, green or even black upon after-treatment.

As the after-treatment is almost without exception carried out with potassium dichromate, the mordant acid colors are often called "chrome dyes." The mordant acid dyes are frequently called "top chrome dyes" to distinguish them from the mordant dyes which are correspondingly known as "bottom chrome dyes."

Metallized Acid Dyes. A number of acid dyes are manufactured which contain chromium in the molecule. Of these the so-called Neolan and Palatine Fast dyes are examples. They possess fastness equal to that of the regular mordant acid dyes. These dyes are soluble in water, but when boiled in a bath containing several times as much sulfuric acid as is commonly used with acid dyes, the dye deposits upon the wool in an insoluble form.

Insoluble Azo Colors—A number of coloring matters of the azo type exist, the insolubility of which renders them non-applicable by any of the methods already described. Fortunately the nature of the process of their formation is such that they may be produced directly upon the fiber. Many insoluble azo colors may be produced, but for many years after their discovery only two, the so-called *para-nitraniline* and *alpha-naphthylamine reds* proved to be of great practical value. These were extensively used upon cotton, the former replacing Turkey-red to a great extent.

The dyestuffs of this class are also known as *developed colors,* because they are developed during the process of application, *ice colors* because ice is frequently used to attain a low temperature during their formation, *ingrain dyes* because they are formed within the grain of the fiber, and naphthol dyes because a naphthol is usually one of the components.

The formation of the insoluble azo dyes depends upon the fact that certain diazotized amino compounds produce insoluble coloring matters when brought into contact with certain naphthols or phenolic bodies. Para-nitraniline red, the most notable example, is produced by padding cotton cloth with sodium beta-naphtholate, prepared by dissolving beta-naphthol in caustic soda solution and then passing the cloth thus prepared through a bath containing a cold solution of diazotized para-nitraniline, the latter being prepared by the action of nitrous acid upon para-nitraniline hydrochloride. As soon as the cloth prepared as above comes in contact with the diazotized para-nitraniline solution, a bright red develops which possesses excellent fastness to light and washing. If diazotized alpha-naphthylamine is substituted for the para-nitraniline, a claret red color is produced of corresponding fastness. Para-nitraniline red on cotton is faster than any of the direct cotton reds of similar character and as regards fastness to light is exceeded only by Turkey-red.

More recently *naphthol AS* (*beta hydroxy naphthoic acid anilide*) has become an important factor in the application of the insoluble azo colors. It possesses one advantage over beta-naphthol, namely, its much greater affinity for cotton. As a result it may be applied by a wet process while beta-naphthol must be thoroughly dried upon the cloth after padding, whereas with naphthol AS the cloth may go directly into the diazo bath without drying. By the addition of formaldehyde to the padding solution of naphthol AS it is possible to keep the cloth wet after the padding for some time. Used in combination with dianisidine it gives a very fast blue. Several other modified naphthol derivatives of a somewhat similar nature have also been introduced. Naphthol AS and similar products have a decided advantage when it is desired to apply the insoluble azo dyes by a machine process wherein the yarn being dyed remains stationary and the dye liquor is forced through it under pressure. High cost as compared with beta-naphthol delayed their introduction to a considerable extent, but now they are quite generally used.

Naphthol AS in combination with Fast Red GL Base (Meta-Nitro-Para-Toluidine) gives a red which in shade and fastness appears nearer to that of Turkey-red than the older para-nitraniline red.

The insoluble azo colors are not applicable to wool, owing to the fact that a strong caustic soda solution must be used in dissolving the naphthol and this would act injuriously upon the fiber.

Fast salts is a name applied to certain stabilized[13] diazo compounds which possess the property of immediately forming diazonium solutions which may then be used the same as a regularly prepared diazo solution for the production of insoluble azo dyes.

The rapid fast dyes and the Rapidogens (Diagens) are the latest developments among the insoluble azo dyes. The Rapid Fast Dyes are stabilized diazo or diazonium compounds (frequently described as nitrosamines) in combination with certain developers as Naphthol AS or related compounds. These have found application in textile printing, but in recent years have been replaced to a considerable extent by the so-called *Rapidogens*.[14] The *Rapidogens* consist of alkaline mixtures of specially stabilized diazonium compounds, combined with suitable naphthols. When a Rapidogen is made into a suitable paste, printed upon cotton cloth, and then submitted to an acid aging process, hydrolysis of the diazonium component is brought about, and an immediate and permanent combination takes place with the naphthol component.

[13] See Chapter 28.
[14] See Chapter 28.

Reduction Vat Dyes—The reduction vat dyes have come into great prominence during recent years owing to their resistance to practically all of the color-destroying agencies, particularly light and washing. The chemistry of their application is the same as that of indigo,[15] in fact indigo is a reduction vat dye in every sense of the word. As a class these colors are insoluble in water, but when strongly reduced in an alkaline bath with sodium hydrosulfite they form soluble, usually colorless or almost colorless, reduction compounds which are easily absorbed by the fiber. Upon subsequent oxidation the reduced compounds pass back to the original insoluble dyestuff which becomes fixed upon the fiber.

From the point of view of composition the vat dyes may be divided into three groups: first, those related to indigo, sometimes designated as the *indigoids;* second, those related to anthracene, sometimes called the *indanthrenes* but more frequently the anthraquinone vat dyes; third, a group of more recently developed colors, sometimes designated as *sulfurized vat dyes,* including a number of the *hydron colors.*

Among the indigoid vat dyes, we have in addition to indigo itself, two quite distinct types: first, those which are *halogenated indigos;* second, those where sulfur has been introduced directly into the molecule, and sometimes called the *thio indigo dyes.* The halogenated indigos for the most part retain a blue or violet color, but with the thio indigo dyes we get an entire change even to the extent of a brilliant scarlet.

Of the anthracene derivatives indanthrene blue is the oldest and in various modified forms still the most important of this type of vat dyes. In addition to blue, however, there are yellow, green, orange, violet, red, brown, and black dyes of this type.

The typical hydron colors are perhaps in some instances more like sulfur dyes than vat dyes, and in some instances may be applied fully as well by the sodium sulfide, as by the reduction, method. Some of the dyes of this group are related to carbazol while others are more closely related to anthracene. The typical dye of this group is hydron blue, but other colors are included such as yellow, brown, and olive. The term hydron, however, has lost much of its class significance by application to dyes which are more strictly of the straight indanthrene type.

The general method of application consists in completely reducing the insoluble dye to a soluble condition by the use of sodium hydrosulfite in a caustic soda solution, and then adding this to the vat already made up to the proper volume with water to which a small amount of hydrosulfite and caustic soda have already been added. It is quite important that the temperature of the dye bath shall be maintained at the proper degree, which varies with different dyes and conditions from 100 to 140° F. Higher temperatures as a rule are detrimental. After dyeing, the material must be sufficiently oxidized to develop fully the color, and in most cases it has been found that finishing in a boiling soap bath increases brilliancy, clearness, and to some extent fastness of the dyeing.

PROPERTIES OF VAT DYES

Among the reduction vat dyes will be found the fastest dyes on cotton, both to light and washing. As a group they possess remarkable fastness to washing,

[15] See p. 1141.

and in some instances to boiling-out with alkali and bleaching with chlorine. While their fastness to light in general is excellent there are instances where it is far from what might be desired. Taking them as a whole it is now possible either by self-colors or combinations to produce almost any desired color with a satisfactory degree of brilliancy.

The vat reds are less satisfactory both as to brilliancy of color, and fastness than the other dyes of this group. For this reason the naphthol reds frequently supplement the vat reds in the production of a more complete line of dyed and printed fabrics.

While the indigoid dyes may be applied to wool, they are not extensively used for this purpose if we except indigo itself. The anthraquinone vat dyes have not been extensively applied to wool on a practical scale owing to the extremely alkaline character of the bath required.

The coloring power of the reduction vat colors is weak and a comparatively large amount must be used in most cases. The vat dyes at first presented many difficulties as far as practical application was concerned, but, through persistent experimentation and study, these have been very largely overcome and today they are extensively used both in dyeing and printing of the highest grades of cotton goods. Commercially the reduction vat colors are variously known as ponsol, anthrene, indanthrene, algol, helindone, ciba, thio indigo, and hydron colors.

Indigosol and Soledon Dyestuffs. These are water-soluble vat dyes virtually stabilized in a reduced form and may be used directly without previous reduction. They are sometimes designated as *solubilized vat dyes.*

Indigosol O, made directly from indigo blue, was the first dyestuff of this type to be introduced. Structurally it consists of reduced or leuco indigo with the hydrogen of the hydroxyl group replaced with a SO_3Na group. Indigosol O was followed by a number of similar dyes prepared from other indigoids. The soledon dyes are corresponding derivatives of the anthraquinone vat dyes and possess properties somewhat similar to the indigosols. The processes for applying these dyes have been improved quite recently, and they are now being used with considerable success. The individual dyes are somewhat more expensive than the corresponding insoluble vat dyes from which they are made and in a few cases they may not retain the equivalent fastness of the corresponding vat dyes. They have, however, many desirable properties such as better penetration in the case of cotton, and indigosol O offers many advantages over indigo in wool dyeing. They also find wide application in textile printing.

In the application of the *indigosols* cotton material is padded or printed with them, and later developed or oxidized with different reagents, such as ferric chloride, in combination with hydrochloric acid and common salt; or a combination of sodium nitrite and sulfuric acid; also by passing through hot acetic acid vapors. Wool material is dyed in a rather strongly acid bath and the color developed by the use of sodium nitrite or bichromate. The *soledon colors* are applied similarly although less acid is used in wool dyeing.

Miscellaneous Dyes—Although the nine classes of dyes which have just been discussed cover the kinds that are most commonly used, there are several dyes that do not fit into any particular category and must be classed as miscellaneous.

Aniline Black. Aniline black is usually classified as one of the *miscellaneous colors,* for it does not belong to any of the other groups. It is, in reality, an insoluble black pigment produced by the oxidation of aniline.

When aniline is oxidized, three consecutive products are formed: (1) *Emeraldine,* a greenish-colored salt insoluble in water. (2) *Nigraniline,* formed by the oxidation of emeraldine, and (3) *Aniline black proper,* or ungreenable black, as it is sometimes called, which is formed by a still further oxidation of nigraniline. The composition of the final product is not definitely known.

Aniline black is extensively used in calico-printing and the dyeing of hosiery, but cannot be used successfully in wool dyeing.

In general, aniline black is applied by preparing or printing the material with a mixture of aniline hydrochloride and certain oxidizing agents and oxygen carriers, such as potassium chlorate, potassium ferrocyanide, copper sulfide, or vanadium salts, and subsequently drying and aging it by passing through an aging chamber. A final oxidation is usually given in a bath of sodium bichromate.

Aniline black is extremely fast to light, bleaching, and washing.

Special Dyes for Acetate Rayon. The cellulose acetate [16] rayons typified by the variety known as "celanese" brought with their introduction entirely new problems in dyeing. It was found that they had no marked affinity for any of the ordinary classes of dyes then on the market, with the exception of the basic dyes, and a slight affinity for some of the vat dyes.

It was not until it was fully realized that the problem of dyeing cellulose acetate rayon could be satisfactorily solved only by devising special dyes for that purpose that any real progress was made.

One of the earliest and most successful attempts to produce a new type of dye suited for acetate rayon was the introduction of the ionamines. The solubility of the ionamines is due to an external or omega sulfonic acid group which splits off gradually during the dyeing process, liberating the insoluble dye base which is readily absorbed by the fiber. The dye base thus formed may in many cases be diazotized and developed with phenolic or naphtholic derivatives, giving a wide range of colors of very good fastness. The introduction of the ionamines was a step in the right direction, but their application involved complications which did not wholly appeal to the practical dyer.

The most important advancement as regards the dyeing of acetate rayon was the introduction of the so-called SRA dyes. It was found that certain dyes, ordinarily insoluble in water, developed an affinity for acetate rayon when they were physically solubilized or perhaps better, colloidally dispersed. Such a dispersion was satisfactorily made through the use of sulfo ricinoleic-acid (sulfonated castor oil), hence the characterizing name of SRA.

It was found that when ricinoleic-acid solutions of a number of such insoluble dyes and certain organic compounds were poured into water that a dispersion of the particles took place which was so fine and so complete as to retain the characteristics of water solutions to such an extent as to pass freely through ordinary filter paper. From such a dispersion acetate rayon readily absorbs the coloring

[16] For a discussion of the composition and manufacture of cellulose acetate, see Chapters 38 and 31.

matter. The principle of thorough dispersion has been utilized in the preparation of other groups of dyes, such for instance as the Duranol colors. The Setacyl, Cibacete, Celatine, Nacelan, and Celanol colors are other groups of dyes especially adapted to acetate rayon.

THE MECHANISM OF DYEING

In the dyeing of textile material we have the following types of material with which to deal:

(1) Raw Stock. Including loose cotton, loose wool, or any other fiber in the uncarded or unspun state.
(2) Carded, combed or partly spun fiber in the form of slubbing, tops, and roving.
(3) Yarn in the form of skeins, continuous chains of warp, or in wound packages.
(4) Piece goods or woven cloth.

In the older methods the dyeing process was carried out by hand. The raw stock was worked, turned over, and more or less constantly kept in motion by long poles. The yarn was dyed in the form of skeins which were suspended above the rectangular dye tubs by means of cross sticks and the skeins were frequently turned end for end and the sticks moved back and forth from one end of the tub to the other.

While these processes are still used, especially for the dyeing of loose wool, most dyeing is now done by means of machines.

These machines are of two types, first, those in which the material being dyed is circulated through the dye liquor which is more or less stationary and second, those in which the material being dyed remains stationary and the dye liquor is forced through it, usually by means of rotary pumps or propeller blades.

Cloth, warps, and skeins are more frequently dyed by the first method, while raw stock, tops, and slubbing are most frequently dyed by the latter.

In recent years, many machines have been devised for dyeing yarn in the form of beams of warp [17] and cops [18] in order to save handling and rewinding. In some instances these processes have been highly successful as, for instance, in the case of the Franklin Process machine, the Brandwood beam dyeing machine, and the Abbott machine, but there are others still in the experimental stage.

Textile Printing—Textile printing differs from dyeing in that the color or colors applied are confined to certain portions of the material, thus producing definite designs or patterns. The chief object of textile printing is the production of a pattern fabric in colors at a low cost, the duplication of which by weaving would be excessively expensive or impracticable for some other reason.

In cotton printing, perfectly plain cotton cloth commonly known as print cloth or calico is used, and the patterns produced are wholly independent of the weave.

[17] Beams are the large tightly rolled cylinders of warp which are placed in the back of a loom.

[18] Cops are small conically wound portions of yarn which are placed in the shuttles of a loom. Yarns wound on various perforated and penetrable cores are frequently described as packages.

There are, however, what might be termed fancy-prints, where the finished design or effect is produced partly in the loom and partly in the printing machine, and other cases by the combined effect of printing and mercerizing, or printing and embossing. Only one side of the cloth is usually printed, but occasionally both sides are printed, either by passing through two different machines, or a special machine arranged so as to print both sides at the same time.

The textile printing process proper is of a mechanical nature, but the preparation of the various printing pastes or colors, as they are called in the works, the methods of applying them, and their actual fixation upon the fiber involve a greater number of chemical principles and a greater variety of dyestuffs and chemicals than any other branch of textile coloring.

Cylinder or Roller Printing. At the present time the cylinder or roll printing machine, which originated in England during the latter part of the 18th Century, is used almost exclusively for textile printing. Although its mechanism has been greatly improved and its range of possibilities wonderfully extended since its introduction, the principle involved remains the same, namely: the passing of the cloth which is to be printed, under some tension, and very great pressure between an engraved (intaglio) metal roll (usually copper), the engraving of which is filled with color paste, and a large cylinder which is well padded with an elastic covering.

The modern textile printing machine, especially one intended for printing a number of different colors at the same time, is complicated and can only be properly handled by one who is acquainted with all its parts and who has had long experience in its use.

To give anything like a complete description of the intricacies of such a printing machine, or discuss the many precautions and rules which must be followed in its use is beyond the purpose of the present consideration. An attempt will, however, be made to explain the principles involved in its use.

Brief Description of Printing Process. By studying Figure 1, which represents a one-color machine in cross-section, the general principles of textile printing by means of the roller printing machine will be apparent:

ER represents the engraved printing roll which bears (sunken below the surface) the design to be printed.

The color box, pan, or trough which holds the color paste that is to be printed upon the cloth is indicated as such.

F represents the color furnisher, which consists of a revolving cylindrical brush or felt-covered roll, half of which is immersed in the color paste. It revolves parallel to the printing roll with which it is brought in contact under sufficient pressure to completely fill the engraving of the roller with the color paste.

The printing roll revolves in the direction indicated by the arrow head and the excess of color is removed, and the unengraved portion of the roller scraped perfectly clean by the color doctor, *CD*, which consists of a metal blade (usually steel) with a very accurately ground edge.

The printing is accomplished at the nip (*N*) between the printing roll and the pressure bowl or roll, *PB*. This pressure roll consists of a large cylinder covered with a number of thicknesses of so-called "lapping" which furnishes an elastic and springy back for the cloth that is being printed. The pressure between the printing roll and the pressure roll is so great that the cloth to be printed is practically forced into the depths of the engraving by the expansive force of the lapping, as well as of the blanket and back cloth which are always run between the cloth and the pressure roll. The color is thus extracted by the cloth from the engraved portion of the roll, while that portion of the cloth coming in contact with the unengraved portion of the roll, from which the color has been removed by the color doctor, remains unprinted.

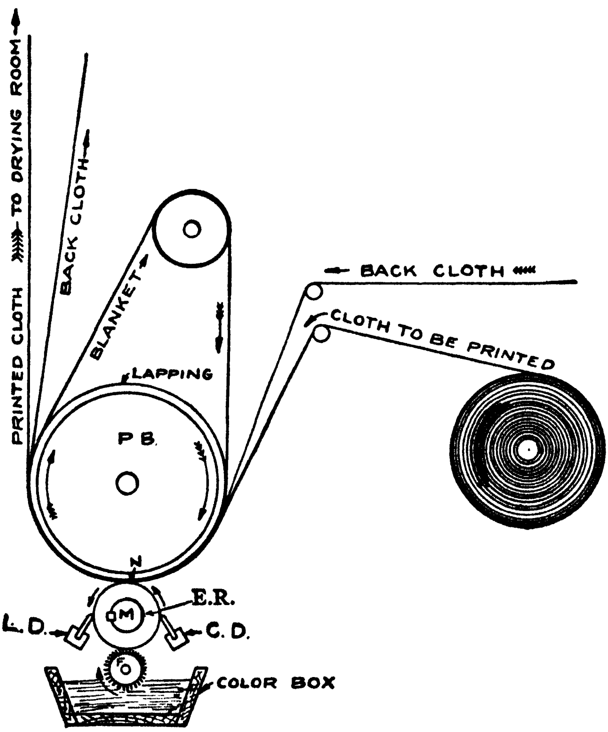

FIG. 1. Textile Printing Machine.

The lint doctor, *LD*, is similar in construction to the color doctor but is located upon the opposite side of the print roll. Its object is to remove lint and threads as well as any particles of partially dried color paste which might be carried into the color box.

After leaving the printing machine the printed cloth is passed as quickly as possible to the dryer.

Styles of Printing. When the term style is used in relation to textile printing, the term refers to the chemist's or colorist's part of the work, rather than the artistic or mechanical. The designer and engraver may determine the exact detail of the design, and perhaps the color combinations desired, but it still remains for the chemist or colorist to determine just how such colors and desired effects can be produced upon the cloth, and it is the particular operation or series of operations producing the effect which the printer designs as style.

There are a dozen or more different styles used in textile printing of which the following are among the more important:

(1) Direct printing style.
(2) Pigment style.
(3) Steam style with tannin mordant.
(4) Steam style with metallic mordant.
(5) Madder or dyed style.
(6) Ingrain or developed azo style.
(7) Vat dye style.
(8) Discharged dye style.
(9) Discharged mordant style.
(10) Resist style.

Style 1. Direct Printing. The term direct printing style has been used differently as well as vaguely by various authorities on printing. Some include the printing of pigment and basic colors, as well as mordant colors under this heading, and as a matter of fact it might rightly be said that every printing process involves direct printing.

To avoid confusion, however, and to make our classification of styles as complete and concise as possible, we shall designate as direct printing only the printing with such dyestuffs as have a direct or self affinity for the fiber without undergoing any chemical change or requiring any special solvent or reducing agent as is the case with the sulfur colors and indigo and its derivatives.

The direct printing style from this point of view includes only the printing of direct cotton colors, upon vegetable fibers and direct cotton, basic, phthalic anhydride, and acid colors upon wool and silk.

The dyestuff is prepared with the necessary thickeners and sometimes with the addition of certain assistants which aid in the penetration and fixation of the dyes. Very little direct printing is done upon cotton, as the only dyestuffs at all suitable are the direct cotton colors, and they cannot be used to any extent on account of their property of bleeding.

Recently a selected number of direct cotton dyes have been successfully printed on cotton in conjunction with urea, and upon aging, the dye is set, through the formation of a resin-like substance.

With wool and silk direct printing is very largely depended upon.

Style 2. Pigment Style. This consists in printing directly upon the material some pigment in a very finely divided condition in conjunction with some adhesive substance which will hold it fast to the fiber. Albumen is commonly used for an adhesive as its property of coagulating renders it especially suitable for the purpose. It is readily soluble in water at ordinary temperatures and can be uniformly incorporated into a printing paste with the desired pigment and the necessary thickeners. After printing, the cloth is subjected to a steaming process during which the albumen coagulates to a very insoluble form which firmly holds the pigment upon the fiber.

The pigment style just described is one of the older forms of printing but in recent years there has been, and still is being developed, a different type of pigment printing. This involves the fixation of the pigment upon the fiber in conjunction with one of the modern resins, which have been so extensively used in the finishing of textile fabrics, as for example in the so-called crease proof finishes. The phthalocyanines, of which the Monastral Blues are typical examples, have found valuable application in pigment printing.

Style 3. Steam Style. Tannin Mordant. This consists in printing upon the material a color paste containing a basic dyestuff, tannic acid, and some volatile acid, usually acetic, but less frequently formic acid, together with a small amount of some non-volatile organic acid, usually tartaric.

After printing, the cloth is steamed and then passed through a solution of some antimony compound, containing chalk in suspension, which completes the fixation of the color. The whole process is followed by a thorough soaping.

Style 4. Steam Style. Metallic Mordant. This style is produced by using a printing paste which contains a mordant dye, some metallic mordanting principle, and, in addition, a small amount of some organic acid, and the proper thickeners. The mordanting principle used must be of such a character as to readily undergo decomposition during the steaming process which follows the printing, thus producing a metallic mordant which will unite with the mordant color and produce an insoluble color lake.

Style 5. The Madder or Dyed Style. The madder or dyed style is produced by first printing upon the material some metallic mordanting principle which will readily liberate the actual mordant when the cloth is subsequently aged or steamed. The fixation of the mordant is completed by a dunging process, which consists in passing the cloth through a bath containing such alkaline fixing agents as chalk, sodium phosphate and silicate. The cloth thus printed and prepared is dyed with a mordant dye which unites with the mordant already present, producing a definite pattern.

Style 6. Ingrain or Developed Azo Style. With this style no actual dyestuff is used in any portion of the process, but the final result is the development of an insoluble azo color upon the fiber.

Two reds, para red, a bright red similar to Turkey-red; and alpha-naphthylamine red, a claret color, were formerly used almost exclusively for this style. The former by printing diazotized para-nitraniline and the latter diazotized alpha-naphthylamine upon cloth previously prepared with beta-naphthol. More recently *Naphthol* AS and related compounds have come into use. In this style of printing the Rapid Fast Dyes and the Rapidogens are extensively used.

Style 7. Vat Dye Style. Vat dyes are being extensively used in the production of fast prints on cotton. The vat dye is made up into a printing paste with a hydrosulfite-aldehyde reducing agent, and a suitable alkali. The printed cloth is then run through an ager, and the color oxidized by passage through a bath of some oxidizing agent usually sodium bichromate or sodium perborate. The prints are then given a hot soaping.

The Indigosols (solubilized vat dyes) have recently come into extensive use in printing. They may be used in conjunction with the *rapidogens* as both require the same treatment after printing.

Style 8. Discharged Dyed Style. In the production of the discharged dyed style the material is first dyed all over, usually by the padding process, or in the jig dyeing machine and less frequently in the ordinary string dyeing machine. Upon the cloth thus dyed there is printed the so-called discharge which is a printing paste carrying some substance capable of completely destroying or decolorizing the dyestuff already present.

A perfectly colorless figure may thus be produced upon a colored ground, or it is possible to introduce into the discharging paste some dyestuff which is not affected by the decolorizing agent, thus producing a colored figure upon a different colored ground. Various hydrosulfite compounds are extensively used for this purpose.

Style 9. Discharged Mordanted Style. This consists in first mordanting the cloth, then discharging the mordant by printing upon it the proper discharge, and subsequently dyeing. There are two quite different types of this style, one in which a tannin mordant is discharged by printing on a caustic soda paste and steaming, the material then being dyed with a basic color and another in which a metallic mordant is discharged by printing on some organic acid, aging and then dyeing with a mordant color.

Style 10. Resist Style. As with the discharge style the object of the resist style is to produce a white or colored pattern upon a different colored ground. The appearance of the two styles may be identical in some instances and the chemistry involved in their production may be the same. The difference between the two lies in the fact that the color-destroying agent is first printed upon the cloth and when the dystuff is subsequently applied absorption and fixation of color is prevented upon the printed portions. Colored resists may be produced by introducing into the printing paste a color not affected by the resisting agent.

Modern Trends in Printing—Whereas twenty-five years ago most cotton printing was done with Styles 3, 4, and 5, to-day they are scarcely used at all and most of the work is done through the application of Styles 6 and 7 with a rapidly increasing tendency towards Style 2.

Leather Dyeing—Leather being a protein resembles wool as regards affinity for dyes. It is colored in two ways, first by coloring only the face, the flesh side remaining undyed, and second by dyeing both sides. In the former treatment the dye is usually applied by means of a brush, and in the second case, the leather is completely immersed in the dye bath, in trays, in revolving drums or in vats equipped with a revolving paddle wheel. Basic and acid dyes are most frequently used, particularly upon vegetable tanned leather. On chrome tanned leather, both acid and basic dyes are used, also certain mordant dyes. Direct cotton dyes are also successfully used in the dyeing of chrome tanned leather.

Paper Dyeing—Paper being cellulosic in character it would naturally be expected to act much the same as cotton during dyeing. There is one difference, however, namely, that dyes must ordinarily be fixed upon cotton so that the material may be washed. Washing is not important as far as paper is concerned, therefore a wider range of dyes is permissible. Acid dyes for instance which cannot be used on cotton may be used in coloring paper. Dependence is placed mostly on basic and direct cotton dyes although acid and eosine dyes may be used. Vat dyes have also been used for producing very permanent tints in paper, particularly writing paper. For the most part, colored paper is produced by dyeing the pulp. The dyestuff and necessary assistants are added directly to the beater. Finished paper is also dyed, usually by applying the color by means of a rotating brush, or the paper is passed over a roller rotating partly in the dye solution.

One side of paper is frequently coated with colored adhesive mixtures, which give a smooth even coloring. Such coated papers are frequently glazed.

READING LIST[19]

Duerr, Geo., and Turnbull, Wm. Bleaching and Calico Printing. London, 1896.
Knecht, E. The Chemistry of the Coal Tar Colors. London, 1900.
Patterson. Science of Color Mixing. London and New York, 1900.
Gardner, Walter M. Wool Dyeing. Philadelphia, 1900.
Collin and Richardson. Chemistry of the Organic Dyestuffs. London, 1892.
Sansone. The Printing of Cotton Fabrics. London, 1901.
Hummel. The Dyeing of Textile Fabrics. London, 1901.
Rawson, Gardner and Laycock. Dictionary of Dyes and Mordants. London, 1901.
Beech, Franklin. The Dyeing of Cotton Fabrics. London, 1901.
Beech, Franklin. The Dyeing of Woolen Fabrics. London, 1902.
Von Georgievics. The Chemical Technology of Textile Fibers. 2d Edition. London, 1920.
Fraps. Principles of Dyeing. New York, 1903.
Cain and Thorp. The Synthetic Dyestuffs. 2d Edition. London, 1913.
Matthews, J. M. Laboratory Manual of Dyeing and Textile Chemistry. New York, 1909.
Patterson, David. Color Matching on Textiles. London and New York, 1909.
Dreaper, W. P. Chemistry and Physics of Dyeing. Philadelphia, 1906.
Mulliken, S. P. Identification of the Commercial Dyestuffs. New York, 1910.
Knecht, Rawson and Lowenthal. Manual of Dyeing. 8th Edition. London, 1925.
Fay, Irving W. The Chemistry of the Coal Tar Dyes. New York, 1911.
Trotman, R. S. The Principles of Bleaching and Finishing Cotton. London, 1911.
Hübner, J. Bleaching and Dyeing of Vegetable Fibrous Material. New York, 1912.
Wood, J. K. The Chemistry of Dyeing. 1913.
Knecht and Fothergill. The Principles and Practice of Chemical Printing. 3d Edition. London, 1936.
Schultz. Farbenstofftabellen. Berlin, 1923.
Wahl, A. Manufacture of Organic Dyestuffs. 1914.
Green, Arthur G. Analysis of Dyestuffs. 1915.
Matthews, J. Merritt. Application of Dyestuffs. 1920.
Gandswindt. Dyeing Mixed Silk Fabrics and Artificial Silk. 1921.
Shreve, J. Norris. Dyes Classified by Intermediates. 1922.
Colour Index. Published by Society Dyers and Colorists. 1923.
Trotman, S. R. and E. R. Bleaching, Dyeing and Chemical Technology of Textile Fibers. 1925.
Hall. Textile Bleaching, Dyeing, Printing and Finishing Machinery. 1926.
Mullin, C. E. Acetate Silk and Its Dyes. 1927.
Horsfall and Lawrie. Dyeing of Textile Fibers. 1928.
Colour Index and Supplement by Society Dyers and Colorists. 1928.
Whittaker, C. M., and Wilcock, C. C. Dyeing with Coal Tar Dyestuffs. 3d Edition. 1938.

Periodicals

Journal of the Society of Dyers and Colorists. England Dyer and Calico Printer. England.
American Dyestuff Reporter, including Proceedings of the American Association of Textile Chemists and Colorists.
Textile Colorist. New York City.

[19] See 1941 Year Book, American Association of Textile Chemists and Colorists, for more complete bibliography.

CHAPTER 30

INDUSTRIAL SOLVENTS

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INTRODUCTION

Solvents and the phenomenon known as solubility have intrigued the scientific mind since antiquity, the alchemist's interest in the universal solvent being exceeded only by his desire to discover the philosopher's stone. Although the discovery of the universal solvent, like that of the philosopher's stone, has not been realized, the interest in solvents and in the mechanism of solution has grown at a tremendous rate during the past century. This is not surprising when one considers that the phenomenon which was scarcely more than an interesting puzzle to the Greek philosopher is of prime importance to the modern chemist and chemical engineer. The selection of the proper solvents for a given process and the development of the proper handling and recovery systems have a profound effect on the process being considered. The degree of success which the chemist or chemical engineer obtains in the solution of these problems often decides the fate of the process in question.

While the interest in solvents dates into antiquity, knowledge concerning the manufacture and usage of the majority of present day industrial solvents is relatively new. If we are allowed to use the legal recognition of one of the most important solvents—ethyl alcohol—as an index of the age of modern solvents, we find that the age of solvents dates back to 1855. It was in this year that the law permitting the use of methylated spirits in England was passed. Passage of a similar law in the United States did not occur until 1906, which indicates the relative youth of the American solvent industry. The World War had a profound effect on the development of the solvent industry in this country. The story of the various measures taken to solve the acute acetone shortage is almost fantastic. The ether-alcohol solvent required in smokeless powder manufacture called for extensive production facilities for industrial alcohol. The post war period with its rapid development of the automobile, airplane, cellulose lacquers and plastic materials in general, sustained and even intensified the development of solvents.

The present demand for solvents is indicated by the following Table 1.

Definition of a Solvent—Because of the wide range of chemical compounds and due to the many and varied uses to which solvents are put, a brief, concise definition of a solvent is extremely difficult, if not impossible. In certain instances the function of the solvent is to reduce various incompatible chemical substances to a homogeneous fluid state so that chemical reaction may take place smoothly and quickly. Another important usage of solvents is the conversion of a solid to a fluid state so that it may be easily removed from one place to another, as in the case of paint removers and solvents for lacquers. A solvent may be a liquid added to a heterogeneous mixture of liquids or liquids and solids to reduce them to a single homogeneous fluid, as in the case of many medicinal preparations. Conversely, a solvent may be a liquid which is added to a homogeneous or heterogeneous mixture of liquids or solids to effect a separation of the mixture;

TABLE 1—PRODUCTION OF MAJOR SOLVENTS IN THE UNITED STATES

Material	*Production*
Tariff Commission Report 1940	
Acetone (lbs.)	201,506,344
Amyl acetates (lbs.)	5,828,497 *
Amyl alcohols (lbs.)	9,096,977 *
Benzol (gals.)	39,151,941
Butyl acetates (lbs.)	86,721,057
Butyl alcohols (lbs.)	164,568,813
Carbon tetrachloride (lbs.)	100,811,330
Diacetone alcohol (lbs.)	4,671,512
Ethyl acetate, 85% (lbs.)	75,368,803
Isopropyl alcohol (lbs.)	219,925,900
Phthalates, total (lbs.)	18,727,424
" dibutyl (lbs.)	8,799,528
" diethyl (lbs.)	2,306,063
Toluol, crude and refined (gals.)	32,579,649
Solvent naphtha (gals.)	10,060,152
Xylol (gals.)	5,645,993
Department of Commerce Report 1940	
Synthetic methanol (gals.)	44,968,447
Wood distillation methanol (gals.)	5,294,020
Department of Treasury Report 1940	
Ethyl alcohol, 95% (gals.)	138,642,016

* These figures taken from the 1939 report because not given in the 1940 report.

for example, the leaching of a solid mixture to remove values therefrom or the separation of the aromatic and paraffinic constituents of a petroleum mixture. It is evident that solvents can best be defined in terms of what they will do rather than what they are. From this point of view a solvent may be defined as:

(a) A substance which is used to bring a solid or semi-solid material into the fluid state.

(b) A substance which when added to a heterogeneous mixture of liquids or liquids and solids will produce homogeneity.

(c) A liquid which when added to a mixture of liquids or solids will, by virtue of its insolubility towards certain of the components of the mixture, result in a heterogeneous mixture and thereby effect a more or less complete separation of the mixture, the separation depending on the mutual solubilities of the components of the mixture and the material added.

Important Solvent Characteristics—The physical properties of a solvent are of paramount interest to the chemist seeking one for some particular purpose.

For example, the vapor pressure of a solvent is largely the result of its molecular weight and the type of molecules present in the liquid state. Comparison of the vapor pressure of a certain solvent with that of a similar compound will indicate whether the compound is associated or not in the liquid state, and therefore give an indication of its polarity. In addition, the vapor pressure gives valuable information on the volatility of a compound and, coupled with knowledge of its chemical structure, gives important information as to its relative toxicity and inflammability. The following are among the important characteristics of solvents:

1. Solvent power.
2. Boiling point and evaporation rate.
3. Inflammability and flash point.
4. Stability.
5. Physiological action.
6. Color.
7. Odor.

A general practice in studying the mechanism of solution and solvent power is to divide the field into two sections, one dealing with the solution of crystalline compounds as, for example, common salt and sugar; the other with lyophilic materials such as cellulose-esters, gums and resins. Without going into the theoretical considerations pertaining to the two types of solubility, it will suffice for present purposes to differentiate between them on the basis of solubility behavior. Lyophilic solids differ from crystalline ones in that they are miscible with their solvents in all proportions, whereas crystalline materials show well defined limits of solubility in their solvents. Since one of the major uses of organic solvents is in connection with solution of lyophilic compounds, this type of solubility is the only one that will be considered here. Those interested in the solubility of crystalline compounds are referred to general texts on physical chemistry and to the A. C. S. Monograph "Solubility," N. Y., 1924, by J. H. Hildebrand, for information and references.

The mechanism of solution of lyophilic compounds, particularly with regard to cellulose esters and various natural and synthetic resins, has been energetically studied within the last two decades. Harkins[1] pointed out that groups which express an affinity for water are usually polar, conferring upon the molecules containing them characteristics of permanent electric moment.[2] Kraemer and Williamson[3] point out if the adhesional energy becomes greater than the cohesional energy at a sufficient number of points in the solid colloid, or xerogel, swelling is unlimited, leading to the formation of a solution.

Highfield[4] considered the nitrocellulose molecule from the viewpoint of polarity and Drummond[5] considered the polarity of many common resins. Hardy[6] illustrated that adhesional energies increase with polarity of organic molecules;

[1] Harkins, J. A. C. S. *39*, 384 (1917).
[2] Debye, "Polar Molecules," Chemical Catalog Co., New York (1929).
[3] Kraemer and Williamson, J. Rheology *1*, 76 (1929).
[4] Highfield, Trans. Faraday Soc. *22*, 57 (1926).
[5] Drummond, India Rubber Journal *125*, 101 (1928).
[6] Hardy, Proc. Royal Soc. Lond. *86-A*, 610 (1912).

esters, alcohols, and acids showing the highest values, the saturated hydrocarbons exhibiting the lowest values.

The theoretical considerations just cited shed considerable light on the mechanism of solution of lyophilic colloids but do not answer all problems of the applicability of distinctive characteristics of individual solvents.

Consideration of application and solvent properties have been studied by use of Gibbs triangular coordinates by Hoffman and Reid [7] in systems of more than one solvent or diluent. Recently Ware and Teeters [8] and Ware and Bruner [9] studied the evaluation of lacquer solvents by constant viscosity procedure.

A. K. Doolittle [10] in a very thorough study has done much in the evaluation of solvents. Table 2 giving the characteristics of the most important industrial solvents is taken from this article.

Testing of Solvents—The American Society for Testing Materials (A.S.T.M.) has done excellent work in standardizing specifications and testing methods for the commonly used solvents and diluents. Solvent manufacturers publish specifications under which they sell their products. Since they are available to anyone interested, no attempt will be made to give these details here.

MONOBASIC ALCOHOLS

The simple aliphatic alcohols constitute one of the most important solvent families. Inspection of their structural formulae shows a water molecule in which one of the hydrogen atoms has been replaced by a hydrocarbon radical. It is not surprising then to find that their solvent powers are those of strongly polar compounds, the polar characteristics being most pronounced in the lower members of the series. They are therefore good solvents for strongly polar materials such as certain resins and dyestuffs but poor solvents for fats, waxes and oils. The influence of the hydroxyl group diminishes as the length of the hydrocarbon radical increases; for example, methyl alcohol is a good solvent for certain types of nitrocellulose while the amyl alcohols are entirely lacking in this ability.

The aliphatic alcohols are narcotic substances whose activity decreases with increasing molecular weight. The acute toxic qualities increase with increasing molecular weight but this factor is more than offset by the decreasing solubility in water and lowering of vapor pressure. All alcohols have an irritating action on the mucous membranes, the effect increasing with the molecular weight of the compound, being most pronounced in the case of the amyl alcohols. The human body develops a decided tolerance towards all the alcohols with the possible exception of methyl. Alcohols are more or less easily absorbed through the skin, the rate of absorption being most pronounced with the lower alcohols. Acute intoxication in the case of ethyl and serious poisoning with methyl may result from repeated skin applications of these alcohols.

[7] Hoffman and Reid, Ind. Eng. Chem. *20*, 431 (1928).
[8] Ware, V. W. and Teeters, W. O., Ind. & Eng. Chem. *31*, 1118 (1939); also *31*, 739 (1939).
[9] Ware, V. W. and Bruner, H. W., Ind. & Eng. Chem. *32*, 78 (1940); also *32*, 519 (1940).
[10] Doolittle, A. K., Ind. & Eng. Chem. *27*, 1169 (1935).

Methanol—Methyl alcohol is decidedly the most poisonous of the alcohols. It is readily absorbed through the lungs by breathing the vapors. Its effects are cumulative and for this reason repeated exposures to this alcohol are to be avoided. Methyl alcohol is very slowly eliminated from the body and its oxidation products in the body are powerful nerve poisons. Perhaps one of the most dangerous characteristics of methyl alcohol is its varying effect on different individuals. Some people seem to be almost entirely immune to methanol poisoning while most people are seriously affected, some even by small amounts.

The major portion of methanol produced today is manufactured from carbon monoxide and hydrogen in a process similar to that used for making ammonia. The process is favored by high pressures and requires high operating temperatures (300-400° C.) for commercial reaction rate. See Tables 3 and 4.

TABLE 3—VALUES OF THE EQUILIBRIUM CONSTANT K, FOR METHANOL FORMATION AT VARIOUS TEMPERATURES[11]

Temperature ° Absolute	*Temperature ° C.*	*K*	*Relative Rates*
300	27	67,000,000	1
400	127	206	10^3
500	227	3.16	10^6
600	327	0.0386	10^9
700	427	0.00154	10^{12}
800	527	0.000138	10^{15}
900	627	0.0000206	10^{18}

TABLE 4—THE PARTIAL PRESSURES, IN ATMOSPHERES, OF CARBON MONOXIDE, HYDROGEN AND METHANOL IN EQUILIBRIUM WITH EACH OTHER AT 700° ABSOLUTE, 427° C., AT VARIOUS PRESSURES[11]

Total Pressures (Atmospheres)	*Partial Pressures (Atmospheres)*		
	CO	H_2	CH_3OH
1	0.333	0.666	0.00023
10	3.26	6.52	0.22
100	19.0	38.0	43.0
200	27.0	54.1	118.9
300	32.6	65.2	202.2
1000	51.6	103.2	845.2

The reaction is exothermic as shown in the following equation:

$$CO + 2H_2 \rightleftarrows CH_3OH + 32{,}100 \text{ cal.}$$

Many catalytic materials have been used in this reaction, some of the most important being chromium and zinc compounds. According to Reid,[11] these compounds exert a preferential action and keep the amount of methane formed at a minimum. Some higher alcohols and polymers are also formed along with the methanol. (For the important features of high pressure synthesis, see Chapter 4, High Pressure Processes.)

Methanol from Wood—The wood distillation industry produces three major products: charcoal, wool alcohol and acetic acid.

The industry began primarily for the purpose of producing charcoal, at a

[11] Reid, E. E., "College Organic Chemistry," third printing, pp. 47, 48, 193, D. Van Nostrand Co. (1931).

time when charcoal iron became an important item in the steel industry. A generation ago many of the larger wood distillation plants also operated blast furnaces producing charcoal iron. Improvements in coke, and technical advances in steel-making have resulted in the production of satisfactory grades of steel without charcoal. With this important market fading, the wood distillation industry had to depend upon its other two major products, methyl alcohol and acetic acid (acetate of lime). During the past ten to fifteen years synthetic production has given the wood distillers severe competition in these two products. As a result, the marginal wood distillation plants closed and liquidated. During this shrinkage process, the progressive members of the industry made a serious effort to widen the market for wood charcoal—their one product not likely to be produced synthetically.

These efforts are bearing fruit. With the improving market for charcoal, it seems evident that what remains of the wood distillation industry will continue in business for many years to come.

The important solvent from the wood distillation industry is methanol.

The distillate (pyroligneous acid) coming from the retort is mainly water but also contains methanol, acetone, oils, tars, organic acids (mainly acetic) and numerous other compounds in minor quantities. The acids were formerly neutralized by the addition of lime. Most of the larger wood distillation plants now recover the acetic acid directly by various extraction methods using solvents. The acetone and methanol are separated from the retort distillate by distillation. The largest single usage for wood methanol is as a denaturant for ethyl alcohol. (For a more detailed discussion of wood distillation products see Chapter 17, Wood Distillation Industry.)

Ethyl Alcohol—Fermentation Process—Ethyl alcohol can be produced by the yeast fermentation of various hexose sugars. Consequently, any raw material containing such sugars or containing materials which may be transformed into them is a potential source of ethyl alcohol. In Germany considerable alcohol has been made from potatoes and in France from sugar beets. Alcohol has been made for years from starchy grains and even sawdust has been used. Sulfite liquor is also used in some of the European countries. Where sawdust or wood flour is employed for the production of alcohol it is necessary to convert the cellulose to fermentable sugars by acid hydrolysis. Where grains are employed the starch is usually converted to sugars by the action of malt. The cheapest source of fermentable sugars is the so-called blackstrap molasses which is a by-product of the manufacture of cane sugar and for which there is no general use other than in the mixed animal feed and in the fermentation industries. The wide utilization of this blackstrap molasses in alcohol plants has proved very helpful to the sugar industry by preventing accumulation of a by-product difficult to dispose of otherwise. Inasmuch as practically all the fermentation industrial alcohol produced in the United States comes from blackstrap molasses, this process will be the only one considered here.

Fermentation. It is necessary first of all to dilute the molasses to reduce the sugar concentration. As ordinarily produced, cane molasses is somewhat acid. Diluted blackstrap usually shows a pH around 5.3. It has been found by long experience that the alcohol production is bettered somewhat if the pH of the diluted solution is reduced to 4.9-5.0. Consequently, following the dilution it is customary in industrial alcohol plants to add small quantities of sulfuric acid in order to bring the pH to the point noted above. Cane molasses, at least the blackstrap type, is surprisingly well provided with nutrients for the yeast—so well supplied that ordinarily it is not necessary to add any nutrients whatever. In some cases a small quantity of nutrient (ammonium sulfate and phosphates) may be necessary. An exception to this rule is found in the so-called invert molasses, of which rather large quantities have been made in the West Indies in recent years. This is not a final molasses but rather an inverted cane juice which has been concentrated by evaporation to a syrup with a sugar content of around 75%. When such material is to be used for alcohol fermentations it is necessary to use considerable quantities of ammonium sulfate since this invert molasses does not have the favorable high ratio of non-sugar yeast nutrients to sugar that is found in the ordinary blackstrap molasses.

Fermentation Steps. The diluted molasses to which has been added a small quantity of sulfuric acid, and perhaps ammonium salts, is run into a large tank for fermentation by yeast. This nutrient medium is known as the "mash." In most plants no attempt is made to run the last stage of the fermentation as a pure culture. The seed yeast mashes, however, which are not unlike the one described above in their make-up, are usually sterilized by heat, cooled, and then inoculated with pure yeast cultures. These seed cultures are built up in volume in the plant by using small preliminary growings in sterile mash and setting successively larger vessels from these until a volume of pure seed is obtained equivalent to about 5% of the final fermenter volume.

The yeast used in industrial alcohol plants is selected in particular for its ability to tolerate high temperatures and high concentrations of alcohol. Obviously, the necessity for maximum economy in distillation requires that the mash contain the maximum amount of sugar which can be efficiently turned into alcohol by the yeast. Since large volumes of liquid fermenting actively generate heat, it is also obvious that a yeast has to stand relatively high fermentation temperatures in order to function satisfactorily. To a limited extent it is possible to cool the fermentations either by placing coils in the fermenters or by running water over the outside surfaces. The sugar concentration is adjusted so that at the completion of fermentation the alcohol content will be from 8-10%. The time required is about 45 hours.

During the fermentation large quantities of carbon dioxide gas are liberated. This gas is scrubbed with water to remove its alcohol content. The alcohol recovered in this manner amounts to from 0.5% to 1% of the total. Fermentation temperature and concentration influence the alcohol content of the CO_2. In many plants the CO_2 is purified by activated carbon or by washing with strong oxidizing solutions, compressed and sold as liquid CO_2 in cylinders or in solid form as dry ice to be used as a refrigerant. The high purity of the fermentation CO_2, together with the low cost of production, makes the production of dry ice from this source particularly attractive. Besides its use as a refrigerant, CO_2 is also used in carbonated beverages, fire extinguishers and to a small extent in chemical processes.

Distillation Step. The alcohol is extracted from the fermented liquor, technically known as beer, by passage through a stripping column known as a beer still. Figure 1 shows a beer still equipped with its own rectifying column. The beer is first preheated in the dephlegmating bodies of the rectifying column and then passes on to the top plate of the beer still. Live steam is fed in at the base of the still, the alcohol being extracted as the beer flows down the stripping column. The dilute vapors coming off the beer still are passed into the base of the rectifying column, wherein they are rectified to 95%.

The alcohol thus obtained is of satisfactory quality for many uses. It does, however, contain traces of impurities boiling near alcohol that have distinctive odors and are difficult to separate from ethyl alcohol.

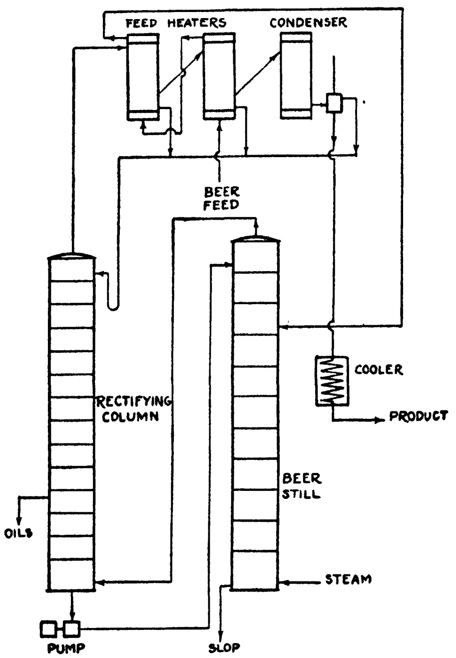


FIG. 1. Continuous Beer Still.

Refined alcohol and cologne spirits are produced by further purification of the product just mentioned. A typical purification unit of this type is shown in Figure 2. Briefly, the operation of this unit is as follows:

Impure alcohol or high wines, together with some dilution water, are fed to the aldehyde column as shown in the diagram. The column is heated by live steam admitted at the base of the unit. As a result of the action of this column the volatile impurities, acetaldehyde, amines, esters, etc., are removed from the alcohol as it flows from tray to tray down the column. These "heads" products are continuously removed along with some alcohol from the aldehyde column condenser as a low grade product.

The purified alcohol issues from the base of the aldehyde column, free of "heads" products but containing higher alcohols and much water, and is fed into the exhausting section of the rectifying column. The higher alcohols, known as fusel oil, accumulate in the exhausting column and are removed continuously from a plate below the feed. The alcohol is rectified to 191-192 proof by action of the rectifying column. During the rectification step some aldehydes and esters are formed by hydrolysis of aldehyde polymers and the action of organic acids on the alcohol. These are removed by passing the alcohol from the rectifying column through a small stripping column. The product issuing from the base of the final purifying column is high grade spirits.

The beer still operation may also be combined with the spirits unit, the vapors from the beer still passing directly to the middle section of the aldehyde column. (For a discussion of the principles of distillation, see Chapter 2, The Unit Operations.)

Synthetic Ethyl Alcohol—For many years considerable ethyl alcohol was used in the preparation of ethylene. This situation has now been reversed, and although considerable ethylene is still made from ethyl alcohol, at the present time a large amount of ethyl alcohol is being produced from ethylene obtained from the cracking of petroleum hydrocarbons. Synthetic ethyl alcohol has been produced in the United States since 1931.

The commercial method used consists of absorbing ethylene in strong sulfuric acid followed by dilution to hydrolyze the ethyl sulfuric acid formed in the first step to ethyl alcohol. This process also produces some valuable by-products such as diethyl ether. One of the serious drawbacks to this process is the necessity for reconcentrating the acid medium.

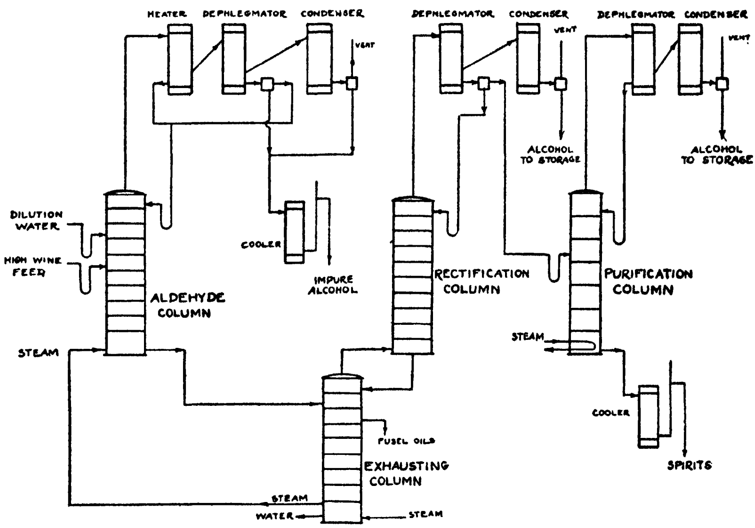


FIG. 2. Continuous Spirit Unit.

This difficulty is overcome by processes described in recent patents. In general, these processes are continuous, operating at relatively high temperatures and pressures and with low acid concentrations.[12] (For further information on the general process of hydrolysis see Chapter 3, The Organic Unit Processes, and Chapter 27, Industrial Organic Chemicals.)

Anhydrous Alcohol—Anhydrous alcohol cannot be made by ordinary rectification alone due to its formation of a low boiling azeotropic mixture with water at atmospheric pressure. Since anhydrous alcohol has several desirable properties not possessed by the azeotrope containing 95% alcohol, considerable effort has been made to develop anhydrous alcohol processes. The most important of these processes are as follows:

(a) The azeotropic process utilizing entraining agents such as benzene, carbon tetrachloride, hexane, ethyl acetate, etc., which form ternary low-boiling mixtures with alcohol and water in which the alcohol-water ratio is lower than in 95% alcohol.[13, 14]

[12] Brooks, B. T., Ind. Eng. Chem. *31*, 518 (1939).
[13] Steffens, J. A., U. S. Patent 1,586,717.
[14] Rodebush, W. H., U. S. Patent 1,583,314.

(b) The anhydrous salt process in which the water is removed by countercurrent washing of the alcoholic vapors with a stream of alcohol containing anhydrous salts.[15]

(c) The processes wherein the water is removed in the vapor phase by the action of water absorbing solids, e.g., hemihydrate of $CaSO_4$, silica gel, alumina, etc.[16, 17]

The major portion of the world's anhydrous alcohol is produced by the azeotropic process which is the only one that will be discussed here.

Anhydrous Alcohol Production Unit. Figure 3 shows the essential units of an azeotropic system using benzene as the entraining agent. The alcohol to be

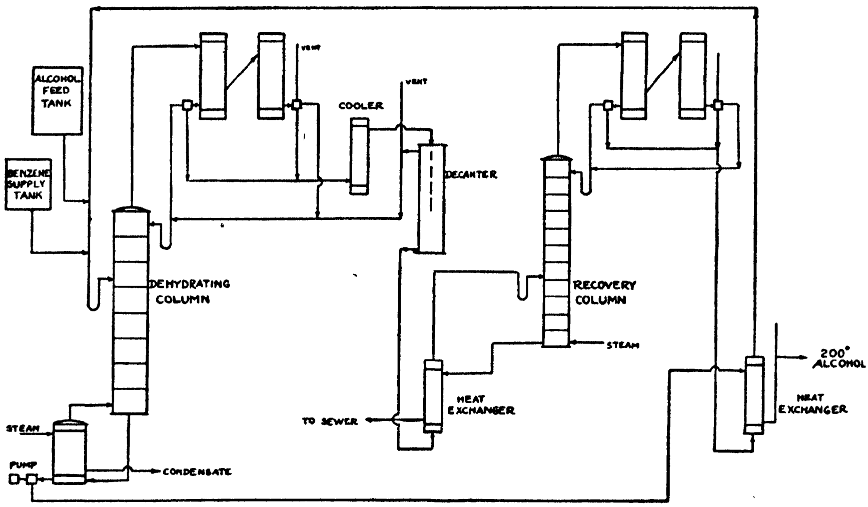


FIG. 3. Anhydrous Alcohol Unit.

dehydrated is fed into a dehydrating column about one-third the way down the column. The dehydrating column contains a large amount of benzene which, with some of the alcohol, forms a low-boiling ternary mixture with the water. The boiling point of this ternary mixture is lower than that of any of the other components or binaries in the system, being 64.5° C. The vapors from the dehydrating column are condensed in the equipment shown, part of the condensate being returned to the column as reflux. The remainder passes through the cooler as shown and then into a decanter or separator. The constant boiling mixture has the following composition by weight:[18] benzene, 74.1%; water, 7.4%; alcohol, 18.5%.

The condensate separates into two layers—a top layer rich in benzene and poor in water, and a water layer rich in alcohol and water and poor in benzene.

[15] Gorhan, A., U. S. Patent 1,936,836.
[16] Hammond, W. A., U. S. Patent 2,008,955.
[17] Schmidt, O., Treppanhauer, M., Fischer, H., German Patent 535,726 (Aug. 30, 1927).
[18] Young, S., "Distillation Principles and Processes," MacMillan & Co., Ltd., London (1922).

The oil layer is returned directly to the column; the water layer is sent to the second column shown, known as the recovery column, for the recovery of the benzene and alcohol contained therein, which is then returned to the system for further work. The water escapes to the sewer along with the condensate from the steam used to heat the column.

The major portion of the alcohol passes slowly through the dehydrating column and becomes anhydrous due to the action of the entraining agent as stated above. In the lower section of the column it is freed of benzene, by virtue of the existence of a low-boiling benzene-alcohol binary, which boils some 10° C. below the boiling point of pure alcohol. The anhydrous alcohol emerges at the base of the column. This column is, of course, heated by indirect steam.

Normal Propyl Alcohol—This alcohol is found to a limited extent in fusel oils obtained in yeast fermentation process for ethyl alcohol. For a long time this was practically the only source of normal propyl alcohol, but recently synthetic normal propanol obtained as a by-product in the manufacture of methanol, has appeared.[19]

Isopropyl Alcohol—Isopropyl alcohol is produced from propylene. Its commercial production began about two decades ago.

The method for its production is similar to that for the production of ethyl alcohol from ethylene. According to recent reports this process has been highly developed and the method now used employs dilute acid and will produce isopropyl alcohol or ether with equal ease depending on conditions.[20]

Butyl Alcohols—During the First World War the demand for acetone far exceeded the supply. In order to meet this demand the fermentation of corn products was started.[21, 22] This process produces normal butyl alcohol, acetone, ethyl alcohol in the following relative amounts:

Normal butanol, 60%; Acetone, 30%; Ethyl alcohol, 10%.

This fermentation process has grown rapidly in the past 15 years but, strangely enough, not because of acetone demand but because of the large amount of normal butyl alcohol required by the solvent industry. A major part of present production of acetone comes from synthetic isopropyl alcohol. The low cost and large quantity of acetone coming from this source have depressed the market to new low levels. The operation of the acetone-butanol fermentation process depends more upon the price of normal butanol than on acetone.

Butyl Fermentation—Formerly butyl alcohol was produced entirely from grain, but in recent years processes have been developed which successfully use molasses as raw material for the fermentation. This fermentation process differs markedly from the ethanol process, although the apparatus employed is similar. The active agent in the ethanol process is the yeast plant; whereas motile anaerobic bacilli are employed in butyl fermentations. A second major difference is that the entire fermentation procedure must be carried out under pure culture conditions. Unless this is done, acid-forming organisms will overgrow the butyl organism and the entire fermentation will fail.

A more dilute sugar solution is used in the butyl-acetone fermentation than

[19] Groves, C. D., Ind. Eng. Chem. *23*, 1381-85 (1931).
[20] Brooks, B. T., Ind. Eng. Chem. *31*, 515-519 (1939).
[21] Killeffer, D. H., Ind. Eng. Chem. *19*, 46 (1927).
[22] Gabriel, C. L., ibid. *20*, 1063 (1928).

in the ethanol process, the concentration being about 5 grams per 100 cc. instead of 15 grams per 100 cc.

The entire mash must be sterilized and kept sterile throughout the run. Fermentation time is approximately 45 hours.

In spite of all the difficulties enumerated above, the butanol fermentation is very reliable when properly handled. The yield is about 30% of mixed solvents on the basis of the sugar charged. The gases produced in this fermentation are hydrogen and carbon dioxide. The hydrogen may be utilized in the production of synthetic methanol or ammonia.

The products are separated from the fermented mash by distillation just as in the case of ethyl alcohol. The crude solvent mixture thus obtained is then subjected to further distillation to obtain the individual products.

Synthetic Butanol—Normal butanol was prepared in Germany during the First World War by condensation of acetaldehyde to form aldol. This important reaction was catalyzed by dilute acids, K_2CO_3, CaO, $ZnCl_2$, and by zinc turnings at a pH of about 8.5. The aldol formed was dehydrated to crotonaldehyde which was then hydrogenated to normal butanol.

Commercial production of normal butyl alcohol by this procedure started in the United States in 1933. A material part of the country's butanol requirements is now supplied by this process.

(For more detailed information concerning the process of condensation see Chapter 3, The Organic Unit Processes, and Chapter 27, Industrial Organic Chemicals.)

Other Butyl Alcohols—Secondary and tertiary butyl alcohols are prepared by absorption of the respective butylenes in dilute sulfuric acid. The secondary alcohol is produced from the alkyl sulfuric acid mixture by simply warming the solution. This procedure does not work well with tertiary butyl alcohol, because it regenerates the isobutylene absorbed. The tertiary alcohol is obtained by adding NaOH solution to the sulfuric acid compound of isobutylene. However, when refinery gases containing a mixture of olefines are scrubbed with sulfuric acid, hydrolysis after dilution results in the production of tertiary butyl alcohol along with the other alcohols.

Isobutyl alcohol cannot be obtained by the direct hydration of isobutylene, but is obtained commercially as a by-product of the synthetic methanol process.

Amyl Alcohols—One of these alcohols, isoamyl, is the main constituent of fusel oils obtained in the alcoholic fermentation of grains and sugars. These oils are carefully collected and refined by chemical treatment followed by distillation.

Synthetic Amyl Alcohols—Chlorinated pentane has for many years been the source of amyl alcohols and their acetates. According to Clark[23] chlorination of gaseous pentanes results in the following products:

1. $CH_3—CH_2—CH_2—CH_2—CH_2Cl$	24%
2. $CH_3—CH_2—CH_2—CHCl—CH_3$	8%
3. $CH_3—CH_2—CHCl—CH_2—CH_3$	18%
4. $(CH_3)_2CH—CH_2—CH_2Cl$	15%
5. $ClCH_2—CH(CH_3)_2—CH_2—CH_3$	30%
6. $(CH_3)_2{=}CCl—CH_2—CH_3$	5%

[23] Clark, L. H., Ind. Eng. Chem. *22*, 439 (1930).

The corresponding alcohols are made by hydrolysis of the above chlorides. A mixture of these alcohols is marketed under the name "Pentasol." The acetates may be prepared by reacting the above named chlorides with sodium acetate under pressure in an autoclave. The method used commercially is esterification of the alcohols with acetic acid. A recently published flow sheet for the amyl alcohol is shown in Figure 4.[24]

Cyclic Alcohols—The only members of this series to be considered here will be those produced by the hydrogenation of phenol and cresols. The reduction proceeds smoothly in the presence of nickel or platinum catalysts. The esters of

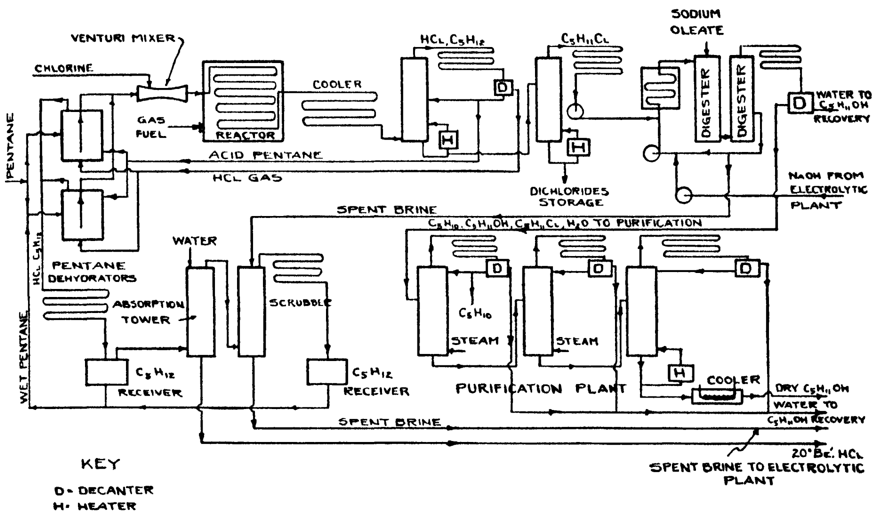


FIG. 4. Amyl Alcohol from Pentane.

these compounds are finding usage as solvents and plasticizers. Cyclohexanol is an important solvent. It has become important recently as the basis for adipic acid which is produced by oxidation of cyclohexanol. (For further information on the process of hydrogenation, see Chapter 3, The Organic Unit Processes.)

Simple Esters—It has been said that the great success of the nitrocellulose lacquer industry was in a large measure due to the successful development of the manufacturing processes for simple esters. Certainly this group contributes more solvents and plasticizers for nitrocellulose lacquers and plastics than any other family of compounds. For example, ethyl acetate is a good solvent for cellulose nitrate, ethyl cellulose, ester gum, certain formaldehyde resins, vinyl resins and cumarons. It is miscible with hydrocarbons and linseed oil, and in the presence of small amounts of alcohol it dissolves certain types of cellulose acetate.

The ester compounds possess the general structure R CO—OR wherein R represents an alkyl group. The only exceptions to this statement are the formates, in which one R represents a hydrogen atom. The majority of the simple esters

[24] Chem. & Met. Eng., "Process Industries Data Book," p. 3, McGraw-Hill Book Co. (1936).

readily dissolve oils and resins, showing that although they possess decided polar characteristics, these are less than in the case of corresponding alcohols.

The toxic effect of all esters is contributed chiefly by the acid present. For example, the esters of formic acid, particularly those of low molecular weight, are several times as toxic as the corresponding esters of acetic acid. All volatile formates have a strong paralytic effect on the central nervous system.

The acetates are relatively innocuous, causing slight headache and vertigo when inhaled strongly. These effects are magnified in the case of the higher alcohols which are in themselves more toxic.

The statements made above in regard to toxicity of esters when inhaled also apply to contact with the skin. Esters of formic and maleic acids, for instance, are powerful skin irritants and poisons, whereas esters of acetic acid have little or no effect on the skin.

All esters tend to hydrolyze in the presence of water, but in many instances the rate at room temperature is so slow as not to be noticeable. Esters of the lower alcohols and acids hydrolyze rapidly, as for example, ethyl formate. In nearly all instances their stability is entirely adequate for the solvent purposes for which they are intended. (For a discussion of the basic principles of the process of esterification see Chapter 3, The Organic Unit Processes.)

Ethyl and Butyl Acetates—Ethyl acetate is manufactured at the present time by two general methods. The first consists in reacting ethyl alcohol with strong or weak acetic acid. In the second method two molecules of acetaldehyde are combined to form ethyl acetate directly. The catalyst used in the latter case is aluminum alcoholate.[11]

The esterification reaction between acetic acid and ethyl alcohol has been thoroughly studied. The classic work of Berthollet and Saint Gilles (1862) on equilibrium was based on esterification studies, and contributed to the mathematical formulation of the law of mass action. They showed that when equal molar quantities of acetic acid and ethyl alcohol are mixed together the reaction does not go to completion, but an equilibrium is established when 65-67% of the reactants have been converted. It was found that this equilibrium could be approached from either direction and that the reaction could only be forced to completion by the removal of one of the products. It is therefore evident that dilute acetic acid could never be used in a straightforward manner for the preparation of ethyl acetate. It is then surprising to one not versed in industrial distillation technique to find that large amounts of ethyl and butyl acetates are prepared annually from ordinary 10% acetic acid vinegar.

Figure 5 gives a flow diagram of the process used for the preparation of ethyl acetate from vinegar and ethyl alcohol.[25]

Vinegar containing alcohol equivalent to the acetic acid and a small amount of sulfuric acid catalyst is fed continuously to a manufacturing column in which a large excess of alcohol is maintained.

This column is heated directly by live steam admitted to its base. As the vinegar-sulfuric acid mixture flows downward through the esterification column the acetic acid reacts with the alcohol present forming ethyl acetate which is then carried away in the vapor phase. The water issuing from the base of the column

[25] Backus, A. A., U. S. Patents 1,403,224 and 1,403,225.

is practically free of acetic acid. The vapors coming from the top of the esterifying column contain ethyl acetate, alcohol and water, and are passed directly to the rectifying column as shown in the diagram.

The rectifying column is heated by means of live steam fed in at its base. The function of the rectifying column is to rectify the vapors from the manufacturing column to a composition approaching that of the constant boiling ternary mixture of ethyl acetate, ethyl alcohol, and water. These vapors are condensed in the condensing bodies shown, and all but a small portion is returned to the

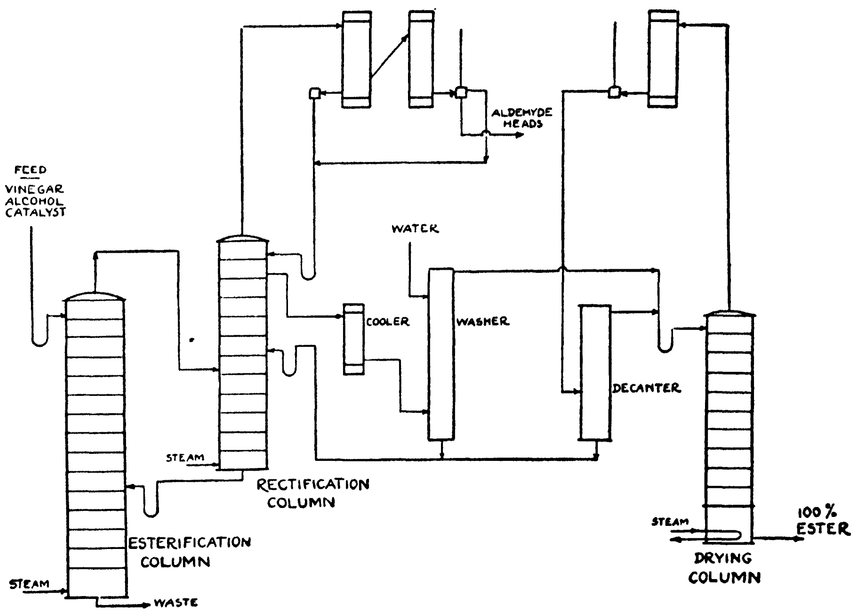


FIG. 5. Manufacture of Ethyl Acetate from Vinegar.

column as reflux. The small portion withdrawn contains acetaldehyde and other "heads" products contained in the vinegar and alcohol feed.

The ethyl acetate manufactured is drawn off as a ternary mixture a short distance from the top of the rectifying column, and is sent to a continuous "washer" to remove the ethyl alcohol. The top or oil layer is rich in ethyl acetate, practically free of ethyl alcohol and saturated with water (about 4%). The oil layer is passed to the top of a drying column wherein its water content is removed by distillation. The binary azeotrope of ethyl acetate and water contains about 8% H_2O. This vapor being richer in water than the 4% solubility separates into an oil and water layer on condensation, thereby providing means for eliminating the water. The dry ethyl acetate issues from the base of the drying column as pure ester.

The excess alcohol contained in the vapor coming from the esterification column and that from the washer passes down the rectifying column and returns as liquid to the lower part of the esterification column, thus providing the alcohol necessary to maintain alcohol concentration in the esterification column.

The Steffens Ester Process[26]—This is a batch process and due to its flexibility and versatility is one of the most important esterification processes. The equipment shown in Figure 6 for the preparation of ethyl lactate gives equally good results on several of the high boiling esters when prepared from relatively concentrated acids, and could, with slight modifications, be made to produce all of the acetates, propionates, butyrates, lactates, etc. The operation in each case will be similar to that described below for ethyl lactate.

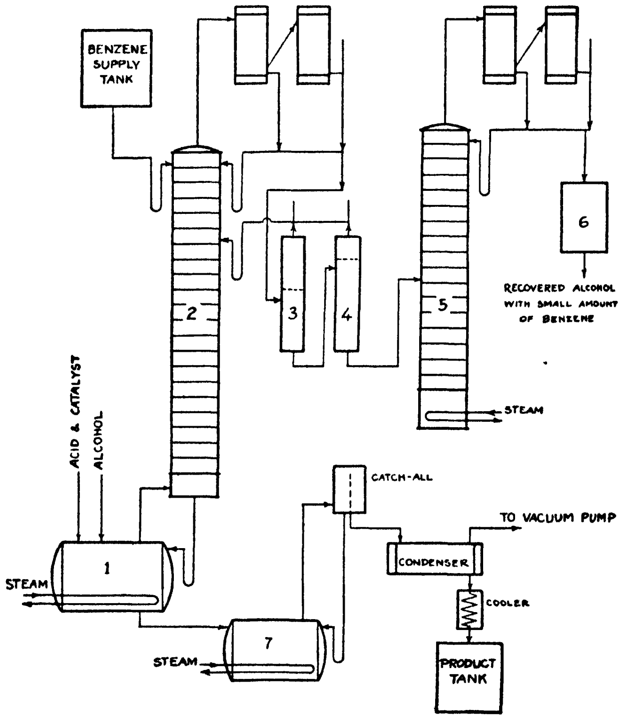


FIG. 6. Batch Esterification Unit.

In the manufacture of ethyl lactate, concentrated lactic acid and ethyl alcohol together with some sulfuric acid are pumped into the still (1). This still is heated indirectly by a steam coil. The vapors pass up through the column (2) and meet not only the regulation reflux but also some benzol which is always present in the column. The benzol has the tendency to drive the excess of alcohol back down into the still (1) while at the same time it carries the water out of the top of the column (2). This is due to the formation of a constant-boiling ternary mixture and also to the fact that the benzol reduces the partial pressure of alcohol.

The ternary mixture of alcohol, water and benzol coming from the top of column (2) is condensed and runs to separator (3). The water layer from this separator passes on to a second separator (4). The oil layer from both separators

[26] Steffens, J. A., U. S. Patents 1,421,604 and 1,421,605.

is returned to a point near the top of the column (2). This oil layer contains most of the benzol. The water layer which consists chiefly of alcohol and water is drawn from separator (4) and passes to column (5). Column (5) is a regulation alcohol rectifying column heated by direct steam. Water collects in the bottom and is sent to the sewer. The vapor coming off the top is 95% to 96% alcohol. This is condensed and sent to a storage tank (6) where it can be used over again in still (1).

As this is a batch process, the time arrives when there is practically nothing in the still (1) except a crude ethyl lactate. In order to purify this product, it is

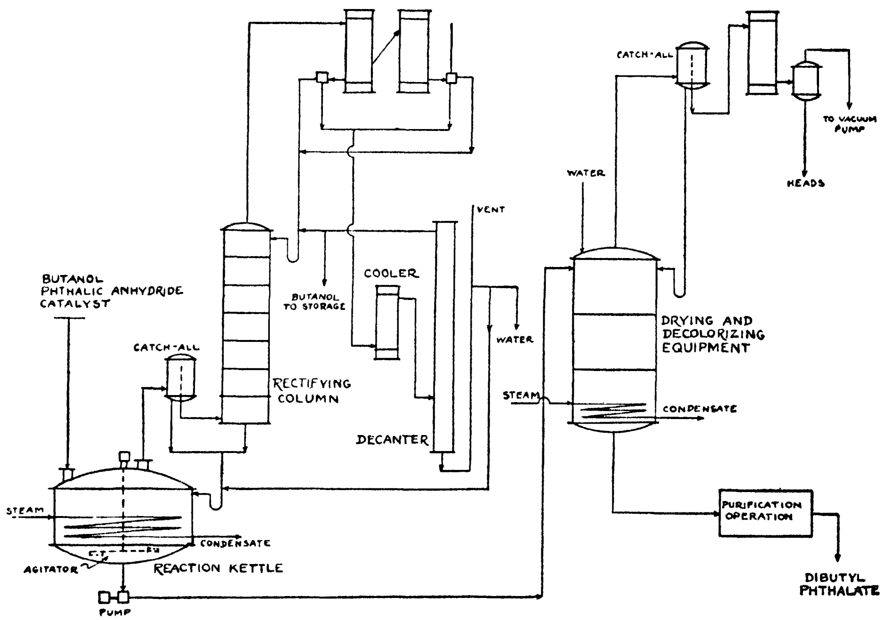


FIG. 7. Dibutyl Phthalate Process.

drawn off the bottom of the still (1) and goes to a vacuum still (7). This still is heated by indirect steam and operates under a high vacuum. The volatile impurities coming off as vapors are condensed and go to the receivers. After these volatile impurities are removed, the ethyl lactate is either drawn from the still (7) without further purification, or it is distilled under high vacuum.

Phthalic Acid Esters of the Lower Aliphatic Alcohols—These esters are formed by the action of phthalic anhydride on the corresponding alcohols. Sulfuric acid is used as the esterification catalyst. A typical apparatus used in the manufacture of dibutyl and diamyl phthalate is shown in Figure 7. An inspection of this process shows it to be the Steffens ester process minus the recovery column. The recovery problem is so slight in the case of the butyl and amyl phthalates that this column is eliminated, the water layer being worked up in some general purpose distillation equipment. In the manufacture of diethyl phthalate the apparatus used is similar to that described under the Steffens process.

Ketones—A ketone consists of a carbonyl group attached to two hydrocarbon chains which may or may not be the same. The polarity of these compounds is less than that of the corresponding alcohols. The hydrocarbon parts of the ketone molecule rapidly overcome the effect of the =CO group as the molecular weight of the compound increases, and, as would be expected, the higher ketones are good solvents for oils. The very lowest ketone-acetone is a fairly polar compound and probably the most widely used of the low boiling solvents.

Very little is known about the physiological action of ketones. Acetone itself does not seem to be very toxic except to certain individuals. On the other hand,

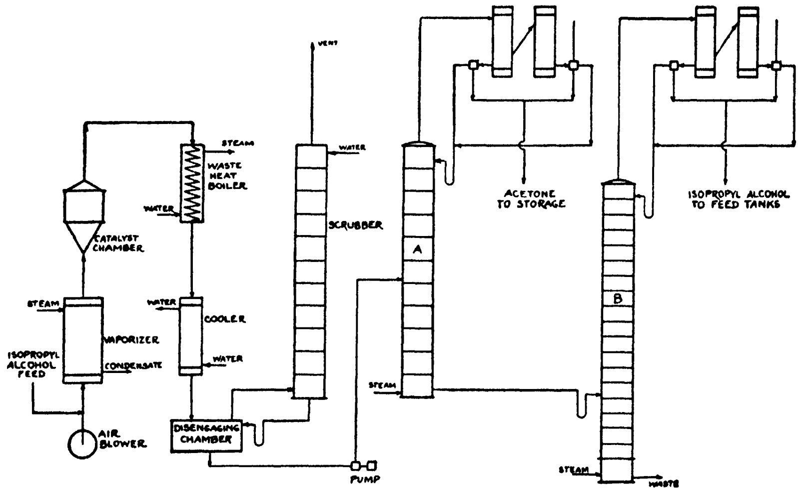


FIG. 8. Manufacture of Acetone from Isopropyl Alcohol.

its unsaturated polymer mesityl oxide is definitely toxic. Its use as a solvent should be undertaken with great care.

Acetone—The chief source of acetone prior to the First World War was the destructive distillation of wood. Some acetone was obtained directly in the vapors issuing from the retort. The larger part, however, came from the calcination of calcium acetate or "grey lime" produced by the neutralization of the pyroligneous acids, obtained during the distillation, with lime.

Acetone at the present time is obtained concurrently with normal butyl alcohol in the normal butyl alcohol fermentation process, and from the catalytic dehydrogenation or oxidation of isopropyl alcohol. Production of acetone by the fermentation process has already been discussed along with the production of normal butanol, and will not be taken up again.

The major source of acetone at the present time is petroleum. Several of the large oil companies are producing alcohols from their cracking gases, and in this manner produce large amounts of isopropyl alcohol from propylene. Isopropanol is readily converted to acetone.

A flow sheet of a typical plant of this type is shown in Figure 8. Air saturated with alcohol vapor is passed through a catalytic bed of copper or silver

Here the oxygen of the air is consumed and a certain portion of the isopropanol is converted to acetone. The hot gases pass to a waste heat boiler and from there into a cooling and separating chamber. The nitrogen is passed through a scrubbing column where it is washed free of alcohol and acetone by a counter-current stream of water.

The water solution of acetone and unconverted isopropyl alcohol is run through rectifying column "A" where the low boiling acetone is taken off in concentrated form as the overhead product and the isopropanol with the water issues at the base of the column and passes to column "B." In this column the isopropanol is concentrated to its binary constant boiling mixture with water, i.e., 91%. The water is discharged at the base of the column. The recovered isopropanol is returned to the vaporizer to be recycled. If high quality acetone is desired, the product from "A" column is refined by redistillation. (A discussion of the general process of oxidation will be found in Chapter 3, The Organic Unit Processes.)

Polymers of Acetone—There have been several attempts recently to establish the use of diacetone alcohol and mesityl oxide as solvents. Diacetone alcohol is readily manufactured from acetone [27] by the use of alkaline condensing agents. This compound has one serious disadvantage: it is easily decomposed in the presence of alkalies. Mesityl oxide,[28] formed by the dehydration of diacetone alcohol, has also been recommended as a solvent. Its use, however, will probably be restricted by its odor and toxicity.

Polybasic Alcohols—The most important members of this series are ethylene glycol, its derivatives, and glycerine. Polar characteristics of these compounds are considerably greater than those of the corresponding monobasic alcohols. They are, therefore, practically insoluble in the non-polar solvents, but are themselves good solvents for water-soluble dyestuffs.

Glycol and certain of its ethers have been found to have definite poisonous effects when taken internally. Ethylene glycol is apparently oxidized in the body to oxalic acid with the resulting damage to nerve centers and internal organs.

Glycerine—At the present time practically all of the glycerine produced is obtained by the hydrolysis of the glycerides of fatty acids occurring in nature as oils and fats. (See Chapter 42.)

Recently a process [29] has been developed for manufacturing glycerine from petroleum.

The future utilization of this process depends upon its economic justification in terms of demand and price.

Glycerine finds important use in the manufacture of explosives and synthetic resins. Large amounts are used in the esterification of polybasic acids to form alkyd type resins. Similarly, large quantities are used to esterify resins acids, such as rosin, to form ester gum.

Ethylene Glycol—Two major processes are in use today for the preparation of ethylene glycol from ethylene. In the first one ethylene is passed into cold chlorine water to form ethylene chlorhydrin. This compound is then hydrolyzed to form ethylene glycol. In the second process ethylene is oxidized to ethylene

[27] McAllister and Bullard, U. S. Patent 2,130,592 (1938).
[28] Fairborn and Engs, U. S. Patent 2,139,560.
[29] Williams, C. C., Trans. Am. Inst. Chem. Eng. 37, (1941).

oxide by passing a mixture of ethylene and air over a silver catalyst. The ethylene oxide is then hydrolyzed to ethylene glycol.[30]

Ethylene glycol is used extensively as a coolant in liquid-cooled airplane engines and as an "antifreeze" in automobile engines. Considerable quantities are used for the preparation of the dinitrate used in the manufacture of low-freezing gelatine dynamite. Ethylene glycol is an excellent anhydrous solvent for many water-soluble substances and is used in the preparation of special pastes used in the manufacture of dry type electrolytic condensers.

Ethers of Ethylene Glycol—These compounds, which in the past few years have become popular solvents, may be prepared by the action of ethylene oxide on the alcohols. The process is usually carried out in the presence of sulfuric acid, although other compounds may be used.

These compounds are good solvents for compounding lacquers, quick-drying varnishes and enamels. Their solvent properties resemble ethyl alcohol. They are also valuable dye solvents, finding use in textile dye baths.

HYDROCARBONS

Petroleum Naphthas—These are mixtures of aliphatic hydrocarbons or mixtures of aliphatic and naphthenic hydrocarbons obtained from petroleum oils.

Their use in lacquer formulations is chiefly that of a diluent to replace toluene in certain formulations. The petroleum hydrocarbons are generally good solvents for paraffin oils and fatty oils, although some of the natural vegetable oils are sparingly soluble in these mixtures. They are used in certain resin extraction processes. (See Chapter 14.)

Cyclic Hydrocarbons—The chief source of these hydrocarbons is from the manufacture of coke and coal gas. The gases passing from the coke ovens during the destructive distillation of bituminous coal contain carbon bisulfide, lower aliphatic hydrocarbons, benzene, toluene, the xylenes, cymenes and naphthalene. These products are stripped from the oven gases, separated and purified by chemical treatment and fractional distillation. (See Chapters 15 and 16.)

A considerable amount of cyclic hydrocarbons is formed in certain gasoline manufacturing processes. These "reforming" processes may soon produce considerable amounts of these hydrocarbons. (For the principles of this general process see Chapter 3, The Organic Unit Processes.)

Benzene—Benzene is an excellent solvent for weakly polar materials such as oils, fats, waxes, ethyl cellulose, rubber and asphalts. In the past it has been used extensively in cleaning and extraction processes and for rubber solutions and lacquers.. At the present time due to its toxicity it is being steadily replaced by toluene which is less toxic and is not a blood poison.

Toluene—Toluene resembles benzene very closely in solvent power. It is the most important diluent used in cellulose lacquers for which purpose it is particularly well suited.

Toluene is a good solvent for bitumins and resins and is used considerably in the manufacture of printing inks. It is an excellent solvent for oil-soluble dyestuffs and is used considerably in the manufacture of colored lacquers.

[30] Balcar, F. R., U. S. Patent 2,135,271 (1938).

A recent very important factor in the production of toluene has been the development of a process and erection of plants to make toluene from hydrocarbons of petroleum.[31, 32]

Xylene—Commercial xylene is a mixture of the three isomeric xylenes. Its use and solvent properties are similar to those of toluene. Its toxicity is much less than that of benzene and probably somewhat less than that of toluene.

Chlorohydrocarbons—The most important members of this group are methylene dichloride, ethylene dichloride and carbon tetrachloride. In the presence of alcohol the first two of this group are used to dissolve cellulose acetates and ethers for preparations of non-inflammable lacquers.

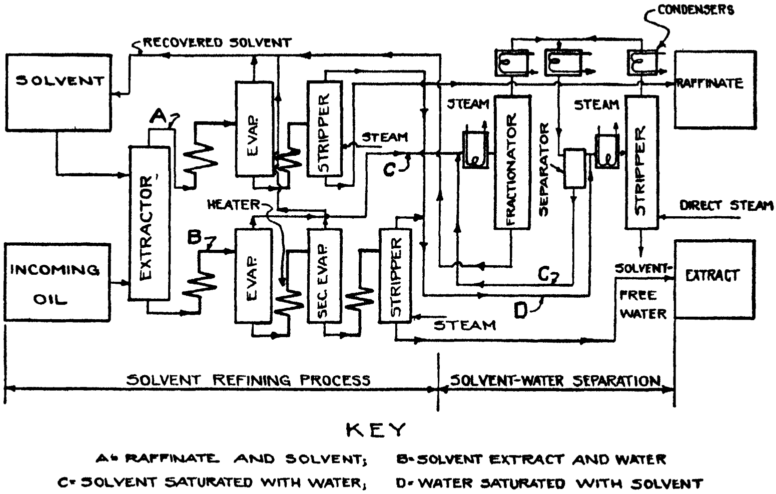


FIG. 9. Typical Solvent-refining Process (with water-solvent separation).

Methylene dichloride is also used as a solvent medium in the manufacture of cellulose acetate.

Carbon tetrachloride is used as a general purpose solvent in cleaning solutions and in fire extinguishers.

Solvent Extraction Process—No chapter on solvents could be complete without the discussion of at least one solvent refining process. This is one of the most powerful tools in the hands of the chemical engineer for the separation of compounds whose solubilities in certain solvents are different but whose other physical properties are so similar as to make separation by older processes impractical if not impossible. For example, certain chemical compounds, the separation of which by distillation is impossible due to the formation of azeotropic mixtures, may be readily separated by the use of a suitable solvent in which one of the compounds is substantially insoluble. A diagrammatic flow sheet of such an extraction process is shown in Figure 9.

The essential requirements of an extracting solvent are (1) a great difference in selective solubility towards the two components of the mixture to be refined,

[31] Ginsburgh, A. R., Chem. & Met. 47, 768 (1940).
[32] Chem. & Met. 47, 535 (1940).

(2) small miscibility with the liquid phase being extracted, (3) availability at low cost, (4) easy recoverability, and (5) non-toxicity. The solubility difference of the solvent towards the extract and raffinate may be obtained either by similarity of molecular structure or by the presence of special groups such as chloride or nitrate, which show a selective solvent action.

Figure 9[33] illustrates the essential steps in any solvent refining process. First, the solvent must be contacted with the liquid mixture to be refined in an apparatus whereby scrubbing of the phases and subsequent separation take place. The scrubbing and separation may be done together in a counter-current packed column or separately in a mixing nozzle and decanting tank. The extract bearing solvent must then be freed of the dissolved material for re-use by a suitable evaporation, distillation or precipitation process. Conversely, for economy and purity of product the extracted liquid phase must be stripped of solvent.

In general, these processes follow the rules of liquid-liquid extraction, the distribution ratio of extract between refining solvent and mother liquor depending on extract concentration, temperature, association of molecules and related factors. Greater solvent efficiency may be obtained by small doses of fresh solvent of equal size rather than a single large application.

Although solvent refining or extraction has long been known to chemists and chemical engineers, it has reached its greatest prominence in the purification of lubricating oils since 1931. Several processes involving this principle have been developed by the major oil companies, all of whose basic flow sheets are similar to Figure 9. They vary in the solvents used and the method of application and recovery. In general, the object in solvent refining of lubricating oils is to extract the "naphthenic" or cyclic and aromatic material from the more paraffinic molecular species. Solvents used for this include acetone, dichloro ethyl ether, phenol, furfural, cresylic acid, benzene and sulfur dioxide combined (the Edeleanu process), and nitrobenzene. The latter solvent is extremely toxic and must be used with great care.

RECOVERY OF SOLVENT VAPORS BY ACTIVATED CARBON

The wide usage of volatile solvents in paint and lacquer application and in the manufacture of coated fabrics makes recovery of the solvent vapors released upon drying highly desirable, both to prevent fires and explosions and to save the solvent values for re-use. Efficient processes have been developed to adsorb solvent vapors from gases by using activated carbon.

A process of this type is illustrated diagrammatically in Figure 10. The solvent vapor-air mixture is drawn from the site of the evaporation by a fan and blown through a bed of activated carbon. In general the amount of air drawn into the system is governed so that the concentration of the solvent in the mixture is below the explosive limit so as to reduce the fire hazard. A second reason for keeping the concentration low is to prevent overheating in the adsorbing beds. This is the governing factor in the case of non-inflammable mixtures. The type of carbon used and the height and diameter of the carbon bed are largely dictated

[33] Chem. & Met., "Process Industries Data Book," p. 32, McGraw-Hill Book Co (1936).

by experience gained in small-scale experiments and in previous installations recovering similar solvents.

In operation the adsorbing bed gradually becomes saturated with solvent and loses its efficiency. When this occurs the vapor-air mixture is then sent to the second adsorber, and the saturated one is reactivated. Reactivation is generally accomplished by passing steam through the spent bed, the direction of the gas flow during reactivation being the reverse of that followed during adsorption. The combined steam and solvent vapors are condensed and separated by distillation or decantation, depending on the type of solvent recovered.

Steaming is stopped when substantially all of the adsorbed solvents have been removed from the carbon. In some installations the beds are allowed to cool

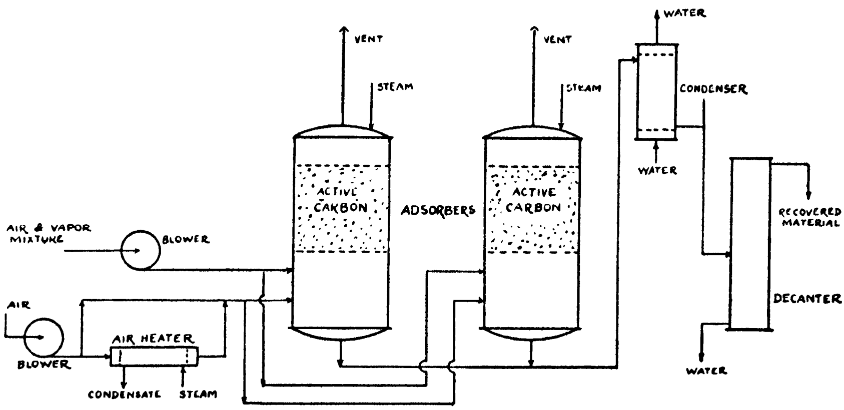


FIG. 10. Recovery by Active Carbon Process.

naturally and the carbon used wet. In others the bed is cooled and partially dried by blowing air through it. A third type of procedure is to completely dry the carbon by sweeping out the water with a stream of hot dry air or other gas. After drying, the carbon is cooled by blowing cool gas through the bed. Conditions for this type of drying must be carefully controlled, as there is considerable danger of setting the carbon on fire. (See Chapter 18.)

This brief chapter has covered merely the high points of the manufacture and use of solvents. For those who wish to investigate the field in more detail, the following brief reading list may prove helpful as a guide.

READING LIST

GENERAL

Jordan, O., "The Technology of Solvents," Chemical Publishing Co. (1938).
Durrans, T. H., "Solvents," fourth edition, D. Van Nostrand Co. (1938).
Mellan, I., "Industrial Solvents," Reinhold Publishing Corp. (1939).

TOXICITY OF SOLVENTS

Browning, E., "Toxicity of Organic Solvents," first American edition, Chemical Publishing Co. of New York (1938).

PRINCIPLES OF SOLUBILITY

Hildebrand, J. H., "Solubility," A. C. S. Monograph No. 17, revised edition, Reinhold Publishing Corp. (1924).

DISTILLATION OF SOLVENTS

Robinson, C. S. and Gilliland, E. R., "The Elements of Fractional Distillation," McGraw-Hill Book Co. (1939).

SOLVENT EXTRACTION

Kalichevsky, V. A., "Modern Methods of Refining Lubricating Oils," Reinhold Publishing Corp. (1938).

Sherwood, T. K., "Absorption and Extraction," McGraw-Hill Book Co. (1937).

SOLVENT RECOVERY

Bulkeley, C. A., Chem. & Met. *45*, 300 (1938).

Mantell, C. L., "Industrial Carbon," D. Van Nostrand Co. (1935).

CHAPTER 31

SYNTHETIC PLASTICS

GEORGE BARSKY
Barsky and Strauss, Inc., New York

The term "plastics" connotes certain physical properties rather than any specific chemical composition or type of composition. The term became a general one in applied chemistry because of the great diversity of chemical materials exhibiting plastic properties, and because the properties rather than the composition are of primary importance in the application to useful purposes. However, physical properties bear a definite relationship to chemical composition and the physical properties are determined principally by the chemical composition.

Plastics are materials or compositions which are capable of being permanently formed into predetermined shapes by means of mechanical force alone, or by means of heat and mechanical force.[1,2] Thus, strictly speaking, clay is a plastic; glass is also a plastic. Many metals have some degree of plastic properties. Ordinarily, however, the term "plastics" is restricted to organic materials formable at temperatures which, though elevated, are seldom above those attainable by means of steam.

Synthetic plastics are new organic materials for fabrication, just as metals, ceramics, glass, etc., are old materials for fabrication. The form in which a plastic is used, the mechanical structure, is important and consequently the adaptability of the composition to the particular mechanical form is important. For example, one plastic material, a drying type alkyd resin, is particularly suitable for use as a protective coating on metal, such as an automobile body. Another plastic, a moldable phenolic resin, is unique in its excellence as a material for the ignition distributor head of the gasoline engine, and entirely unsuited for use as a coating material. Chemical properties are critical for many uses just as they are with old materials. Methods of fabrication play an important role in determining final cost, as they do with metals.

Thus, synthetic plastics compete with many other materials such as wood, glass, metals of all sorts, as well as with natural resins. In addition, synthetic plastics compete with one another. Just as there is no one metal adaptable for all purposes, there is no universal plastic. There is usually a definite reason for the use of a particular plastic. The cost of the finished piece may be below that of a similar article made from competitive materials, or the particular plastic may have properties sufficiently superior to warrant the price differential over other materials, or qualities so unique or in such indispensable combination that cost is not a deciding factor.

[1] Bingham, E. C., "Fluidity and Plasticity," McGraw-Hill, New York (1922).
[2] Houwink, R., "Plasticity, Elasticity and Structure of Matter," Macmillan, New York (1937).

In general, formed plastics offer lightness of weight, resistance to corrosion, elimination of necessity for protective coatings, variety of decorative effects, and cheapness in fabrication of intricate shapes. Synthetic plastics in coating materials offer improved durability, speed of application, uniformity and variation of properties beyond that obtainable with natural materials.

The synthetic plastics industry is still in its early stages. Plastics have the great value of simplifying mass production by making possible adjustments of composition to facilitate fabrication, and therefore are being adopted more and more by mass production industries. For example, the automobile industry is steadily increasing the number of parts made from plastics, and in addition is using more and more coatings containing synthetic material for finishing bodies. The airplane industry is becoming a mass production industry and experimentation with plastics for construction of wings, fuselages and small parts is going forward, with probable success sometime in the future.

HISTORICAL

Natural plastic materials were used many centuries ago. Asphalt was used by the Babylonians; amber was well known to the ancient Greeks. Various fossil resins have been used by primitive peoples all over the world. The rise of the science of chemistry was accompanied by increased use of natural materials and the development of synthetics, first as substitutes for natural materials of limited supply and later because synthetics offered combinations of properties not obtainable with natural materials. The oldest synthetic plastic is probably nitrocellulose plasticized with camphor (Celluloid), developed by the Hyatt Brothers about 1868. The next synthetics to appear were the casein plastics (1890). Spilleler is generally credited with their first commercial production under the trade name "Galalith." About the same time ester gum, rosin esterified with glycerine, was developed by Schaal.[3] This material appeared on the New York market about 1893. It is interesting to note that so far all the synthetics that had appeared were modified natural products, although resinous material had often formed as by-products in the conduct of organic reactions. Such resins were considered by chemists as a nuisance, which interfered with their researches on preparation of new materials, usually crystalline, and caused trouble in factories.

In 1909 Baekeland[4] announced a new type of synthetic material, later known as Bakelite, a plastic prepared from entirely non-plastic, non-resinous raw materials. He had been seeking a substitute for shellac, a widely used natural resin, the price of which had been rising steadily. Actually he produced an entirely new type of product and started a new branch of the chemical industry.

The pyroxylin or nitrocellulose plastics in the meantime had progressed steadily, but the two principal disadvantages, a tendency to turn brown on exposure, and great inflammability, induced a search for improved materials. Attempts to substitute cellulose acetate for nitrate met with little success because of the expensive solvents required. In 1903, Miles[5] discovered that by hydrolyzing the tri-acetate a product of better stability and solubility could be obtained.

[3] U. S. Patent 335,485 (1886).
[4] Baekeland, L. H., Ind. Eng. Chem. *1*, 149 (1909); U. S. Patent 942,809 (1909).
[5] U. S. Patents 733,729 (1903); 828,350 (1907).

This discovery was the beginning of both the acetate plastics industry and of that of acetate silk.

The advent of plastics from synthetic raw materials and the increased knowledge of colloid chemistry stimulated the industry and resulted in commercial development of many new synthetic plastics, such as the alkyd resins (originating with Watson Smith),[6] urea resins (Johns,[7] Pollak[8] and others), vinyl resins, polystyrene, acrylates and others.

PRODUCTION AND USE

The synthetic plastics industry has grown at a rapid rate and is expected to continue its growth for many years in the future. Statistics are available for

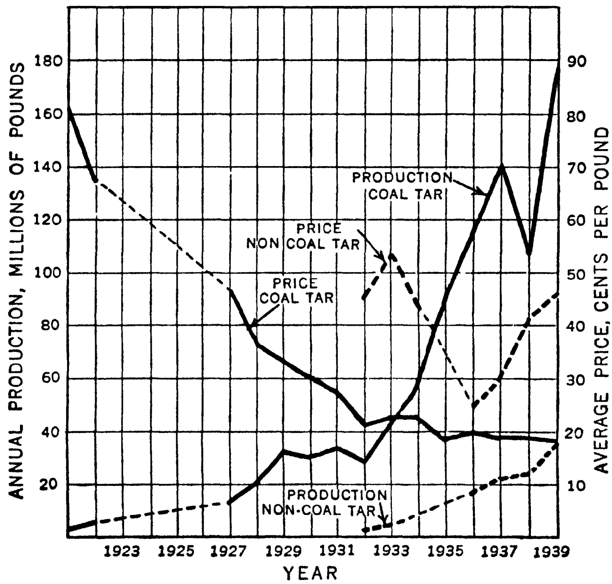


FIG. 1. U. S. Production of Synthetic Resins, 1921-1939. [U. S. Tariff Commission: Census of Dyes and Other Synthetic Organic Chemicals (Annual, for the years 1921-1930).] [Dyes and Other Synthetic Organic Chemicals (Annual, for the years 1933-1939).]

three divisions of synthetic plastics: coal-tar resins, non-coal-tar resins and modified cellulose plastics, excluding regenerated cellulose. Figure 1 shows the growth of the synthetic resin branch, divided into two groups. Coal-tar resins, which are products made from raw materials derived from coal tar, such as phenol-formaldehyde resins (Bakelite), have shown a remarkable increase in volume of production and a decrease in average price. The non-coal-tar resins are of more recent origin and are growing rapidly. The average price is of less significance as it is changed as new and unusual resins come into the market.

Figure 2 shows the production history of the principal modified natural

[6] Smith, W., Jour. Soc. Chem. Ind. 20, 1075 (1901).
[7] Johns, H., U. S. Patent 1,355,834 (1920).
[8] Pollak, F., U. S. Patent 1,458,543 (1923).

plastics, cellulose nitrate and cellulose acetate. Nitrocellulose plastics have shown a decline in production, while the volume of cellulose acetate has increased sharply. Practically all nitrocellulose plastics and about half the cellulose acetate are sold

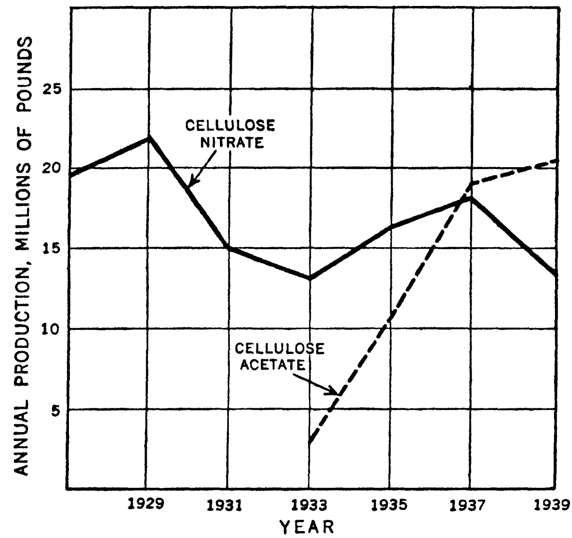


FIG. 2. U. S. Production of Cellulose Plastics, 1927-1939. (Regenerated cellulose and wrapping materials not included.) (U. S. Dept. of Commerce: Biennial Census of Manufacturers for Various Years)

as sheets, tubes and rods. The prices vary, depending upon the size and shape. Acetate molding composition sells from $.36 to $.52 per pound, depending upon the grade and color.

Table 1 gives more detailed information on the production of the different classes of synthetic resins.

TABLE 1—SYNTHETIC RESINS: U. S. PRODUCTION FOR 1939

(A) *Coal-tar:*	*No. of Manufacturers*	*Production, Millions of lbs.*	*Average Unit Sales, Value, $/lb.*
Alkyd			
Maleic anhydride	12	6.3	0.19
Phthalic anhydride	34	70.2	0.21
Coumarone and indene	2	(1)	(2)
Polystyrene	1	(6)	...
Phenolic			
Cresols or cresylic acid	14	10.5	0.13
Phenol			
For casting	6	8.5	0.38
For molding	11	19.4	0.15
For other uses	19	27.8	0.14
Phenols and cresols	8	...	...
Xylenols	5	0.4	...
Xylenol and cresols	4	...	...
Total Coal-tar		179.0	0.18

TABLE 1—SYNTHETIC RESINS: U. S. PRODUCTION FOR 1939—*Continued*

	No. of Manufacturers	*Production, Millions of lbs.*	*Average Unit Sales, Value, $/lb.*
(*B*) *Non-Coal-tar:*			
Acrylates	3	(3)	...
Polyamide	1	(4)	...
Urea	8	16.6	0.36
Vinyl	4	(5)	...
Total Non-Coal-tar		33.7	0.46

Source: U. S. Tariff Commission Report 140, second series, Synthetic Organic Chemicals, U. S. Production and Sales (1939).

Notes:

(1) Not available. Estimated by the author at about 20 million pounds.
(2) Quoted price $.04 to $.13 per pound, depending on the grade.
(3) Not available. Prices for molding powder about $.85 per pound.
(4) Sold principally as fiber. Production about 4 million pounds.
(5) Prices $.40 to $1.25, depending on the variety.
(6) Not available. Estimated by the author at 4 million pounds. Prices $.52 to $.58 per pound of molding compound.

The uses of the 1939 production of synthetic resins were as follows:

TABLE 2—USES OF SYNTHETIC RESINS, 1939 *

Use	*Millions of Pounds*
For molding and casting †	54.8
For laminating †	18.4
For paints and varnishes	100.2
Other uses	39.6
Total	213.0

* For information on regenerated cellulose materials see Chapter 38, Cellulose Industries.

† See p. 1199 and following for explanation of these terms.

Table 3 gives further data on cellulose plastics.

TABLE 3—CELLULOSE PLASTICS: * U. S. PRODUCTION FOR 1939

	Production, Millions of lbs.	*Average Unit Value $/lb.* †
Cellulose nitrate:		
Sheets, tubes and rods	13.4	0.76
Cellulose acetate:		
Sheets, tubes and rods	8.7	0.75
Molding composition	11.5	0.45
Total cellulose acetate plastics ‡	20.2	

Source: U. S. Dept. of Commerce Biennial Census of Manufactures (1939).

* Regenerated cellulose and wrapping materials not included.
† Calculated from census data.
‡ Acetate yarn production was 97.3 million pounds in 1939.

GENERAL CHEMISTRY OF SYNTHETIC PLASTICS

In general, two types of materials are embraced by the term "synthetic plastics": (1) modified natural materials, and (2) plastics made from non-resinous, non-plastic raw materials. Certain generalizations are applicable to both classes.

Chemical Structure—Plastic materials are usually mixtures of compounds of high molecular weight, often termed macro-molecules. Nature has provided many materials of such character and these are often useful in their natural state, as is the case with natural resins. These and other macro-molecules of nature may be modified by chemical reaction, as will be discussed below. However, the modifications that natural materials may be made to undergo are limited and the resultant plastic often retains characteristics for which the original natural material is responsible. In addition to the plastics based on natural material there are the macro-molecules that are synthesized from non-resinous raw materials of low molecular weight by the chemical reactions of condensation and polymerization, details of which are given below.

The structure of the macro-molecules of plastics may be long chains or long chains with cross linkages, or more complicated configurations. Physical properties such as flexibility and elasticity appear to be related to such structure. For example, the helix type of structure is probably responsible for elasticity. Cross linkages in many directions tend to give a more rigid, brittle structure. Various linkages and groups in the molecule impart other properties. For example, hydroxyl groups and amino groups are responsible for poor water resistance; long carbon chains tend to give hydrocarbon solubility; ester groups give products subject to hydrolysis; phenyl groups tend to decrease elasticity.

Synthetic plastics must consist of compounds which can be produced in a liquid or semi-liquid condition prior to being given their final form. It is this ability to exist temporarily in the liquid or plastic state that permits forming to shape.

Modification of Natural Materials—Many natural materials, such as cellulose, are made up of macro-molecules, which when unmodified are incapable of conversion to a plastic state without decomposition. They cannot therefore be formed by heat and pressure, nor can they be plasticized or deposited from solution. However, by the proper chemical modification these deficiencies can be remedied.

The most extensively modified natural material is cellulose, which in itself has three deficiencies: its water resistance is poor because of the large number of hydroxyl groups per structural unit; it cannot be softened by heat because of its relatively low temperature of decomposition; and it is insoluble in solvents. By chemical reaction cellulose may be modified to overcome these three deficiencies. Such modifications are: esterification with nitric acid to give nitrocellulose, or with acetic anhydride to give cellulose acetate, or with other fatty acids or mixtures; etherification of the hydroxyl groups with ethyl or benzyl groups. (See Chapter 3, The Organic Unit Processes.) These derivatives of cellulose are soluble in various solvents, miscible with plasticizers, have improved water resistance, can be softened by heat, etc.

The chemical action by means of which the natural occurring cellulose is converted to a synthetic plastic material may be explained as follows: Cellulose fibers are considered to be made up of bundles of chains in which the chains are parallel and tightly held to one another. Cellulose itself is not thermoplastic because the chain structures are so firmly held in the bundles that increase in the kinetic energy of the units cannot be made great enough to separate the chains from one another at temperatures below chemical decomposition. In chemically modified cellulose the chain structure is maintained, but the length of the chain reduced. The cohesional forces between chains is reduced by replacement of hydroxyl groups, which have a strong tendency to association, by ether or ester groups. These effects result in a lower tensile strength, but also in a more pronounced response to temperature change. Similarly the reduction in size of chain and in the cohesion between chains makes for more ready solubility.

Other examples of modification of natural materials are the esterification of rosin by means of glycerine, treatment of casein with formaldehyde, chlorination of rubber, etc. Modifications brought about by treatment of natural materials may be in properties such as water resistance, solubility in solvents, miscibility with plasticizers, hardness, ductility, tensile strength, softening point, chemical resistance.

Synthetic Resins—Plastics made from non-resinous raw materials are generally referred to as synthetic resins. Like the term "plastic," the term "resin" is characteristic of the physical state rather than of a particular type of chemical composition, although, of course, chemical composition and organization is responsible for particular physical properties.

In synthesizing resins from simple units a succession of reactions is required to get the high molecular weight necessary for plastic properties. The molecular weight goes up very rapidly as the reactions progress and the reacting units themselves increase in molecular size. With the use of synthetic materials, there is a large choice of structural units and it is possible, as has been recently demonstrated commercially in a variety of products on the market, to introduce a larger variation of properties than was possible only by modification of natural materials. In the synthesis of resins, reactions which result in the formation of compounds of high molecular weight are of two classes: (1) condensation and (2) polymerization.

Condensation is the union of two molecules with the elimination of water or its equivalent. (See Chapter 3, The Organic Unit Processes.) Esterification of an alcohol with an acid is a condensation reaction. Where the alcohol and the acid have at least two reactive groups each, long chains can be built up. For example, a typical condensation reaction is that between ethylene glycol and phthalic acid anhydride which forms a viscous balsam-like resin:

If one reactant has more than two active groups (for example, if the alcohol is glycerol instead of glycol) a more complex structure may be built up, one with cross linkages and therefore very different properties. (See "Alkyd Resins," p. 1213 ff.)

The rate at which some condensations take place is often affected by the acidity or alkalinity of the medium. In many cases, however, no catalytic effect is required. Heating to drive off water is sufficient for many condensations.

Polymerization is the formation of higher molecular weight compounds by interaction of two or more molecules of the same or similar compounds without the formation of by-products. (See Chapter 3, The Organic Unit Processes.) For polymerization to take place, unsaturated linkages must be present. There may be homo-polymers, that is, high molecular weight compounds made up entirely of the same monomeric units, or hetero-polymers, where the units are varied. The position of the unsaturated linkage in relationship to the rest of the molecule is

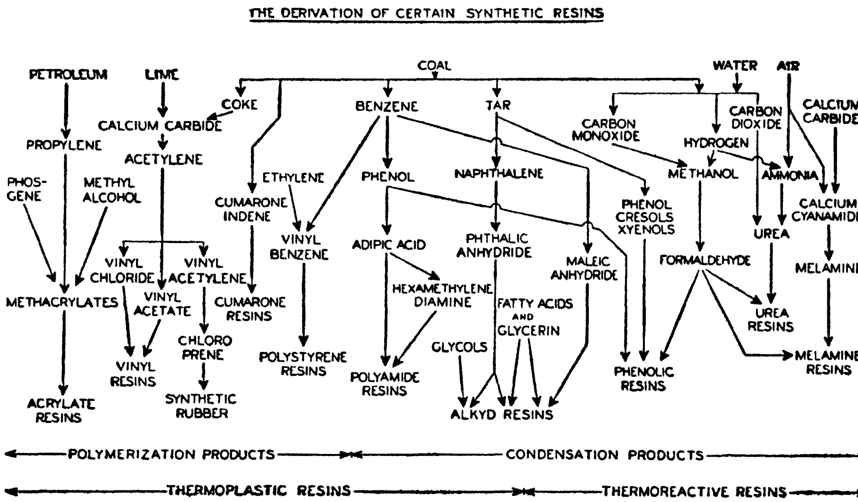


FIG. 3. The Derivation of Certain Synthetic Resins.

important. Apparently it is the electrical unbalance of the molecule, due to the difference in the groups on both sides of the double bond, that causes polymerization to take place. Compounds having conjugated double bonds, that is, two double bonds separated by a single saturated linkage such as in butadiene, polymerize most rapidly.

Sometimes there occurs a splitting out of the elements of water or its equivalent from adjacent carbon atoms in a structural unit during the course of a reaction, resulting in a double bond which may be responsible for the sudden polymerization that may occur in some resin forming processes, such as the gelling that may occur with alkyd resins.

Polymerization is catalyzed by a large number of materials. Small traces of oxygen or oxidizing agents catalyze many polymerizations; acid is another catalyst sometimes used; metallic sodium is a catalyst for some compositions. Acceleration of a polymerization reaction, either by elevation of the temperature or by use of catalysts, usually results in a lower average molecular weight of polymers formed.

Stabilization of plastic materials in an intermediate form or in the form of the simple monomer is effected by adding a negative catalyst, that is, a compound which will render inactive catalysts which are accidentally present. For example, methyl methacrylate may be stabilized by adding small amounts of hydroquinone, the hydroquinone acting as the reducing agent to neutralize the effect of traces of any oxidizer, such as dissolved oxygen or a peroxide formed from oxygen and the monomer.

As the large molecules are built up from the smaller ones by condensation or polymerization, or both, there occurs a progressive increase in viscosity, ending, in the case of thermoreactive materials, with a rigid solid incapable of being deformed at temperatures below that of destructive decomposition. (See section on Thermoreactive Plastics, p. 1199.) Here, there is taking place the reverse of the type of reactions that are used to modify cellulose. We have the formation of more and longer linkages resulting in greater cohesion.

Plasticizers—Plasticizers are materials added to compositions to improve their plastic properties. True plasticizers are solvents for the basic plastic material and remain permanently in the composition. Some plastics, for example, nitrocellulose, are not workable without plasticizers. Other plastics do not require any plasticizers as they have sufficient flow. In general, plasticizers lower the temperature at which the plastic may be worked. The use of properly selected plasticizers often results in the improvement of other properties, such as toughness, resistance to temperature change, flexibility, water resistance, etc.

The effect of plasticizer may be explained on the basis of gel structure, the common example of which is gelatin. A sheet of dry gelatin is quite brittle and cannot be flexed or made to undergo deformation without shattering. Water swollen gelatin, on the other hand, can undergo considerable elastic deformation. Plastic materials may be considered to be a similar structure of "solid" and "liquid" particles. When the solid and liquid are the same composition, the colloid chemist calls the system an isogel. Glass is a typical isogel; so are unplasticized plastics. Swollen gelatin is a heterogel. The effect of plasticizers is to allow easier deformation of the heterogel because the molecules of the resin or basic plastic are not so closely packed, but are distributed throughout the plasticizer separating them.

The relationship of plastic and plasticizer is the intimate one of dispersed and dispersing phases and a plasticizer for one material may not be effective with another. Thus dibutyl phthalate will plasticize cellulose nitrate but is not very effective with cellulose acetate.[9] Plasticizers usually contain active solvent groups such as ester, ether or ketone groups, as well as hydrocarbon groups. Some plasticizers, such as triethylene glycol dihexoate, are both esters and ethers. Plasticizers must have very low vapor pressures at ordinary temperatures so that there will be little tendency to evaporate from the composition, and should remain compatible at low temperature and not crystallize. They should not sweat out at slightly elevated temperature. Stability on long exposure to light and air are often important requirements.

[9] For a list of plasticizers see Fordyce, C. R. and Meyer, L. W. A., Ind. Eng. Chem. *32*, 1053 (1940).

PROPERTIES OF PLASTICS AND METHODS OF FABRICATION

As has been pointed out previously, plastics are materials for fabrication, and therefore certain of their properties determine the method of fabrication. From this viewpoint they may be conveniently classified as:

(a) thermoplastic
(b) thermoreactive or heat-hardening
(c) oxygen-hardening

Thermoplastic Materials—Thermoplastic materials soften or melt with the application of heat, and become rigid again when cool. On reheating, they become soft again. By the application of heat and pressure, such materials can be

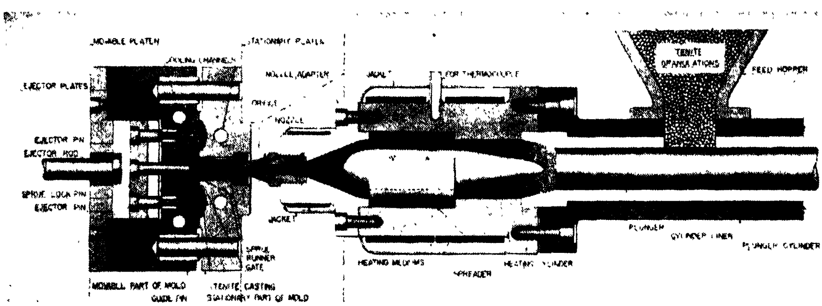


FIG. 4. Sectional View Illustrating General Method of Injection Molding. (Courtesy of Tennessee Eastman Corp.)

made to flow and fill out a metal mold. Before the molded piece can be removed, however, the mold must be chilled to harden it. Otherwise the shape will be distorted. This results in a comparatively long and often complicated molding cycle with alternate heating and cooling of the mold, and charge and discharge. For this reason, molding of thermoplastic materials is now largely done in injection molding machines. This operation is very similar to that of the die casting of metals. The plastic material, previously compounded with plasticizer and coloring material, and usually in the form of granules, is heated in a reservoir, from which it is forced by pressure into a cold mold, usually multicavity, where it cools and sets to shape. The mold then opens up, mechanically ejects the piece and closes for the next cycle. This method of molding has the advantage of rapid production and low mold expense. It is particularly adapted to the production of small pieces.

Cellulose acetate, polystyrene, vinyl resins, and acrylates are examples of thermoplastics.

Some thermoplastic materials, particularly those formed by polymerization reactions, may be shaped by pouring the monomer or intermediate liquid product into a mold and then curing, that is, continuing the reaction in the mold. Thermoplastic materials may also be extruded as a continuous sheet, tube or rod by forcing the heated mass through the properly shaped opening or die into a cooler atmosphere. In some cases, such as that of nitrocellulose, it is necessary to have volatile solvents present to facilitate the forming operation, and a seasoning period is required for the evaporation of the solvent, usually at slightly elevated temperatures. If the plastic is extruded as a thin thread which may then be further stretched, the resulting product may be suitable for use as a textile fiber. Fibers may also be formed, as in the case with cellulose acetate, by extruding a solution into a warm atmosphere which carries away the solvents.

Thermoplastic materials are often dissolved in solvents to make lacquers. For example, the vinyl resins used as linings for beer cans are applied to the tinplate as a lacquer. Nitrocellulose lacquer is another example of this application. (See Chapter 25, Surface Coatings.)

Thermoreactive Plastics—Thermoreactive plastics differ from the thermoplastic in one important property. When heated, they also soften and may be caused to flow, but while in the heated state they undergo profound chemical changes which result in loss of plasticity. Therefore, they remain rigid even at the temperature at which they showed flow properties when first heated. Thus, in the manufacture of thermoreactive materials, there occurs an intermediate stage at which the course of reactions taking place is interrupted and some residual reactivity is reserved for the final hardening during fabrication. This residual reaction is probably the formation of cross linkages. All thermoreactive plastics now on the market are synthetic resins, except shellac, a natural resin which shows some thermoreactive properties.

Thermoreactive plastics are used to make objects by:

(a) casting
(b) molding
(c) laminating

Casting—In the manufacture of castings, the reactions between the ingredients are carried as far as possible in the hot fluid mass. The liquid or pasty resin, with or without fillers and coloring matter, is then poured into molds which are placed in ovens to cure. There the final reactions take place, resulting in the infusible, insoluble final product. The curing operation may take several days. The product is usually furnished in the shape of rods, bars, cylinders, plates, etc., which are subsequently cut by machine tools to desired shapes. Examples of these resins are the cast phenolic resins (Catalin, Marblette) and some of the alkyd resins, such as the unmodified glycerol phthalates.

Molding—Another thermoreactive resin application is in heat and pressure molding. In this operation the resin, usually mixed with an inert filling material, is subjected to heat and pressure in metal molds. The resin softens due to the temperature. The effect of the pressure is to cause it to flow and fill out the mold space. At the same time chemical change is taking place, resulting in the conversion of the flowing resin into a hard, infusible product which when finally removed from the mold is, though still hot, rigid and which reproduces exactly the shape of the mold. In practice the molding time cycle may be as low as ninety seconds. The principal examples of this type are the phenolics (Bakelite, Durez) and the urea molding resins (Beetle, Plaskon).

Inert fillers, such as wood flour, asbestos, paper pulp, are practically always used in such molding compositions. These reduce the cost, and in addition improve the shock resistance of the molded article. The choice of filler depends upon the properties required in the finished piece. Asbestos is used for high temperature resistance; mica for its electrical properties; wood flour for strength; paper pulp for light color. Pigments are used to give desired colors.

The material is supplied to the molder in the form of powder or granules; the latter is easier to handle, less dusty, and not so bulky in the mold before pressing. Instead of weighing out the charges of powder or granules for each mold, preforming may be resorted to. In this operation, the molding compound is pressed into tablets in automatic machines and a fixed number of pills used per charge. Metal

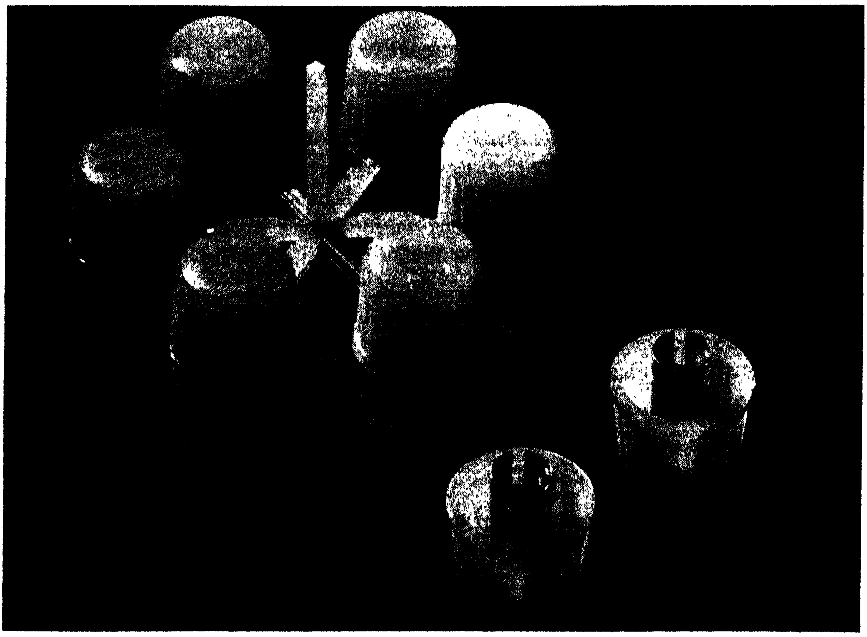


FIG. 5. Injection Castings of Cellulose Acetate. (Courtesy of Tennessee Eastman Corp.)

Control knobs as they come from the mold, with sprue and runners attached. The plastic is injected around metal inserts as shown by the two knobs in the foreground.

parts may be set in the mold and the resin molded around these parts. Molds are usually multicavity; that is, several pieces are cured in one operation. Hardened steel and often alloy steels are used for the molds. Heating is usually accomplished by means of steam. Temperatures from 250° F. to 320° F. are used; pressures are from 1500 to 4000 pounds per square inch. These are usually obtained hydraulically. A tremendous variety of articles are produced by molding, from door knobs and bottle closures to automobile distributor heads and camera cases.

Laminating—Laminating is really a form of molding in which simple forms are made. Paper or cloth is impregnated with resin, usually by passing it through a bath of resin dissolved in a solvent. The solvent is then evaporated and the sheet cut to size, stacked in bundles of several sheets. These are then placed in hydraulic presses between steam heated metal platens and cured under heat and pressure. Standard sheets as large as 36 in. × 110 in. and ranging in thickness from 1/64 in. up to 2 in. are produced commercially. Sheets can be cut and punched. Shapes with some variation from flat sheets can be produced by this method; for example, serving trays such as are common in cafeterias and in households.

Tubes, rods and cable conduit also can be made from the impregnated sheets. By using cloth, such as canvas, and alternating the direction of the weave in the layers, a material of much greater shock resistance can be obtained. Such material is used in gears of various kinds. Cutting from blanks may be done by the ordinary gear cutting machines such as are used for metal gears.

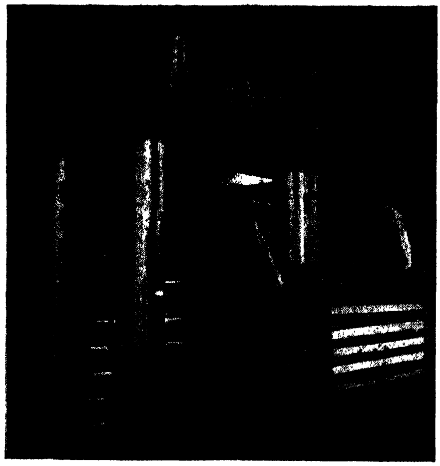


FIG. 6. Fabrication of Laminated Sheets. (Courtesy of Bakelite Corp.)

Bundles of paper sheets impregnated with resin being loaded into the press.

Miscellaneous Uses of Thermoreactive Resins — Thermoreactive resins have recently come into fairly extensive use in the bonding of plywood, replacing glue and blood albumin. A thin film of resin or a sheet of paper impregnated with phenolic resin is placed between the layers of plywood and the structure heated between platens. The resulting plywood is waterproof and proof against bacterial action. It is used in boats, for exterior building construction and experimentally in airplane and automobile body construction.

Another recent development is the use of thermoreactive resins in the crush proofing of fabrics, such as velvet. The fabric is impregnated with a water solution of resin, usually urea-formaldehyde, dried and then stretched and heated as it passes through an oven. The resulting finish is remarkably resistant to the wrinkling effect of casual crushing. Care must be taken to avoid tenderizing the fabric. The use of resinous finishes improves the durability of the fabric, the washing qualities, and resistance to certain stains.

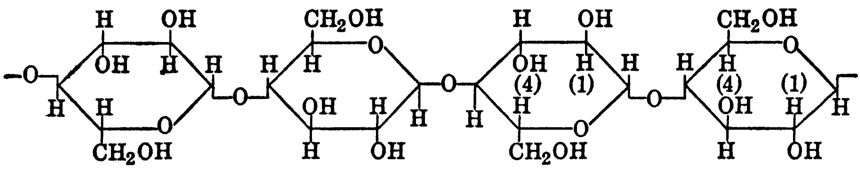
Thermoreactive resins in some cases may be applied as a film deposited by evaporation of a solvent and subsequently baked to form a coating. They are also often used where high temperatures would cause other materials to soften. For example, phenolic resins are used to bond abrasive particles to make wheels which become hot in use, due to friction.

Oxygen Hardening Plastics—Oxygen convertible resins require the presence of air for the final chemical transformation to the insoluble stage. In these cases the reaction is similar to that of the drying of a linseed oil film. The oil takes up oxygen and is thus converted to a solid substance or mixture of substances. The principal example of this type is the oxygen hardening alkyd resin made from a mixture of glycerol, phthalic anhydride and linseed fatty acids (Rezyl, Glyptal, Beckosol). The oxygen absorption make take place at ordinary temperatures or at elevated temperatures, i.e., on baking. Owing to the requirement of oxygen contact for hardening, these resins are used mostly in films; that is, in coatings such as varnishes and enamels.

METHODS OF MANUFACTURE

The manufacture of synthetic plastics involves the ordinary unit processes of the chemical industry, and much of the ordinary types of equipment is used. (See Chapter 3, The Organic Unit Processes. See Figure 9, Flow Sheet, Manufacture of Urea Molding Resins.) The use of stainless steel equipment is becoming more usual and is imperative with the light colored plastics. The plastics industry employs heavy mixing, kneading, and extruding equipment. A brief description will be given of the principal points in the manufacture of the most important types of plastics.

Modified Cellulose Plastics—The cellulose molecule is generally considered to be made up of glucose residues linked together according to the following formula:



Each glucose residue has three hydroxyl groups which may be esterified or etherified. (For the description of these two processes with cellulose see pp. 1203 and 1204.) The number of these hydroxyl groups which are substituted, and the nature of the substituent has a marked effect on the properties of the product. Moreover, the chain of glucose residues may be broken during reaction, and thus further modification of properties occurs.

Cellulose Nitrate—Cellulose nitrate plastics resulted from the discovery by Hyatt in 1869 that nitrocellulose, by itself too hard and brittle, could be successfully plasticized by means of camphor. The many improvements that have been made since Hyatt's day have been in the mechanical handling of material and in the manufacture and stabilization of the nitrocellulose itself. Camphor is still the most important plasticizer. (See compound 198, Chapter 27.)

For the manufacture of cellulose nitrate plastics a suitable grade of nitrocellulose (10.5 to 11.5% N_2) is treated with alcohol and camphor to make a plastic dough-like mass which is kneaded in a dough mixer. (See Chapter 32, Explosives, and Chapter 27, Industrial Organic Chemicals.) The kneaded product is forced through a filter to remove foreign matter, is manipulated between a pair of rolls to effect a better dispersion of ingredients, and is finally smoothed up into a sheet. A number of rolled sheets are placed upon one another in a steel box, where they are consolidated under pressure into a solid block. At various stages in the mixing, and before cutting, dyes and pigments may be added to produce various color effects.

The blocks are cut into sheets by a planer knife, and thereafter subjected to a seasoning process at slightly elevated temperature to remove volatile solvent which is not recovered. The seasoning period varies from a few hours to several months, depending on the thickness of the stock. The seasoned sheets are polished and finished in various ways to improve the transparency and brilliancy, and to produce different surface effects. Continuous tubes or rods are made with stuffing machines, and are then cut to desired length.

These plastics are characterized by toughness and strength. A great variety of decorative effects is possible. Cellulose nitrate plastics are very inflammable and have a definite odor and taste. They are unaffected by oils, and only very slightly affected by water. They are not resistant to acids and alkalies. On exposure to light, discoloration takes place. Sheets may be punched, but shaping operations that may be used are more limited than with any other plastic except casein.

Common applications are automobile curtain windows, toothbrush and other handles, fountain pen barrels, piano keys, buttons, toilet sets, radio dials, eyeglass frames, etc. Wooden heels and similar wooden forms may be covered by softening sheets of the plastic by means of an alcohol-water mixture, stretching over the form and allowing the sheet to dry. Tubes, etc., may be expanded by warming in hot water and then shrunk on metal.

Cellulose Acetate—In recent years cellulose acetate has become increasingly important in the plastic field. Its low rate of combustion and its light stability attracted attention to it as a substitute for nitrocellulose, first for non-inflammable photographic film and later for plastics. When used in conjunction with plasticizers, it can be extruded and molded into shapes not possible with nitrocellulose.

The manufacture of acetate sheets, etc., follows the general procedure of the nitrocellulose plastics. The acetate plus plasticizers is worked into a dough with acetone; colors are added, and the usual processes of rolling, blocking and slicing are carried out. These are followed by seasoning to remove solvent, which is lost. Acetate plastics may also be mixed and extruded without the use of solvents to form sheets which can be cut into blanks or granules (chips) for molding composition.

Cellulose acetate itself is prepared by acetylating cellulose, usually purified cotton linters, with acetic anhydride, glacial acetic acid and a catalytic agent (sulfuric acid) in copper or stainless steel mixers equipped with heavy agitators at 68-86° F. The acetylation goes to the triacetate stage, at which point the reaction is stopped by the addition of dilute acetic acid recovered from a later operation. (See compound 28, Chapter 27.) The triacetate is then hydrolyzed by heating after addition of more sulfuric acid. The acetic acid content is reduced from 61% to between 52 and 56%, depending on the use for which the product is intended. When the saponification has proceeded to the desired stage, the acetate is precipitated by running the charge into water or dilute acid. The acetate is then filtered, washed and dried. Recovery of the acetic acid not consumed in the reaction is important in the economics of the process. This is concentrated by distillation and a part is converted back to acetic anhydride.[10]

The plasticizing of cellulose acetate is a problem on which much work has been done. The literature is full of patents on substances proposed for such use.

[10] Othmer, D. F., Chem. & Met. *40,* 631 (1933); *41,* 81 (1934).

There is no universal plasticizer as in the case of camphor with nitrocellulose plastics. The variety of plasticizers used is very great. Among the more commonly used plasticizers are triphenyl phosphate, tricresyl phosphate, the dialkyl phthalates, phthalyl glycolates and sulfonamides. (See compounds 332, 326, 232.)

Cellulose acetate plastics have unusual light stability, light base color, excellent finish, and transparency when desired. Their softening point permits them to be worked at elevated temperatures and, with the addition of plasticizers, to be molded. Cellulose acetate varies in properties, depending upon the percentage of combined acetic acid. The higher the acetyl content (above a certain limit), the poorer the plasticity and the poorer the solubility. On the other hand, the lower the acetyl content, the greater the water absorption.

Cellulose acetate molding compositions are available in all colors, from water white transparent to opaque. They can be used in thin walled sections where other molding materials cannot because of brittleness. Because of their water absorption, cellulose acetate plastics are not suitable for uses bringing them into contact with water. They are not as tough as cellulose nitrate, and are not nearly as inflammable. They lend themselves very readily to injection molding and may also be extruded. Their machining qualities are good; they can be sawed, punched and turned. The cellulose acetate plastics may be molded around metal cores, a great advantage for certain shapes, such as automobile steering wheels.

A large proportion of the molding material goes to automobile hardware, and a considerable proportion to buttons, buckles and similar novelty and decorative uses, office machine keys, combs, door knobs, golf tees, etc.

Other Cellulose Esters—Cellulose aceto-butyrate, a mixed ester, is similar to cellulose acetate in properties, but is superior in compatibility with resins and plasticizers, is less limited in choice of solvents, and has a higher degree of moisture resistance. It is especially adapted for injection molding, and for use in coatings.

Cellulose aceto-propionate is a similar mixed ester.

Cellulose Ethers—The hydroxyl groups of cellulose can be etherified with aliphatic or aromatic radicals. (See Chapter 3, The Organic Unit Processes.) Several of these ethers have been proposed as plastics, but only one of them, ethyl cellulose, has been in commercial production in the United States.

Ethyl Cellulose—The properties of ethyl cellulose vary with the proportion of the ethoxy group, $-OC_2H_5$, combined with the cellulose molecule. Three types of ethyl cellulose are known, their properties varying with the degree of ethylation. The lower ethers, with an ethoxyl content as low as 5%, are soluble in caustic soda after freezing. With an ethoxyl content of 27%, the ethers are water soluble. Ethers with an ethoxyl content of 47% and above are soluble in alcohol and aromatic hydrocarbons. Only the first and third types are on the market.

The low ethoxyl type of ethyl cellulose, soluble in alkali, has recently been introduced to the American market as a permanent sizing for textiles. Highly etherified ethyl cellulose containing 2.4 to 2.5 ethoxy groups per glucose residue and soluble in organic solvents, is marketed for use in coating materials for leather, paper, fabrics and polished metal, and as an addition agent to speed up drying of varnish. The fact that it softens at temperatures as low as 120° C may adapt it to use as a thermoplastic molding material.

In the manufacture of ethyl cellulose, cellulose in the form of highly purified wood cellulose or cotton linters is treated with caustic soda solution (16-18%) by steeping combined with mastication or grinding. An alkali-cellulose compound results which is subjected to the action of ethyl chloride under heat (120-130° C.) and pressure (200 lbs. per sq. inch) for 8-12 hours.[11] Diethyl sulfate may also be used as the ethylating agent (see compound 49, Chapter 27). The excess reactants and by-products are removed by distillation and washing. To secure a highly etherified product, the material may be repeatedly subjected to the ethylating reaction. The highly ethylated grades are made in a range of viscosities.

Other Cellulose Ethers—The commercial production of methyl cellulose of a water-soluble type has recently been announced. It has been used abroad as a thickening agent, size and adhesive. Alkali soluble methyl cellulose has been suggested as a substitute for viscose. Benzyl cellulose has been manufactured on an experimental scale abroad.

Ester Gum—Of the natural resins, the most important is common rosin, or colophony, obtained from various species of pine trees (see Chapter 17, Wood Distillation Industry). The principal constituent of rosin is abietic acid, $C_{19}H_{29}COOH$. Rosin is readily soluble in oil, but its use in varnish is objectionable because of its acidic nature. The presence of the carboxyl group is a disadvantage with regard to durability, moisture resistance, and reactivity with such basic pigments as zinc oxide which are used in enamels. By esterification of rosin with glycerol the carboxyl group is blocked and the resulting modified rosin presents improved properties. The following formula represents the resulting structure:

$$
\begin{array}{l}
CH_2O\,\boxed{H \quad HO}\,OCC_{19}H_{29}\\
|\\
CH\ O\,\boxed{H \quad HO}\,OCC_{19}H_{29}\\
|\\
CH_2O\,\boxed{H \quad HO}\,OCC_{19}H_{29}
\end{array}
$$

In the manufacture of ester gum, stainless steel or aluminum kettles are used. These usually hold about 10,000 lbs. per charge. They are oil fired and connected to vacuum equipment. The rosin is first charged through a manhole, melted, and its temperature raised to about 240° C. At this point, high gravity glycerine amounting to 10 to 12% of the rosin is run in slowly, the temperature raised over a period of about six hours to 280° C., and held until a cooled sample is clear. Any unreacted glycerine, and the small amount of volatile material present in the original rosin are then distilled off under vacuum. The kettle is discharged by blowing the molten resin onto a concrete floor, where it solidifies as a glassy layer, which is broken up with a sledge when cool. (See Chapter 40, The Natural Resins, Gums, and Gum Resins.)

Ester gum is used principally as an ingredient of varnishes and of nitrocellulose lacquers. It is soluble in a wide variety of solvents, alcohols, esters, aliphatic and aromatic hydrocarbons, etc.

Casein Plastics—The casein plastics industry is more highly developed in Europe than in the United States. The basic raw material is casein, a protein

[11] Traill, D., J. Soc. Chem. Ind. *53*, 338 (1934).

comprising the major portion of the solids of milk. Casein reacts with formaldehyde to give a hard, horny material. The mechanism of the reaction is probably a condensation between amino groups of the protein and the formaldehyde.

Casein plastics are hard, non-inflammable, odorless, and of light color. Their water resistance is poor and they have a marked tendency to warp with changing atmospheric conditions. They cannot be molded, and fabrication is almost entirely by machining. Because of these disadvantages, they are being largely displaced by the newer plastics. Casein plastics find their principal use in buckles, buttons, and small ornamental objects. (For a description of the manufacture of casein plastics see Chapter 44, Casein and Allied Materials.)

Soybean Plastics—Soybean meal, the product left after pressing of the oil, contains protein material similar to casein and has been used to produce a similar plastic with the same disadvantages. The meal has also been used as a filler for phenolic resins. (See Chapter 44, Casein and Allied Materials.)

Lignin Plastics—These are made from lignin, the principal non-cellulose constituent of wood. It is recovered from waste liquor of sulfite pulp mills as a sulfonate by precipitation with lime. (See Chapter 37, The Pulp and Paper Industry.) Sheets of this product with wood fiber filler are produced commercially and are used to manufacture laminated sheets by pressing in hydraulic presses with steam heated platens. The sheet is black in color. It can be punched and nailed. Molding compositions are said to be in the development stage. To obtain a thermosetting plastic, a reactive resin such as phenol-formaldehyde must be added.

Modified Rubbers—Rubber itself, when compounded with sulfur, behaves as a thermoreactive plastic. It is discussed elsewhere. (See Chapter 39, Rubber and Rubber-like Products.) Two other modifications of rubber are in commercial use as plastics: chlorinated rubber and isomerized rubber.

Chlorinated rubber is made by chlorination of rubber in solution in carbon tetrachloride and in the presence of a catalyst such as iodine. Practically all of the current production of chlorinated rubber is compounded with ester plasticizers and volatile hydrocarbon solvents and used in coatings. Rubber derivative finishes have proved successful principally in three types of service: in floor paints and enamels, in protective coatings subject to contact with chemicals or corrosive gases, and for painting over fresh concrete. In floor paints, their toughness, adhesion and wearing qualities, combined with resistance to moisture and the free alkali of concrete, make them useful under conditions where oleoresinous finishes are unsatisfactory.

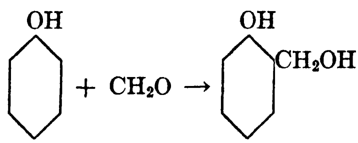
Isomerized rubber (rubber that has undergone an internal structural rearrangement) is made by mixing rubber with a metal-chlorine compound such as stannic or antimony chloride on rubber rolls, curing the mix at an elevated temperature to effect the reaction, and then removing the isomerizing agent by washing with alcohol. Isomerized rubber is used principally in the form of thin transparent sheets for ladies' raincoats, umbrellas, and household novelties.

Resins from Cashew-nut Oil—Cashew-nut shell liquid contains a high molecular weight phenol, cardanol o—$C_{14}H_{27} \cdot C_6H_5OH$, in which the side chain is unsaturated. It reacts with formaldehyde directly, and also after polymerization. Such products become slightly soft at elevated temperatures and have found use in automobile brake linings and oil-resistant coatings. (See Chapter 40, The Natural Resins, Gums, and Gum Resins.)

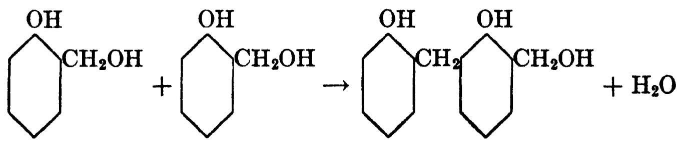
PHENOL-FORMALDEHYDE RESINS

Phenol-formaldehyde resins, the most important of the resins now being produced, are well known to the general public, which is very familiar with the trade name: Bakelite. The reaction of phenol and formaldehyde to form resinous products was observed by Baeyer about 1872. However, Baekeland is generally considered the first to discover methods for the control of the condensation of phenols and formaldehyde for the manufacture of useful articles. He devised the method of rapid curing of the resin by heat and pressure molding, and of reinforcing by the use of fillers.

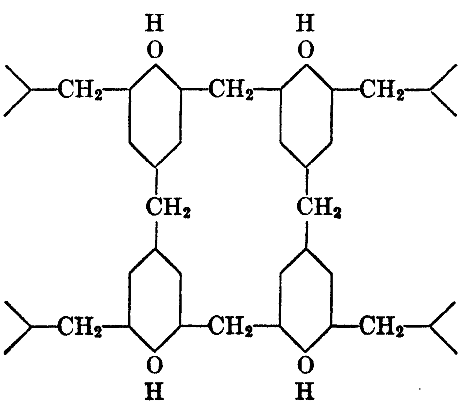
Structure of the Resin—There has been much speculation concerning the reactions involved in the formation of these resins. The first step in the alkaline condensation is the formation of phenol mono-alcohols, *o*-, *m*- and *p*-hydroxy benzyl alcohol (saligenins), and of polyalcohols. (See Chapter 3, The Organic Unit Processes.)



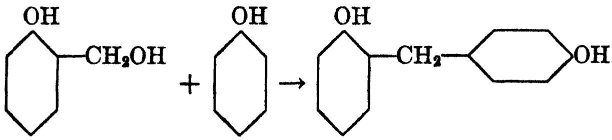
These compounds undergo further condensation represented by the simplified equation:



Still larger molecules are built up by similar reaction to the final infusible insoluble product whose structure is three-dimensional. The following highly simplified two-dimensional formula gives a general idea of the structure:



Modified Forms—When phenol and formaldehyde are condensed in the presence of an acid catalyst, phenol alcohols are formed, but the acid also catalyzes the reaction of the phenol alcohols with phenol:



This reaction of phenol reduces the proportion of phenol alcohols formed and, in a sense, blocks the condensation to higher molecular weight bodies. Thus the acid condensation results in thermoplastic, soluble compounds. If, however, alkali and more formaldehyde are added to the acid condensate, for example, in the form of hexamethylene tetramine (see compound 91, Chapter 27), and heat is applied, two things happen. The alkali catalyzes combination of the formaldehyde to form additional —CH_2OH groups and the heat causes condensation of the new products to the final infusible stage.

By using homologues of phenol, particularly para-substituted phenols, it is possible to avoid final reactivity and obtain products exhibiting thermoplastic and little or no thermoreactive properties. For example, para-cresol has the para position on the ring blocked by a methyl group. Therefore, only the two ortho groups react with formaldehyde and the resultant product is essentially a long chain or ring with reduced thermoreactivity. The side chain also imparts increased oil solubility. Such products from para-substituted phenols are cooked with vegetable drying oil such as tung oil to form varnishes.

Method of Manufacture—Phenol itself is usually used for the manufacture of molding compounds; for laminating solutions, cresols and phenols are employed; for the coating resins, phenol and its homologues, including specially synthesized para-substituted higher phenols, are used. Formaldehyde is the aldehyde principally employed; furfuraldehyde (see compound 462, Chapter 27) is used only to a small extent.

The reaction between the phenol and formaldehyde takes place in steel kettles equipped with reflux and distillation condensers. A charge is usually about 500 gallons and consists of approximately equal volumes of phenol and formaldehyde (37% solution). In the so-called two-stage process, 0.1% hydrochloric acid is the catalyst used. The reaction is started by passing steam through the jacket of the still. It is exothermic and the temperature is controlled in the beginning by circulation of water through the jacket. The reaction is allowed to take place at slight pressure (temp. 105° C.) with the reflux condenser connected. The first phase of the reaction is over in about two hours. The water is then evaporated under vacuum. The hot liquid resin is finally discharged into trays or cans and allowed to cool and solidify.

The resin is dumped from the cans and broken with sledge hammers, ground in ball mills with lime (to neutralize the acid catalyst), with hexamethylene tetramine (to accelerate the curing rate in molding) and with mold lubricant, usually zinc stearate. The material is then further ground in ball mills with filler and brown or black coloring matter. Sienna is the usual brown pigment.

For black, nigrosine is the common coloring agent. As nigrosine is alcohol soluble, carbon black is used where the finished molding is expected to come into contact with alcohol, but carbon is objectionable in electrical insulating parts.

The complete mixture is compacted by very brief treatment on steam-heated rolls, similar to rubber compounding rolls, into uneven sheets about one-quarter inch in thickness, known as blankets. The blankets are stripped from the rolls, allowed to cool, and crushed coarsely by a mill. The particles then pass to a hammer mill in circuit with a vibrating screen and in series with a dust collector. The compound, in the form of a powder or granules, is packed in drums for shipment to the molding shop.

Varnish—A large quantity of resin is converted into varnish for shipment to factories impregnating cloth or paper for laminated products. To make varnish, the resin in the kettle is dissolved in alcohol.

Cast Phenolics—In the manufacture of cast phenolics, nickel or copper kettles of about 200 gallons capacity are used. Pure phenol and more than its equivalent of formaldehyde (about two and a half mols per mol of phenol) are condensed at 100° C. for one hour in the presence of a small amount of alkali. The reaction is highly exothermic and water is circulated in the jacket of the kettle to keep the mixture under control. The alkali is then neutralized by means of lactic acid. The resin solution is then concentrated in vacuo with agitation and becomes more and more viscous. Glycerine is added during the concentration to keep the mass more fluid and to improve the transparency and reduce the brittleness of the cured resin. Toward the end of the concentration dyes are added.

The resin is drawn off from the kettles in small pots from which it is poured by hand into gang molds made of cast lead, and cured for about one week at 72-85° C. From the standard shapes so cast, the final piece is machined by a fabricator.

Cast phenolics may be made brilliantly clear and colorless and lend themselves to a variety of mottled decorative effects.

Molded Resins—The molded resins are strong, oil and water resistant, very durable, quite heat resistant, and have excellent electrical properties. Properties vary, depending upon the filler used. Wood flour filler material is usually used for common articles such as switch plates, electrical plugs, bottle caps, telephones, etc. It is characterized by high dielectric strength, excellent finish and accuracy of form. Where higher heat resistance and better water resistance are required, mineral fillers are used. For strength and toughness, fabric fillers are used, as the long fibers of the filler impart greater impact strength. Molded phenolics are slightly attacked by weak alkalies and sometimes have a slight phenolic odor. The usual colors available are brown, black and mottles of these two.

The properties of the resin portion of the laminated sheet are, of course, similar to those of the molded phenolic, the differences in the product being due to the filler, which may be paper, canvas or linen. Laminated sheet is characterized by strength, impact resistance, imperviousness to oil and moisture, good electrical properties, and good machining qualities. In certain properties, one grade may excel at the expense of other properties. Thin sheets may be punched.

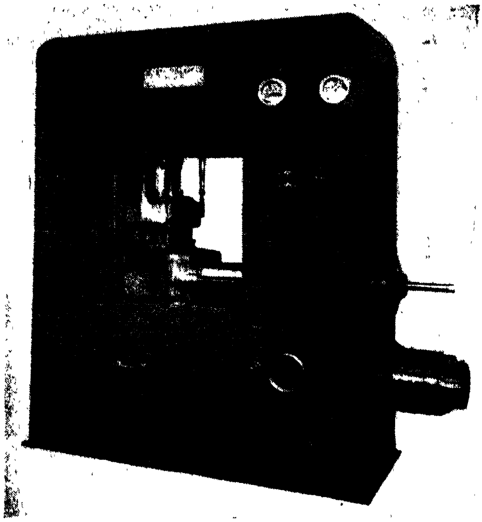


FIG. 7. A Modern 25-Ton Automatic Molding Press. (Courtesy The Watson-Stillman Co.)

Pressure may be applied both vertically and horizontally as is shown by the two plungers.

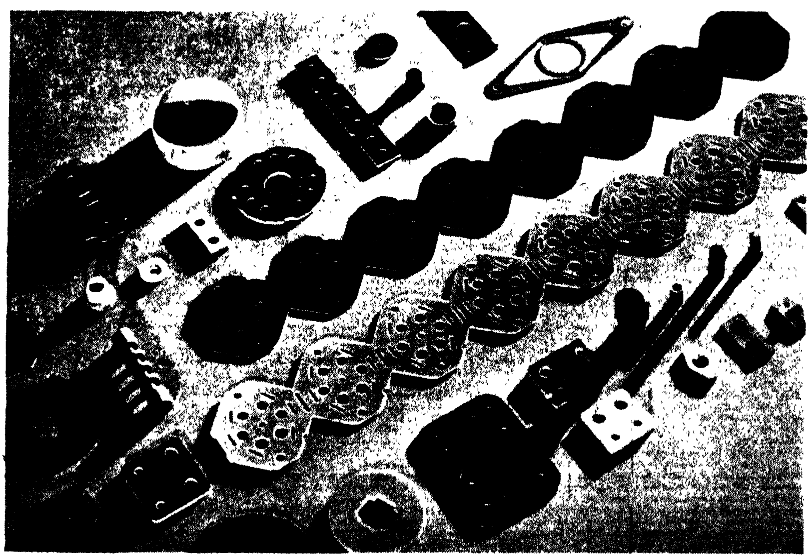


FIG. 8. Pieces Stamped from Laminated Material. (Courtesy Bakelite Corp.)

By facing the outside with printed sheets, decorative products can be made for many purposes.

UREA-FORMALDEHYDE RESINS

Urea has, according to its conventional carbamide formula, two amino groups and is therefore capable of reacting with formaldehyde (methylene glycol) to form compounds of high molecular weight.

$$-\underset{H_2}{C}-\boxed{OH\quad H}HN-\underset{\underset{O}{\|}}{C}-NH\boxed{H\quad HO}-\underset{H_2}{C}-\boxed{OH\quad H}HN-\underset{\underset{O}{\|}}{C}-NH\boxed{H\quad HO}-\underset{H_2}{C}-$$

Macromolecules can also be formed by the following series of reactions.

$$\begin{array}{l} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{array} + 2CH_2O \rightarrow \begin{array}{l} NHCH_2OH \\ | \\ C{=}O \\ | \\ NHCH_2OH \end{array}$$

$$\begin{array}{ccc} HNCH_2 & \boxed{OH\quad H} & -NCH_2OH \\ | & & | \\ C{=}O & & C{=}O \\ | & & | \\ HNCH_2 & \boxed{OH\quad H} & -NCH_2OH \end{array}$$

Probably a mixture of the two types of linkages are formed during manufacture, with many cross linkages forming during molding. These cross linkages are responsible for the thermosetting.

Thiourea and guanidine (imino urea) behave similarly. These latter two are much more expensive than urea and offer little, if any, advantage. Mixed urea-thiourea molding composition was manufactured a few years ago, but was abandoned both because of high cost of thiourea and because it caused staining of the molds.

Manufacture—The manufacture of urea-formaldehyde molding compound is shown in the accompanying flow sheet. The resin solution is prepared in a closed 500 gal. glass-lined or aluminum jacketed kettle equipped with an agitator. A typical charge would comprise:

Urea	1200 lbs.
Formaldehyde	2160 lbs.
Aqua Ammonia	70 lbs.

The reaction mass is cooled by circulating water in the jacket of the kettle, the maximum temperature reached being about 100° F. The syrup so produced is mixed in a stainless steel Baker-Perkins mixer, with a filler, usually a high grade alpha cellulose paper pulp.

The mixture is then dried in steam heated tray driers at 175-180° F. for 4 to 8 hours. The degree of drying is finally controlled by a molding test on the unground material. The dried material is ground in brine cooled porcelain mills with the addition of zinc stearate (used as a mold lubricant), a small amount of molding accelerator and the pigments required for the desired shade.

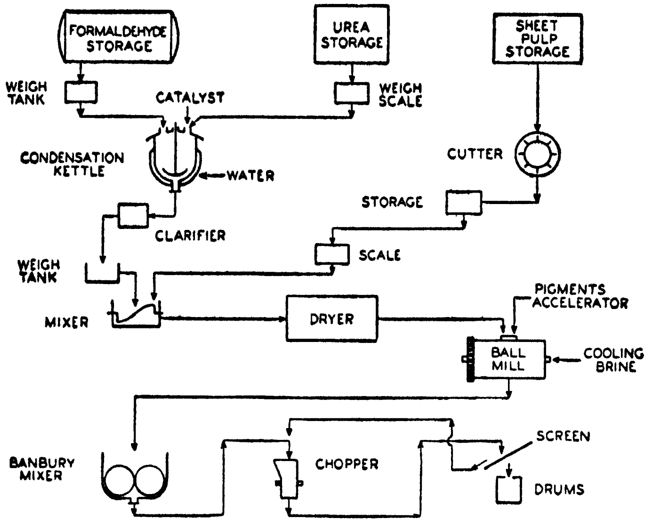


FIG. 9. Flow Sheet. Manufacture of Urea Molding Resins.

For many molding operations, especially where pre-forms or tablets are made for ease of loading multiple molds, a fluffy powder is objectionable. In other cases, powder will trap air and cause blistering or haze easily noted in the translucent composition. For such purposes, the molding powder is agglomerated in a Banbury mixer. After agglomeration, the charge is chopped in a chopper, run through a coarse screen and packed.

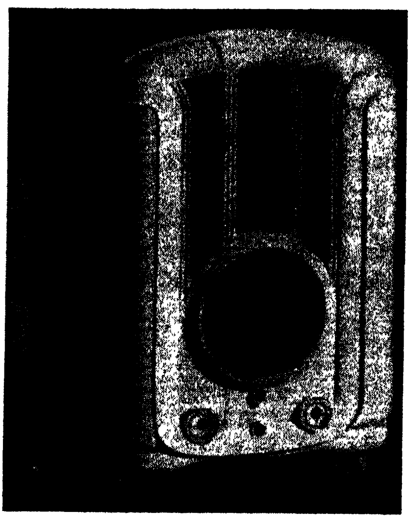


FIG. 10. A Urea Resin Molding. (Courtesy American Cyanamid Co., Beetle Products Division)

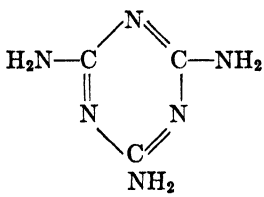
Urea resins, unlike phenolic molding resins, do not discolor with light or time. Because of the very white cellulose used as filler, very light shades are obtainable. The final molded resin contains a small percentage of water, the evaporation of which on exposure causes a slight distortion of shape, which is not objectionable in many cases. The cured resin does not burn on exposure to free flames, but chars and emits disagreeable odors. Its water resistance is fair, but it must not be subjected continuously to the action of water.

The ultimate uses to which the molded articles go are very varied. Among the molded products are the following: buttons, buckles, bottle caps, radio cabinets, clock cases, picnic dishes, cutlery handles, automobile hardware, lighting shades, electrical plugs, switch plates, scale housings, boxes, novelties.

The urea-formaldehyde coating resin is made by the reaction of urea and formaldehyde in slightly alkaline solution, followed by dissolution in an alcohol such as butyl alcohol and further reaction in slightly acid solution with the alcohol which combines with a hydroxyl group to form an ether linkage. Blended with alkyd resins, it produces excellent coating films. The addition to the alkyd resin imparts hardness, gloss, improves the color and baking characteristics. Such films cure in one hour or less at 250° F., and in a few minutes at temperatures of 300° F. or above. They exhibit little or no discoloration when cured at these high temperatures and no yellowing on age or light exposure.

MELAMINE RESINS

Melamine is a compound containing three amino groups attached to a triazine ring:



Like urea it can react with formaldehyde, but having three reactive groups to two for urea, the structures obtainable are more complicated. It can also react with polyhydric alcohols. Melamine is the trimer of cyanamide and is made commercially from calcium cyanamide.

Melamine-formaldehyde resins in varieties similar to urea resins have recently come on the market and have been widely accepted. They are thermoreactive. Methods of manufacture and uses are similar to those of urea resins. Melamine resins have superior heat resistance and superior water resistance. Both these improvements are probably due to the absence of the carbonyl group present in urea.

ALKYD RESINS

When a polyhydric alcohol is esterified with a polybasic acid, a complex resinous ester of high molecular weight generally results. The resins thus formed are known as alkyd resins. In the simple case, ethylene glycol is reacted with phthalic acid (or its anhydride, see compound 307, Chapter 27) to form long chains of alternating ethylene and phthalyl groups (see p. 1195). There is a large variety of such resins because of the large number of polyhydric alcohols and polybasic acids available. In addition, modifying agents are used and these, of course, increase the variety possible. The ethylene glycol phthalic anhydride product cited above is non-hardening and of balsam-like appearance. The presence of the three hydroxy groups in glycerol gives a resin which on prolonged heating becomes insoluble and infusible, probably because of the linking of chains one to the other and to the cross linking in the same chains. This resin is not molded by the ordinary method because it has a very slow rate of cure. It must be cured in an oven with a very slowly rising temperature in such a way that the volatile products can escape. Glycerol phthalate resins may be plasticized by the addition of substances such as succinic acid and diethylene glycol (see compounds 44 and 128, Chapter 27) to the reaction mass. In this case we have long chains of the nonconvertible resin attached to the heat convertible resin molecules, resulting in flexible products.

Ordinarily, the heat convertible glycerol phthalate resin is modified by the addition of a monobasic acid. This may be perhaps most clearly visualized by considering the monoglyceride of the modifying acid as a dihydric alcohol. It has only two available groups for reaction and therefore gives products similar to those obtained with ethylene glycol. Properties obtained depend upon the nature of the modifying agent used and the amount. For example, if stearic acid is used one type of product is obtained; if benzoic, there is a change in properties. But both resins are non-hardening.

The non-hardening resins are used in the formulation of nitrocellulose lacquers and for other purposes. Their particular value in nitrocellulose lacquer formulation is the great durability they impart to the film. This may be due to their opacity to ultra-violet light, which has a deleterious effect on nitrocellulose.

Unsaturated acids, such as acids of linseed or tung oil, may be used to modify glycerol phthalate resins and the resulting product is an oxygen hardening resin, the action of the oxygen of the air probably causing cross linkages. Oxygen hardening alkyds are extensively used for quick drying varnishes and enamels for finishes on automobiles. They have unusual durability on exposure to the weather and, in addition, excellent adhesion and retention of elasticity with age. The discoloration on baking or on light exposure is relatively slight.

Glycerine is the most extensively used polyhydric alcohol; phthalic anhydride the most extensively used polybasic acid. Fatty acids from linseed, tung, soya and sunflower oil are the drying fatty acids employed for oxidizing resins; cottonseed and cocoanut oil fatty acids for the non-drying, lacquer type. (See Chapter 41, Natural Oils, Fats and Waxes.)

Manufacture—Alkyd resins are manufactured by heating together the polybasic acid, the polyhydric alcohol and the modifying agent in an open kettle, or in a reaction vessel provided with a vent. A current of carbon dioxide is often passed through the reaction mixture to maintain an inert atmosphere, assist in thorough agitation, and carry off water vapor. Temperature of reaction is about 500° F.

In its simplest form, the equipment consists of a varnish kettle of the usual cylindrical type. This kettle is mounted on a wheeled buggy and is rolled over an oil or coke fire level with the floor in a varnish "stack." Sometimes the kettle is partially closed by a loosely fitting cover. On completion of the cook, the batch is allowed to cool to a safe temperature and then thinned or "reduced" with the desired amount of coal-tar or petroleum solvent.

The principal resin manufacturers and a few of the larger varnish makers use more elaborate equipment. Closed stainless steel stills holding up to 10,000 lbs. of charge are employed. They are oil or gas fired. Agitation with carbon dioxide and sometimes with mechanical stirrers is usual. The finished resin is usually blown or run into a separate thinning tank where thinning is carried out under a reflux condenser to conserve solvent. Production by this method entails a larger capital expenditure and more intelligent control, but results in a superior product and in lower production costs where operations are on a large scale.

POLYAMIDE RESINS

These bear a structural resemblance to the thermoplastic alkyds. They are made from a dibasic acid such as adipic acid (see compound 8, Chapter 27) and a dibasic amine such as 1,6-diamino hexane. The structure of the resin is as follows:

$$\begin{array}{cccccccccccc} -\mathrm{N}- & (\mathrm{CH_2})_x & -\mathrm{N}- & \mathrm{C} & -(\mathrm{CH_2})_y- & \mathrm{C} & -\mathrm{N}- & (\mathrm{CH_2})_x & -\mathrm{N}- & \mathrm{C} & -(\mathrm{CH_2})_y- & \mathrm{C}- \\ \mathrm{H} & & \mathrm{H} & \| & & \| & \mathrm{H} & & \mathrm{H} & \| & & \| \\ & & & \mathrm{O} & & \mathrm{O} & & & & \mathrm{O} & & \mathrm{O} \end{array}$$

Such products have found uses as fibers for artificial silk under the name of "Nylon" and as bristles for brushes under the name of "Exton." They have unusual elasticity and wearing qualities.

VINYL RESINS

Compounds containing the vinyl linkage, i.e., $CH_2{=}CHX$, where X is a strongly negative group, polymerize to give hard, thermoplastic products, the vinyl resins. Common usage has generally restricted the term vinyl resins to those derived from vinyl chloride, vinyl acetate, vinyl alcohol and vinyl acetal, in which the negative group X is respectively Cl, $OCOCH_3$, OH, and $RC(O-)_2$. Vinyl chloride and vinyl acetate especially have been extensively investigated.

The structure of vinyl polymers is probably:

$$\begin{array}{cccccc} -\mathrm{CH_2}- & \mathrm{CH} & -\mathrm{CH_2}- & \mathrm{CH} & -\mathrm{CH_2}- & \mathrm{CH}- \\ & | & & | & & | \\ & \mathrm{X} & & \mathrm{X} & & \mathrm{X} \end{array}$$

One of the first uses of vinyl resins was as the molding composition in the manufacture of records for the electrical transcription of sound. Vinyl resins are used in the lining of food and beer tins, for lining food container caps, and for the impregnation of paper used in wrapping foods. Recently vinyl resins have come into use in the inner layer of safety glass and as a synthetic fiber, Vinyon.

Vinyl resins are prepared by the thermal polymerization of vinyl derivatives in the presence of an oxygen yielding compound, usually benzoyl peroxide (see compound 189, Chapter 27) or acetyl peroxide. Polymerized vinyl acetate and chloride and mixed polymers are the more common products. The vinyl resin used in the new safety glass is an acetal prepared by reacting polyvinyl alcohol with butyraldehyde (see compound 21, Chapter 27). The break resistance claimed for this new safety glass is superior to that of the old cellulose acetate glass, especially at low temperatures. Sheets of the plasticized resin are prepared by an extrusion process and the glass laminated by application of heat and pressure. No adhesive is required and no edge-sealing.

Vinyl chloride is produced by the reaction of acetylene with hydrogen chloride in the presence of a tin or copper chloride.[12] The mixture of acetylene and vinyl chloride can be separated by fractional distillation and the acetylene recycled. Vinyl acetate is prepared by the reaction of acetylene with acetic acid in the presence of a mercury-oleum catalyst:

$$CH\vdots CH + HX \rightarrow CH_2{:}CHX$$

Acetylene is circulated continuously through a Duriron or stainless steel kettle at 70 to 90° C., removing the product as formed. A continuous still separates the vinyl acetate from unreacted acetic acid, which is returned to the kettle. Ethylidene diacetate (see compound 76, Chapter 27) is produced as a by-product and is recovered for conversion to acetic anhydride.[13] Polymerized vinyl alcohol is produced by hydrolysis of polymerized acetate.

VINYLIDENE CHLORIDE RESINS

A new variation of the vinyl type is the polymerized vinylidene chloride resin. The liquid monomer has a structural formula, $CH_2{:}CCl_2$, related to vinyl chloride, and forms similar long chains. Co-polymers with vinyl chloride range from flexible, moderately soluble products to hard thermoplastic solids. Unusually high tensile strengths are possible. These resins contain a high proportion of chlorine. They exhibit great chemical inertness and abrasion resistance. The base resin is clear and has limited compatibility with plasticizers. Applications are as substitutes for gut leaders on fishing lines, as rattan-like strands used for weaving seats of vehicles. Its high dielectric strength makes it look promising for electrical insulation.

ACRYLATE RESINS

Acrylate resins are closely related to the vinyl resins and to the hydrocarbon resins, such as polystyrene, polybutylene, etc. The presence of any negative group, in this case the carboxyl group, attached to an ethylenic carbon atom promotes the polymerization tendency of the ethylenic double bond. Acrylates have the general formula $CH_2{=}CR'COOR''$, where R′ represents either hydrogen or an alkyl group. In the only derivatives of commercial importance, that is the acrylates and methacrylates, R′ is hydrogen or the methyl group. R″ is usually a methyl group. The polymer is generally considered to have a chain structure as follows:

$$\begin{array}{l} -CH_2-\underset{\displaystyle COOR''}{\underset{|}{CR'}}-CH_2-\underset{\displaystyle COOR''}{\underset{|}{CR'}}-CH_2-\underset{\displaystyle COOR''}{\underset{|}{CR'}}- \end{array}$$

Variation in R′ and R″ results in variation of the hardness of the resin.

Acrylic resins are outstanding in their light weight, water white transparency, clarity, water and chemical resistance, electrical properties, heat and light stabil-

[12] Toussaint, W. J., U. S. Patent 1,926,638 (1933); Perkins, G. A., U. S. Patent 1,934,324 (1933).

[13] Morrison, G. O. and Shaw, T. P., Trans. Electrochem. Soc. 63, 197 (1933).

ity, toughness, and high softening point. Their scratch resistance, although good for thermoplastic resins, is not excellent and they exhibit brittleness at low temperatures. They can be compressed or injection molded. In machining cast forms, the general precautions necessary when working with thermoplastic materials must be exercised to avoid over-heating and gumming.

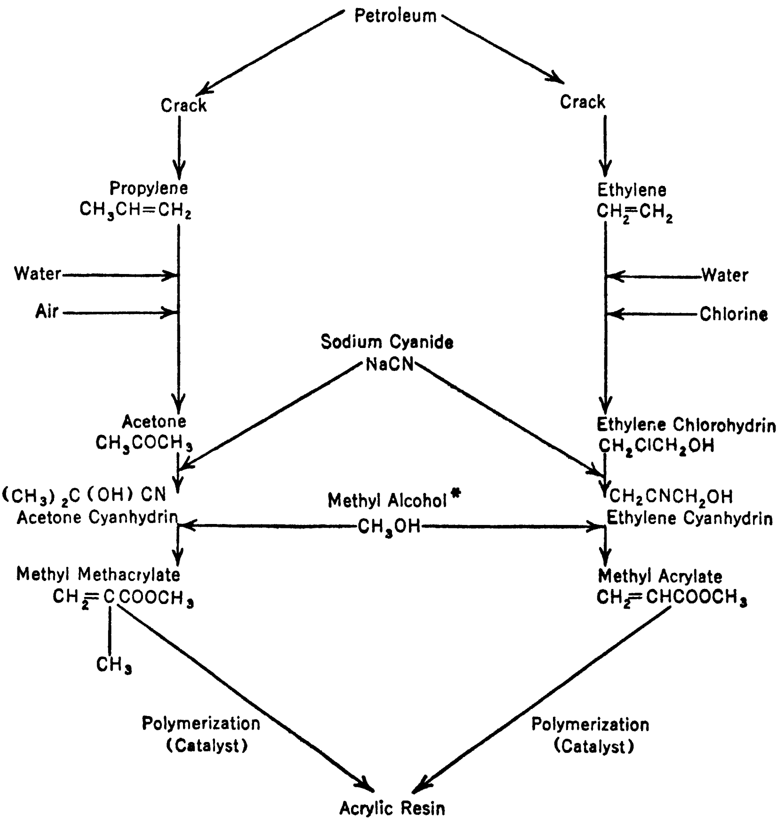
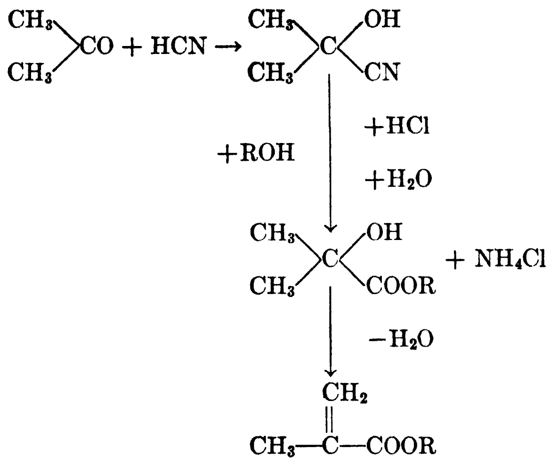


FIG. 11. Manufacture of Acrylate Resins. (Courtesy Rohm & Hass Co.)

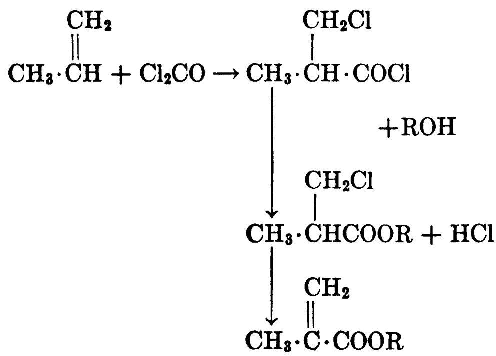
* By substituting other alcohols at this point, other esters of acrylic acid and methacrylic acid are obtainable. Varying the relative amounts of these esters and control of polymerization conditions yields resins varying from tacky liquids to hard solids.

Manufacture—Acrylate resins are manufactured from acrylate esters by thermal polymerization in the presence of benzoyl peroxide or a similar catalyst. Special technique has been devéloped for polymerization into cast products which are bubble-free and flawless.

There are two methods of manufacturing acrylate esters: the cyanide method and the phosgene method. In the first method, acetone and hydrogen cyanide are reacted to give acetone cyanhydrin which is hydrolyzed in the presence of methanol and hydrochloric acid to give α-hydroxy isobutyric methyl ester. Dehydration of this ester with a strong dehydrating agent gives methyl methacrylate. Ethanol instead of methanol gives ethyl methacrylate.



In the second method, phosgene, prepared from carbon monoxide and chlorine, is condensed with propylene to α-chlor-isobutyryl chloride, which is easily esterified with methanol and is then dehydrohalogenated with alkali or catalytically to give methyl methacrylate.



Sheets of polymerized methyl methacrylate are used for windows and cockpit enclosures of aircraft. In the textile field, aqueous dispersions of acrylate resins are used as finishing materials. Various ornamental and decorative objects are made by injection molding or by casting. A recent development is molded reflectors for highway warning signals.

POLYSTYRENE RESINS

Polystyrene resin is the polymerization product of styrene, an unsaturated compound with the formula $C_6H_5CH{=}CH_2$. The phenyl group, C_6H_5, is a strongly negative group, and in its position in relation to the ethylene linkage accounts for the strong tendency of styrene to polymerize. Polystyrene is a colorless, odorless, tough thermoplastic resin which is generally considered to have a chain structure as follows:

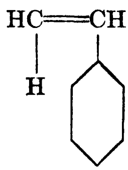
$$\begin{array}{cccccccccccc} -CH_2- & CH & -CH_2- & CH & -CH_2- & CH- \\ & | & & | & & | \\ & C_6H_5 & & C_6H_5 & & C_6H_5 \end{array}$$

Polystyrene resin is outstanding as an electrical insulator and is unique in its resistance to breakdown and in low loss factor in high frequency fields. It is well known for its waterproofness, resistance to corrosive chemicals, light weight, lack of odor, and its water white transparency. At temperatures above 300° C. it depolymerizes to a large extent.

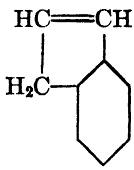
The monomer occurs in cracked hydrocarbons and is also formed by dehydrogenation of ethyl benzene which may be made from ethylene and benzene with aluminum chloride as a catalyst. The dehydrogenation takes place at 600-700° C.[14]

COUMARONE RESINS

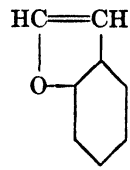
Indene is an unsaturated hydrocarbon with an ethylene bond; coumarone is a similar compound with oxygen replacing a CH_2 group. The polymerization reaction is similar to that of styrene.



styrene



indene



coumarone

Coumarone resin is a clear, amber, brittle solid. There are various grades classified according to softening point, which varies from 50° C. to 160° C. for the different grades. Color is also an important factor, the lighter colors commanding higher prices. The resins are thermoplastic and soluble in aromatic solvents, esters and petroleum hydrocarbons containing some aromatics. Coumarone resins are neutral in reaction and fairly resistant to dilute solutions of acids and alkalies. They are used in the manufacture of varnish and of printing ink. They are also used in compounding rubber compositions, in the manufacture of floor tiles and as an ingredient in chewing gum.

The resins are produced from a fraction of coal-tar solvent naphtha boiling between 150 to 200° C. Such a naphtha contains large proportions of coumarone and indene bodies. The naphtha is refined by alkali washing to remove phenols, tar acids, etc. Pyridine bases are removed by treatment with dilute acid, which also removes certain readily polymerizable hydrocarbons that yield dark tars. The naphtha may then be redistilled.

The polymerization reaction is carried out by the addition of concentrated sulfuric acid catalyst with thorough agitation and temperature control. At the end of the reaction, the sulfuric acid is allowed to settle and drained off with some tar. The oil is then neutralized with alkali and washed with water.

[14] Natelson, S., Ind. Eng. Chem. *25*, 1391 (1933).

The naphtha is distilled over. The resin remaining behind is run into containers where it solidifies.

HYDROCARBON RESINS FROM PETROLEUM DISTILLATES

Cracked-gasoline distillates contain considerable quantities of mono-olefins, di-olefins, and aromatic compounds which can be polymerized to resins by aluminum chloride. The temperature is controlled by cooling during the reaction, and after its completion the aluminum chloride is decomposed with water. The unreacted gasoline is recovered by distillation. This resin has had some experimental use as a varnish resin. For this purpose it resembles coumarone-indene resin in many of its properties.

SULFUR DIOXIDE-OLEFIN RESINS

These resins are easily formed from the two raw materials. They are thermoplastic, but tend to dissociate back to their components at elevated temperatures. The resins are brilliantly clear and somewhat brittle, the properties varying with the different olefins.

TRADE NAMES OF COMMON PLASTICS ON THE AMERICAN MARKET *

TRADE NAME	COMPANY	TYPE OF PLASTIC	REMARKS
Acryloid	Resinous Products & Chemical Co.	Acrylate	Solution for coatings
Alvar	Shawinigan Products Corp.	Vinyl	
Amberol	Resinous Products & Chemical Co.	Modified Phenolic	For coatings
Ameroid	American Plastics Corp.	Casein	Sheets, rods, etc.
Aquaplex	Resinous Products & Chemical Co.	Alkyd	Water emulsions for coatings
Arochem	Strook & Wittenberg Corp.	Modified Phenolic	For coatings
Arofine	Strook & Wittenberg Corp.	Phenolic	For coatings
Aroplaz	Strook & Wittenberg Corp.	Alkyd	
Bakelite	Bakelite Corp.	Phenol-Formaldehyde Urea-Formaldehyde Polystyrene Cellulose Acetate	Cast, molding compounds, laminating solution and solids for coatings
Beckacite	Reichhold Chemicals, Inc.	Phenolic and Rosin Maleic Glyceride	For coatings
Beckamine	Reichhold Chemicals, Inc.	Urea-Formaldehyde	Solution for coatings
Beckolin	Reichhold Chemicals, Inc.	Alkyd	Liquid for coatings
Beckosol	Reichhold Chemicals, Inc.	Alkyd	Solution for coatings

* For a more complete list of trade names see the Modern Plastics Annual Catalog and Directory.

TRADE NAME	COMPANY	TYPE OF PLASTIC	REMARKS
Beetle	American Cyanamid Co.	Urea-Formaldehyde	Molding compounds, laminating solutions and coating resins
Beetleware	American Cyanamid Co.	Urea-Formaldehyde	Molded ware
Bonnyware	Reynolds Spring Co.	Phenol-Formaldehyde Urea-Formaldehyde	Fabricator's name
Butacite	du Pont	Vinyl Acetal	Safety glass inner layer
Butvar	Shawinigan Products Corp.	Vinyl	
Catalin	Catalin Corp.	Phenol-Formaldehyde	Cast
Celluloid	Celluloid Corp.	Cellulose Nitrate	Sheets, rods, tubes
Cumar	Barrett Co.	Indene-Paracoumarone	For coatings
Dilecto	Continental Diamond Fibre Co.	Phenol-Formaldehyde	Laminated
Dulux	du Pont	Alkyd	Finished coating materials
Duraplex	Resinous Products & Chemical Co.	Alkyd	For coatings
Durez	Durez Plastics & Chemicals, Inc.	Phenol-Formaldehyde	Solids for coatings, laminating solutions, molding compounds
Durite	Durite Plastics	Phenol-Furfural	Molding compound
Esterol	Paramet Chem. Corp.	Alkyd	For coatings
Ethocel	Dow Chemical Co.	Ethyl Cellulose	
Exton	Weco Products Co.	Polyamide	Bristles
Formica	Formica Insulation Co.	Urea-Formaldehyde Phenol-Formaldehyde	Fabricator's name, laminated product
Formvar	Shawinigan Products Corp.	Vinyl	
Glyptal	General Electric Co.	Alkyds	Solids and solutions for coatings
Halowax	Bakelite Corp.	Chlorinated Naphthalene	Solids and liquids for impregnation
Harvel	Harvel Corp. Irvington Varnish & Insulator Co.	Cashew Nut Oil Derivative	For coatings
Haveg	Haveg Corp.	Phenol-Formaldehyde	Cast with filler for chemical equipment
Hemcoware	Bryant Electric Co.	Urea-Formaldehyde Phenol-Formaldehyde	Molded ware
Hercose AP	Hercules Powder Co.	Cellulose Aceto-Propionate	For coatings and molding
Hercose C	Hercules Powder Co.	Cellulose Aceto-Butyrate	For coatings and molding
Indur	Reilly Tar & Chemical Corp.	Phenol-Formaldehyde	Molding compound, laminating solution
Karolith	American Plastics Corp.	Casein	Sheets, rods

TRADE NAME	COMPANY	TYPE OF PLASTIC	REMARKS
Kodapak	Eastman Kodak Co.	Cellulose Acetate	Sheets for wrapping
Korolac	B. F. Goodrich Co.	Vinyl	Solutions for coatings
Koroseal	B. F. Goodrich Co.	Vinyl	Molded product
Lamicoid	Mica Insulator Corp.	Phenol-Formaldehyde Urea-Formaldehyde	Laminated product
Lewisol	J. D. Lewis, Inc.	Modified Phenol-Formaldehyde, Rosin Maleic Ester	Solids for coating
Lucite	du Pont	Acrylate	Molding compound, sheets, rods, tubes
Lumarith	Celluloid Corp.	Cellulose Acetate	Molding compound
Luxene	Bakelite Corp.	Phenol-Formaldehyde	Denture material
Marblette	Marblette Corp.	Phenol-Formaldehyde	Cast
Masuron	J. W. Masury	Cellulose Acetate	Molding compound
Melamac	American Cyanamid Co.	Melamine	Coating
Micabond	Continental Diamond Fibre Co.	Alkyd	Laminated mica
Micarta	Westinghouse Elec. & Mfg. Co.	Phenol-Formaldehyde Urea-Formaldehyde	Laminated product
Monsanto CA	Monsanto Chemical Co.	Cellulose Acetate	
Monsanto CP	Monsanto Chemical Co.	Phenolic	Cast
Monsanto NC	Monsanto Chemical Co.	Nitrocellulose	
Neoprene	du Pont	Butadiene Derivative	Synthetic rubber
Nevindene	Neville Co.	Coumarone-Indene	For coating
Nixonite	Nixton Nitration Works	Cellulose Acetate	Molding compound
Nixonoid	Nixton Nitration Works	Cellulose Nitrate	Sheets, rods, tubes
Nylon	du Pont	Polyamide	Fiber
Panelyte	Panelyte Corp.	Phenol-Formaldehyde	Laminated product
Paradura	Paramet Chemical Corp.	Phenol-Formaldehyde	Solids for coatings
Paranol	Paramet Chemical Corp.	Modified Phenol-Formaldehyde	Solids for coatings
Paraplex	Resinous Products & Chemical Co.	Alkyd	Solutions for coatings
Parlon	Hercules Powder Co.	Chlorinated Rubber	For coatings
Petrex	Hercules Powder Co.	Alkyd from Terpene-Maleic Anhydride	For coatings
Phenac	American Cyanamid Co.	Modified Phenol-Formaldehyde	For coatings
Phenolite	National Vulcanized Fibre Co.	Phenol-Formaldehyde Urea-Formaldehyde	Laminated product
Plaskon	Plaskon Corp.	Urea-Formaldehyde	Molding compound
Plastacele	du Pont	Cellulose Acetate	Molding compound, sheets, rods, tubes
Plexiglas	Rohm & Haas	Acrylate	Sheets
Plexigum	Rohm & Haas	Acrylate	Solution for safety
Pliofilm	Goodyear Tire & Rubber Co.	Isomerized Rubber	Molding compound

TRADE NAME	COMPANY	TYPE OF PLASTIC	REMARKS
Pliolite	Goodyear Tire & Rubber Co.	Isomerized Rubber	Solid for coatings
Protectoid	Celluloid Corp.	Cellulose Acetate	Sheets for wrapping
Redmanol	Bakelite Corp.	Phenol-Formaldehyde	Cast, molding compound
Resibend	Bakelite Corp.	Phenol-Formaldehyde	Impregnated paper for bonding plywood
Resinox	Monsanto Chemical Co.	Phenol-Formaldehyde	Molding compound
Resoglaz	Advance Solvents & Chem. Co.	Polystyrene	Molding compound, solids for coatings
Resovin	S. S. White Dental Mfg. Co.	Vinyl	Denture material
Revolite	Atlas Powder Co.	Phenol-Formaldehyde	Coated cloth
Rezyl	American Cyanamid Co.	Alkyd	Solids and solutions for coatings
Saran	Dow Chemical Co.	Vinylidene Chloride	For molding and extrusion
Spauldite	Spaulding Fibre Co.	Phenol-Formaldehyde	Laminated product
Styron	Dow Chemical Co.	Polystyrene	
Sylphrap	Sylvania Industrial Corp.	Cellulose	Transparent film
Sylvanic	Sylvania Industrial Corp.	Ethyl Cellulose	Solid for sizing
Syntex	Devoe & Raynolds Co.	Alkyd	Solids and solutions for coatings
Synthane	Synthane Corp.	Phenol-Formaldehyde	Laminated product
Teglac	American Cyanamid Co.	Rosin Modified Alkyd	Solid for coatings
Tego Glue Film	Resinous Products & Chemical Co.	Phenol-Formaldehyde	Adhesive for plywood
Tenite	Tennessee Eastman Corp.	Cellulose Acetate	Molding compound, sheets
Textolite	General Electric Co.	Phenol-Formaldehyde	Molded and laminated material
Thiokol	Thiokol Corp.	Alkene Polysulphide	Molding compound and rubber substitute
Tornesit	Hercules Powder Co.	Chlorinated Rubber	Solid for coatings
Uformite	Resinous Products & Chemical Co.	Urea-Formaldehyde	Solutions for coatings and laminating
Victron	U. S. Rubber Products, Inc.	Polystyrene	Molding compound, solid for coatings
Vinal	Carbide & Carbon Chem. Corp.	Vinyl	For safety glass
Vinylite	Carbide & Carbon Chem. Corp.	Vinyl	Molding compound, solids for coatings
Viscoloid	du Pont	Cellulose Nitrate	Sheets, rods, tubes
Vulcoid	Continental Diamond Fibre Co.	Phenol-Formaldehyde	Laminated product

READING LIST

GENERAL

Ellis, C., "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York (1935).

Morrell, R. S. and others, "Synthetic Resins and Allied Plastics," Oxford University Press, New York (1937).

Rahm, L. F., "Plastic Molding," McGraw-Hill Book Co., Inc., New York (1933).

Scheiber, J. and Sändig, K., "Artificial Resins," translated by Fyleman, E., Pitman Publishing Co., New York (1931).

U. S. Tariff Commission, "Synthetic Resins and Their Raw Materials," Government Printing Office, Washington (1938).

"British Plastics" (monthly), Plastics Press, Ltd., London.

"Modern Plastics" (monthly), Breskin Publishing Corp., New York. (Annual catalog and directory contains a trade name list and extensive data on properties of plastics.)

CHEMISTRY OF PLASTICS

Burk, R. E., Thompson, H. E., Weith, A. J. and Williams, I., "Polymerization," A. C. S. Monograph 75, Reinhold Publishing Corp., New York (1937).

Carothers, W. H., "Polymerization," Chem Rev. *8*, 353 (1931).

Houwink, R., "Elasticity, Plasticity and Structure of Matter," Cambridge University Press (1937).

Standinger, H., Mark, H., Carothers, W., Houwink, R., Meyer, K. H. and others. "The Phenomena of Polymerization and Condensation," Trans. Faraday Soc. *32* (1936).

MODIFIED CELLULOSE PLASTICS

Clewell, J. H. and Paine, H. W., "Pigments, Lakes and Other Coloring Materials in Plastics" (Nitrocellulose and acetate), Ind. Eng. Chem. *29*, 750 (1937).

Cohoe, W. P., "Permanent Sizing with Alkali Soluble Celluose Ethers," Chem. & Ind. *56*, 381 (1937).

Fordyce, C. R. and Meyer, L. W. A., "Plasticizers for Cellulose Acetate and Cellulose Acetate Butyrate," Ind. Eng. Chem. *32*, 1053 (1940).

Jenkins, W. J., "Plastics with Special Reference to Cellulose Materials," British Plastics Yearbook, p. 108 (1934).

Kirkpatrick, S. D., "Building an Integrated Industry in Times of Depression" (Cellulose acetate), Chem. & Met. *40*, 236 (1933).

Koch, W., "Properties and Uses of Ethylcellulose," Ind. Eng. Chem. *29*, 687 (1937).

Lorand, E. J., "Cellulose Ethers, Variation of Physical Properties with Composition," Ind. Eng. Chem. *30*, 527 (1938).

White, H. C., "How to Avoid Difficulties in Cellulose Acetate Production," Chem. & Met. *41*, 307 (1934).

Worden, E. C., "Technology of Cellulose Ethers," 5 volumes, Worden Laboratory and Library, Millburn, N. J. (1933).

OTHER MODIFIED NATURAL MATERIALS

Brother, G. H., "Casein Plastics," Ind. Eng. Chem. *32*, 31 (1940).

Brother, G. H., and McKinney, L. L., "Protein Plastics from Soybean Products," Ind. Eng. Chem. *31*, 84 (1939).

Harvey, M. T. and Caplan, S., "Cashew Nut Shell Liquid," Ind. Eng. Chem. *32*, 1306 (1940).

Howard, G. C., "Lignin Plastics Created from Pulp Liquor Wastes," Modern Plastics, Vol. 17, No. 3, 96 (November, 1939).

PHENOLIC RESINS

Anon., "Producing Phenolic Resins for Molding," Chem. & Met. *42*, 661 (1935).

Anon., "Phenolic Resin Production," Chem. & Met. *46*. 519 (1939).

Anon., "Laminating Phenolic Plastic," Chem. & Met. *47*, 183 (1940).
Baekeland, L. H. and Bender, H. L., "Phenol Resins and Resinoids," Ind. Eng. Chem. *17*, 225 (1925).
Granger, F. S., "Condensation of Phenols with Formaldehyde"
I. Formation of Phenol Alcohols, Ind. Eng. Chem. *24*, 442 (1932).
II. Resinification of Phenol Alcohols, Ind. Eng. Chem. *29*, 860 (1937).
III. Direct Resinification, Ind. Eng. Chem. *29*, 1125 (1937).
IV. Variation of Phenols, Ind. Eng. Chem. *29*, 1305 (1937).

UREA AND MELAMINE RESINS

Hodgins, T. S., Hovey, A. G. and Ryan, P. J., "Urea-Formaldehyde Film-Forming Compositions," Ind. Eng. Chem. *32*, 334 (1940).
Hodgins, T. S., Hovey, A. G., et al., "Melamine-Formaldehyde Film-Forming Compositions," paper presented at meeting of A. C. S., Detroit, Sept. 10, 1940.
McClellan, P. P., "Melamine Preparation," Ind. Eng. Chem. *32*, 1181 (1940).
Stockfisch, H. E., "Urea Resin Varnish for Laminating," Chem. & Met *41*, 302 (1934).

ALKYD RESINS

Kienle, R. H., "Observations as to the Formation of Synthetic Resins," Ind. Eng. Chem. *22*, 590 (1930).
Kienle, R. H. and Ferguson, C. S., "Alkyd Resins as Film-Forming Materials," Ind. Eng. Chem. *21*, 349 (1929).

VINYL, ACRYLATE AND POLYSTYRENE RESINS

Blaikie, K. G. and Crozier, R. N., "Polymerization of Vinyl Acetate," Ind. Eng. Chem. *28*, 1155 (1936).
Curme, G. O., Jr., and Douglas, S. D., "Resinous Derivatives of Vinyl Alcohol," Ind. Eng. Chem. *28*, 1123 (1936).
du Pont Company Staff, "Methacrylate Resins," Ind. Eng Chem. *28*, 1160 (1936).
Goggin, W. C., "New Vinylidene Chloride Resins," News Edition A. C. S. *18*, 923 (1940).
Klein, L. and Pearce, W. T., "Polymerized Acrylic Acid Derivatives," Ind. Eng. Chem. *28*, 635 (1936).
Neher, H. T., "Acrylic Resins," Ind. Eng. Chem. *28*, 267 (1936).
Skirrow, F. W., "Vinyl Esters: Their Origin, Transformations, and Applications," Chem. & Ind. *57*, 1117 (1938).
Weith, A. J., Turkington, V. H. and Allen, I., Jr., "Polystyrene," Ind. Eng. Chem. *32*, 1301 (1940).

HYDROCARBON RESINS

Carmody, W. H., Sheehan, W. and Kelly, H., "Synthetic Resins for Coal-Tar Hydrocarbons," Ind. Eng. Chem. *30*, 245 (1938).
Frolich, Per K. and others, "Plastics and Resins from Hydrocarbons," Ind. Eng. Chem. *32*, 293 (1940).
Thomas, C. A. and Soday, F. J., "Resins from Cracked Distillates," Ind. Eng. Chem. *28*, 1174 (1936).

MISCELLANEOUS

Houwink, R., "Resins as Colloids," Brit. Plastics Yearbook, p. 51 (1935).
Lee, J. A., "Synthetic Resins for Surface Coatings," Chem. & Met. *47*, 334 (1940).
Merrill, L. K., "Thermal Efficiency in Injection Molding," Modern Plastics *18*, No. 3, p. 65 (November, 1940).
Snow, R. D. and Frey, F. E., "Reaction of Sulfur Dioxide with Olefins," Ind. Eng Chem. *30*, 176 (1938).
Weidlein, E. R., "History and Development of Laminated Safety Glass," Ind Eng. Chem. *31*, 563 (1939).

CHAPTER 32

EXPLOSIVES

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INTRODUCTION

An explosive is a material which, on proper initiation, becomes rapidly converted into products of greatly increased volume. Ordinarily the original material is solid or liquid in form, whether a single chemical compound or a mixture, and becomes gasified during the explosion reaction. The conversion to gaseous form is accompanied by intense heat, which increases the volume of gases still more. The rapid expansion taking place at the time of explosion gives the accompanying disruptive or propelling effect.

Explosives are destructive in action when they decompose within a completely confined space or in close proximity to other objects. If this decomposition takes place inadvertently, the results may be disastrous. When, however, predetermined amounts of explosives are used under controlled conditions of time and place, they may become constructive agents for accomplishing definite objectives. By such control of their disruptive power, explosives function in blasting ores of iron and other metals, breaking down coal, mining salt, quarrying limestone for use in road construction, and in performing a multitude of useful tasks.

POTENTIAL ENERGY OF EXPLOSIVES

Explosives are so disruptive in effect that they are commonly reputed to be highly superior reservoirs of energy. The fact is that, pound for pound, commercial blasting explosives contain considerably less potential energy than, for example, liquid fuels. The shattering action of explosives comes from the extremely rapid conversion of solids or liquids to gaseous products; in other words from the oxidation of carbon and hydrogen to carbon dioxide and water vapor. In the case of explosives, the oxygen for this combustion is a chemically combined portion of the material, while with fuels the oxygen of the air is utilized. With most explosives also, there is a considerable content of inert material not convertible into gaseous products.

The explanation of the effectiveness of explosives comes in the almost instantaneous release of the pent-up energy. While the combustion of fuels is a relatively slow procedure, the progress of which can be followed by the eye, the decomposition of explosives takes place at tremendous speed. Black powder is considered a slow explosive, but even this has a velocity of combustion, when shot in long cylindrical columns, upward of around 1000 feet per second. The higher velocity dynamites, on the other hand, detonate at rates of between 5000 and 20,000 feet per second.

Data are given in Table 1 to show comparatively the temperatures attained theoretically in the combustion of fuels and explosives, the volume of gas produced, both at the maximum temperature and when cooled to 0°, and the energy released per pound of material employed. Because of various assumptions made, the calculated values must be taken as only approximate.

The volume of hot gases is greater than that of the cold gases both because of thermal expansion and because of the fact that water, which is in liquid state in the cold gases, is in vapor form in the hot gases and has been assumed to follow the gas laws.

TABLE 1—ENERGY VALUES OF EXPLOSIVES

Material	*Theoretical Temp. Combustion ° C.*	*Volume of Gases Cu. ft. /100 lbs.*		*Potential Energy*
		Cold	*Hot*	*Ft. lbs./lb.*
Gasoline	3900	2500	83,000	16,000,000
Nitroglycerin	3150	750	14,400	2,050,000
40% Straight dynamite	2620	560	9,100	1,520,000
Black powder	2350	514	5,200	958,000

PROPERTIES OF EXPLOSIVES

In peace times the explosives industry is chiefly concerned with commercial blasting explosives, and the standardization and control of their properties are of prime importance. This is particularly true of dynamites. Since these must be applied to all kinds of blasting work, a great many different types must be designed and their properties must be varied widely, to adapt them to do their work effectively.

Strength and Velocity—The two properties which are most important in assuring the proper execution of an explosive in blasting work are strength and velocity. Probably it is a combination of the two properties which determines the shattering effect. This combined effect has sometimes been termed "brisance." Strength is the property on which explosives are graded primarily, and this may be considered to depend on the gas pressure developed from a given weight or volume of material. Velocity denotes the rate at which the effective strength is developed. Obviously, very hard rock can be blasted down only by a high strength explosive and by one which possesses high velocity of detonation. For softer rock and material offering less resistance, lower strengths and particularly lower velocities give more satisfactory results.

Sensitiveness—Sensitiveness to propagation is a property which must be accurately controlled and maintained, as failure to propagate will mean the presence of a certain amount of unexploded material in the borehole, a very hazardous condition. Other properties, such as fumes and water resistance, are likewise important and are matters of routine test by manufacturers of explosives.

Tests—The final judgment as to the efficiency of an explosive must be based on its execution in actual blasting work. Laboratory and proving ground tests have been developed, however, which allow a good preliminary evaluation.[1] Propellent explosives such as smokeless powder, are given very extensive tests, particularly with respect to ballistic properties and stability under storage conditions.[2] It is essential that the explosive give the desired velocity to the projectile, but that this pressure shall not be developed so rapidly as to burst the gun barrel. Because of the fact that smokeless powder may be stored for years, it is important that there be no deterioration in quality and properties over this period.

Military explosives of the disruptive type used for shell filling and like purposes, TNT for example, are tested mainly for purity and freedom from contamination. Melting point tests and determinations of percentages insoluble in certain solvents, acidity, nitrogen content, amount of ash are the important criteria for such compounds.[3]

Role of Nitrogen in Explosives[4]—The chemistry of explosives is closely bound up with that of nitrogen compounds. The alkali nitrates are the oxidizing agents used in black powder compositions, while ammonium nitrate is perhaps the most important ingredient of dynamites, functioning both as a strength producer and as oxygen supplier. Practically all the high explosive compounds important in the commercial and military fields contain nitrogen.

The explanation for the adaptability of the nitrogen compounds as explosives seems to lie in their degree of instability and sensitiveness to shock. A practical explosive compound must be sufficiently stable to permit safe handling and storage, yet must be capable of almost instantaneous decomposition when subjected to impact of definite intensity. In certain nitrogen compounds, the strength of the bond linking the nitrogen atoms to adjacent atoms is such as to give a practical sensitiveness. Since explosive decomposition is essentially a combustion process, the organic nitrates and nitro-compounds fit well into the requirements. Nitrogen itself is usually found in elemental form in the products of explosion, while the attached oxygen is available for the combustion of the carbon and hydrogen present. As additional NO_2 groups are introduced into organic formulas, the sensitiveness of the nitrated compound increases.

MANUFACTURE OF EXPLOSIVES

Black Powder[5]—The story of black powder goes back many centuries, so far back that its origin is a matter of tradition. While some of the very early investigators may have experienced the explosively violent action of intimate mixtures of ingredients similar to those in black powder, its authentic history appears to have begun in the 14th century, when it was first used in firearms.

[1] Munroe, C. E. and Tiffany, J. E., "Physical Testing of Explosives at the Bureau of Mines Explosives Experiment Station," U. S. Bureau of Mines, Bulletin 346 (1931); Gillie, B. A., J. Chem. Education *5*, 1213-1223 (1928).

[2] Tschappat, W. H., "Textbook of Ordnance and Gunnery," Wiley (1917); Marshall, A., "Explosives," second edition, Vol. 1, pp. 289-335, Blakiston (1917).

[3] Taylor, C. A. and Rinkenbach, W. H., "Explosives: Their Materials, Constitution and Analysis," U. S. Bureau of Mines, Bulletin 219 (1923).

[4] Sidgwick, N. V., "Organic Chemistry of Nitrogen," second edition, Clarendon Press (1937).

[5] Guttmann, O., "Manufacture of Explosives," Vol. 1, p. 24, Whittaker & Co. (1895); Marshall, A., "Explosives," second edition, Vol. 1, p. 53, Blakiston (1917).

Berthold Schwartz is frequently given credit for the invention of firearms and for the use of black powder or gunpowder as the propellent charge.

Black powder started out as gunpowder and is said to have been first used for military purposes at the battle of Crécy in 1346. It was not until 1627 that this powder is known to have been used in mining, in Hungary. Gunpowder remained the accepted name for black powder down practically to the end of the 19th century, regardless of the method of use.

Black powder is an excellent explosive for the blasting down of coal, as its low velocity gives it a slow, heaving action that does not shatter the coal unduly. For safety reasons, however, black powder cannot be used in mines in which inflammable gases are present or suspected, as its long flame of considerable duration makes it more hazardous than the higher velocity safety dynamites designated as "permissible" explosives.

Composition. The composition of black powder has changed very little over the course of many centuries. An English powder of the year 1350 is given the composition of 66.6% saltpeter, 11.1% sulfur, and 22.3% charcoal, while a French powder of 1650 had these ingredients present in the respective amounts of 75.6%, 10.8%, and 13.6%. This latter composition would be satisfactory for a present-day powder. Where potassium nitrate was formerly used exclusively as oxidizing agent, it has been replaced in American black blasting powders by sodium nitrate. Because of the higher weight percentage of oxygen in the latter, about 2% less of the sodium salt may be desirably used than of the potassium, for comparable results.

Black powder, therefore, is essentially an intimate mixture of (1) sodium or potassium nitrate, (2) sulfur and (3) charcoal, in the approximate compositions given above. The replacement of potassium nitrate took place in American powders about the middle of the 19th century. At the present time, all American black blasting powders contain sodium nitrate, which is considerably cheaper as an ingredient than potassium nitrate and possesses greater potential strength. It has the disadvantage of being hygroscopic, hence potassium nitrate is retained in black sporting powders and in fuse powders, where uniformity of burning and of moisture content is essential.

Raw Materials for Black Powder. Sodium nitrate is the ingredient used in much the largest amount in American black powder. Until the last few years, this material was obtained almost entirely by importation from Chile. Now synthetic sodium nitrate has largely replaced the natural product, and is available free from impurities.

Charcoal is one of the most important ingredients and one that requires most careful control as to uniformity, freedom from undesirable impurities and general excellence. Any marked deviation from the standard in the properties of the charcoal will affect the properties of the finished powder. Charcoal may be obtained from various non-resinous woods, for example, maple, and results from a charring and a dry distillation process. (See Chapter 17, Wood Distillation Industry.)

Sulfur is available in the United States in a high state of purity, the only specifications generally being that it shall be free from grit and acidity.

Decomposition Reactions of Black Powder. Black powder comprises a combustion mixture of oxidizing and reducing agents. Assuming a black powder composition of 73% $NaNO_3$, 13% sulfur, and 14% charcoal, the following reaction would represent the approximate molecular proportions present:

$$2NaNO_3 + S + 3C = Na_2S + N_2 + 3CO_2$$

Actually the reaction is much more complex. Some formation of sodium sulfate and sodium carbonate will take place. Those familiar with black powder blasting know also that some carbon monoxide is always formed. Under conditions of use in mining operations, it is noted that there is substantially no formation of free hydrogen sulfide, this gas being fixed by the alkali element present. Black powder is not completely gasified on explosion, and in the reaction shown the solid residue in the reaction products represents about ⅓ of the total by weight.

The sulfur in the black powder composition is not simply an alternative combustible material. It appears to have a characteristic action in facilitating ignition of the powder and promoting combustion.

Manufacturing Operations. The manufacture of black powder comprises a number of steps or mechanical operations which are carried out in separated buildings for safety reasons. These operations briefly are as follows:

1. Preliminary pulverizing of ingredients
2. Incorporation under wheels
3. Pressing
4. Cutting of press cake
5. Granulation, or "corning"
6. Drying and glazing
7. Packing

Pulverizing. The ingredients are prepared initially in a state of fine subdivision. Ordinarily the sulfur and charcoal are first ground together in a drum containing steel balls, while the nitrate is disintegrated either in a ball mill or under steel crusher rolls. Care is taken at the end of this preliminary grinding that the materials are free from foreign particles of matter, particularly of a metallic nature, and this is accomplished by screening or passing over a magnetic separator.

Wheeling. The finely divided ingredients are given a more intimate and thorough incorporation in the "wheeling" operation. The materials are introduced into a cylindrical bowl, having ordinarily a metal bed plate and wooden side walls. Within this bowl two heavy broad-edged runners or wheels connected by a short horizontal axis rotate continuously. (See Crushing and Grinding in Chapter 2, The Unit Operations.) These wheels may be over 7 feet in diameter and around 2 feet in width of rim. At the same time the wheels revolve slowly about their own axes. The wheels are preferably driven from below and have a certain amount of clearance above the bed plate. Metal plows are arranged in front of each wheel to move the mixture from the sides and centers of the bowl under the path of the wheels. Water is added to the charge to ensure the proper final moisture content. The operation is continued for several hours, at which time very intimate incorporation has resulted. The product of this operation is designated "wheel cake."

Pressing. The wheeled and incorporated mixture is subjected to the action of crusher rolls or other devices for breaking up the lumps and is then introduced into hydraulic presses where pressures of over 1200 pounds per square inch may be applied. The pressing operation gives a hard mass, designated "press cake," in which there is no longer any tendency for segregation of the separate ingredients.

Cutting and Granulation. The pressed cake is broken up into pieces of about 1 to 2 inches in diameter and passes to the "corning" or granulating operation, in which the fragments of powder are caused to go through consecutive sets of steel crusher rolls, provided with teeth. The powder is gradually reduced to grains of the desired size, and screens beneath the rolls separate the material into the various desired granulations. The corning operation is one of the most hazardous of black powder steps, but in all stages of black powder manufacture care is taken that no workers are present in the buildings while the powder is in course of treatment.

Drying, Glazing and Packing. If granular black powder is to be produced, the "green grain" powder from the corning operation is run into the revolving drying and glazing drums, which may have a length of 12 feet and a diameter of 4 feet. The powder is in these drums for several hours, during which time the grains have their edges rounded off. Heated air is blown in and the moisture content is reduced to about 0.5%. A small amount of graphite is added during the latter part of the rotation of the drum to glaze the particles and give the grains a polished surface. The finished powder is sorted by means of screens into the desired granulations and is packed in metal kegs, usually holding 25 pounds each.

Pellet Powder. Black powder is now prepared in two commercial forms, (1) in the form of free-flowing grains and (2) in the form of pellets or cylindrical columns enclosed in a paper wrapper. The preparation of the granular powder has been described in the preceding paragraph.

Pellet powder originated in Europe and was introduced by American manufacturers about 1925. In its usual form, it consists of cylindrical agglomerated pellets 2 inches in length and of diameters up to 2½ inches, each pellet having a longitudinal center hole. Ordinarily four such pellets are placed end to end and enclosed in a paper wrapper to form a cartridge 8 inches in length.

In the manufacture of pellet powder, the same materials are taken as for granular powder. The "green grain" powder resulting from the "corning" step is commonly used and is fed from a hopper into a die or hole in a charging block of the diameter desired for the pellet. A center pin is introduced previous to pressing of the powder and two plungers compress the powder from above and below respectively, until the desired density has been obtained. About 4.5% of water is present in the powder being compressed. The pressed pellets are transferred from the press house to another building, where they are dried on trays by means of hot air, to a moisture content of about 0.5%. The finished pellets are wrapped in paper, waterproofed by dipping in paraffin, and packed in 25- or 50-pound boxes.

Pellet powder is in a form very convenient for use and very adaptable for accurate measurement of the desired explosive charge. It is safer to handle than granular powder because no pouring of the powder is necessary and spilling is unlikely. In the presence of inflammable gases, however, it is no safer for use in coal mining than the granular form, since it possesses the same long-flame characteristics on combustion.

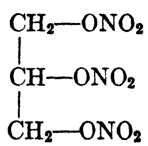
Potassium Nitrate Powders. The blasting powders already described have contained sodium nitrate as oxidizing ingredient. For certain types of use, fuse powder for example, it is desirable to use potassium nitrate as the oxidizing agent.

Black propellent powder for use in firearms, though largely displaced by smokeless powder, is likewise a potassium nitrate composition, since uniformity of pressure development is an absolute requirement here.

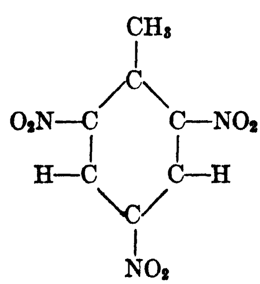
THE ROLE OF NITRATION

In black powder the nitrogen of the explosive is supplied as an intimate mechanical mixture. With the development of the studies of chemical reactions it was found that many explosives could advantageously be made by the incorporation of nitrogen in organic molecules. Hence, nitration has assumed a role of paramount importance in this field (see Chapter 3, The Organic Unit Processes.)

Nitrates and Nitro-Compounds—Two types of organic high explosive compounds are obtained by the action of nitric acid on organic materials, i.e., by nitration. These are (1) the organic nitrates or nitric esters and (2) the nitro-compounds. Both of these types contain one or more NO_2 groups replacing hydrogen atoms of the unnitrated compounds. In the case of the nitric esters, the NO_2 group is attached to an oxygen atom, while in the nitro-compounds it is linked to a carbon atom. The nitric esters are obtained by the nitric esterification of alcohols, while the nitro-compounds are ordinarily prepared by the nitration of hydrocarbons or their derivatives. Nitroglycerin is an example of the nitric esters,



As is apparent from the above formula, the name nitroglycerin is a misnomer, the correct designation being glyceryl trinitrate. Trinitrotoluene (TNT), on the other hand, is a true nitro-compound:



In addition to the above types of nitrated products, the primary detonating compounds, commonly used in blasting caps as initiating explosives, are likewise nitrogen-containing compounds. Mercury fulminate has the formula $(CNO)_2Hg$, while lead azide is PbN_6.

Nitration Processes[6]—Nitration is the term commonly employed to designate the action of nitric acid on organic compounds whereby the nitro group (NO_2) is introduced, usually in place of a hydrogen atom. Thus it includes both the preparation of the true nitro-compounds, where the NO_2 group is attached to a carbon atom, and esterification by means of nitric acid.

The nitration agent in commercial operations is ordinarily one of the following forms:

1. Mixed acid, comprising nitric acid associated with a dehydrating agent such as sulfuric acid.[7]
2. Concentrated nitric acid, for example, around 95%.[8]
3. Nitrogen tetroxide, preferably in vapor form.[9]

Nitration products are important in organic industries generally and particularly as dye intermediates. (See Chapter 28, Manufacture of Intermediates and Dyes.) Many of such nitro-compounds are not explosive compounds, having perhaps one or two nitro groups in their formulas. Generally it is the compounds having three or more nitro groups that are important as explosives, though ethylene glycol dinitrate is a conspicuous exception. Thus the mononitrophenols and mononitrotoluenes are lacking in explosive properties, but are useful as dye intermediates. The corresponding dinitro-compounds are relatively insensitive explosive compounds, while trinitrophenol (picric acid) and trinitrotoluene are outstanding explosive compounds. The lower nitro-compounds are readily obtained by treatment of the starting material with low strength nitric acid, while the compounds containing three or more nitro groups require a higher nitric concentration in the nitration acid, or higher temperature treatment. The replacement of hydrogen by a nitro group results in the formation of water as a reaction product:

$$R - H + HO - NO_2 \rightarrow R - NO_2 + H_2O$$

Hence the presence of sulfuric acid or other dehydrating agent in the mixed acid helps maintain a high concentration of nitric acid.

EXPLOSIVES MADE BY NITRATION

Manufacture of Nitroglycerin[10]—Nitroglycerin is the ingredient which, from the beginning of the dynamite industry, has given such explosives their characteristic high velocity, as distinguished from low-velocity black powder, the commercial blasting powder previously in use. Nitroglycerin is obtained by the action of nitric acid on glycerin:

[6] Groggins, P. H., "Unit Processes in Organic Synthesis," second edition, p. 1, McGraw-Hill Book Co. (1938).

[7] Naoum, P., "Nitroglycerin and Nitroglycerin Explosives," American translation by E. M. Symmes, p. 51, Williams & Wilkins Co. (1928).

[8] Naoum, P., ibid., p. 244 (PETN).

[9] Wilhelm, R. H., U. S. Patent 2,109,873 (March 1, 1938) (Aromatic Nitro-Compounds).

[10] Naoum, P., "Nitroglycerin and Nitroglycerin Explosives," American translation by E. M. Symmes, Williams & Wilkins Co. (1928); Groggins, P. H., "Unit Processes in Organic Synthesis," second edition, p. 583.

$$\begin{array}{l} CH_2OH \\ | \\ CH \cdot OH \\ | \\ CH_2OH \end{array} + 3HNO_3 \rightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array} + 3H_2O$$

It will thus be seen that nitroglycerin is not a true nitro-compound, but actually is a nitric ester, glyceryl trinitrate.

Nitroglycerin resembles glycerin in appearance, and is a white to yellowish, viscous liquid, having a specific gravity of 1.6.

The raw materials employed in the manufacture of nitroglycerin are glycerin, sulfuric acid, and nitric acid. So-called dynamite glycerin is a high-grade product of around 99% purity, having a specific gravity of about 1.262 and a high viscosity. The mixed acid used in the nitration has a composition of about equal parts of sulfuric acid and nitric acid, with possibly a slight excess of the former, and is substantially free from water. For information on the manufacture of these raw materials see Chapters 7, 8 and 42.

In carrying out the nitration, the proper amount of mixed acid is introduced into the steel nitrating vessel, in which brine coils serve to cool the acid. (See Chapter 2, The Unit Operation.) After agitation has been started, glycerin is added at such a rate that the temperature rise is only moderate. The temperature range is maintained generally between 50° and 37° F. (10-3° C.). Nitroglycerin itself may freeze at about 55° F. (12.8° C.) and its freezing in the nitrator would constitute a hazard, but various conditions present make operation safe at somewhat lower temperatures. Actually it is the practice to make low freezing or difficultly freezable nitroglycerin by nitrating, instead of glycerin alone, a solution in glycerin of ethylene glycol, diglycerin or other similar nitratable material. The nitrated product then is a solution in nitroglycerin of ethylene glycol dinitrate, tetranitrodiglycerin or other freezing point depressant. In addition to the formation of glyceryl trinitrate, therefore, one of the following reactions may be proceeding simultaneously in the nitrator:

$$\underset{\text{Ethylene Glycol}}{\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}} + 2HNO_3 = \underset{\text{Ethylene Glycol Dinitrates}}{\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}} + 2H_2O$$

$$\underset{\text{Diglycerin (polymerised glycerin)}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2\diagdown \\ \quad\quad O \\ CH_2\diagup \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + 4HNO_3 = \underset{\text{Diglyceryl Tetranitrate}}{\begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2\diagdown \\ \quad\quad O \\ CH_2\diagup \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array}}$$

The resulting nitroglycerin and spent acid, having a composition of about 76% H_2SO_4, 7% HNO_3, and 17% H_2O, are run from the nitrator into a separating vessel. In the course of about ¾ of an hour, the nitroglycerin and spent acid form separate layers, with the nitroglycerin on top and with a clear line between the two layers, which may be observed through a sight glass. Usually the separation into layers is hastened by the addition to the nitration mixture of a facilitating material such as a mixture of sodium fluoride and kieselguhr. The nitroglycerin is drawn off from the separator, given a preliminary water wash, and treated in the neutralizer with a weak solution of sodium carbonate during vigorous agitation to remove the last traces of acidity from the nitroglycerin.

It needs to be strongly emphasized that the manufacture of nitroglycerin is a hazardous operation, and one that should never be attempted by inexperienced persons. Such care is taken, however, in commercial production in the control of temperature, the purity of materials and the avoidance of dangerous practices that explosions are uncommon. If there is an unduly rapid rise of temperature in the nitrator, or if, for any reason, a nitration must be interrupted before completion, the entire charge is drowned, that is, dropped into an excess of water directly beneath the nitrator.

The yield is commonly calculated on the basis of glycerin as 100, and the theoretical yield would be 245; in practice, yields of around 230 are commonly obtained under best operating conditions. Charges of around 3000 pounds nitroglycerin and over are frequently obtained in one nitration.

In recent years, continuous processes for the nitration, separation, and washing of nitroglycerin have been adopted in a number of European plants.[11] These have replaced the former batch processes.

Nitrocellulose[12]—The nitration of cellulose follows the same principles as in the case of glycerin, namely the treatment of cellulose with nitric acid and the introduction of nitro groups in place of hydrogen atoms. Nitrocellulose, like nitroglycerin, is misnamed and actually is a nitric ester, cellulose nitrate. Its formation is shown by the following reaction:

$$C_6H_{10}O_5 + 3HNO_3 \rightarrow C_6H_7O_2(ONO_2)_3 + 3H_2O$$

In reality, the nitration reaction is much more complicated than this, as the size of the cellulose molecule is doubtless very much larger than indicated and should be written $(C_6H_{10}O_5)_n$. In the case of nitroglycerin, a single relatively pure product is formed. In the nitration of cellulose, on the other hand, a mixture of cellulose nitrates may be obtained, varying in nitrogen content and solubility in organic solvents, depending on the composition of the mixed acids and the conditions of nitration.

Prior to nitration, the cotton linters are purified by digestion under pressure with a dilute solution of caustic soda. This serves to reduce the content of vegetable oils, resins, and other removable impurities.

In one method of nitration, the purified cellulose is immersed in a mixed acid, having, for example, the approximate composition 63% H_2SO_4, 22% HNO_3,

[11] Gassner, O., Chem. Ztg. *57*, 201-2 (1933); Schmid, A. U. S. Patents 1,893,447, 1,901,003, 1,939,634, 1,946,414-5.

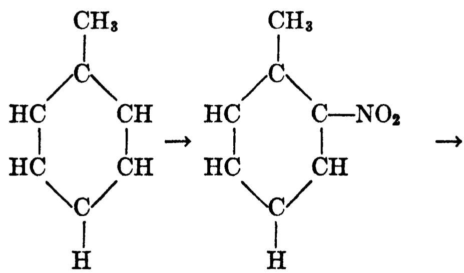
[12] Marshall, A., "Explosives," second edition, Vol. 1, p. 168, Blakiston (1917).

15% H_2O. It is common to nitrate 30 pounds of cotton as one charge for about 30 minutes, with agitation, using about 1500 pounds of mixed acid and maintaining a temperature of 30-35° C.

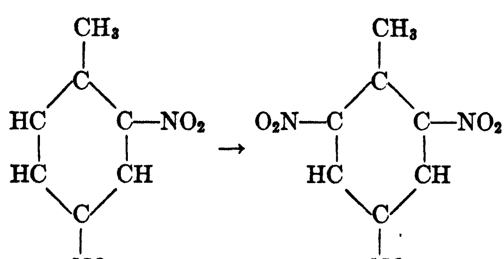
When nitration is complete, the nitrocellulose and the spent acid are run into a centrifugal wringer, which revolves slowly at first and then at a high speed of around 1100 RPM. This causes the separation of the acid, which can be sent to mixing tanks for fortification and subsequent re-utilization, or to the denitrator. The centrifuged nitrocotton, with its acid content, is drowned in an excess of water.

The purification treatment consists of a prolonged boiling in water, slightly acidified with sulfuric acid in order to break down unstable esters, a mechanical pulping treatment to reduce the length of the fibers, and an alkaline boiling (poacher) treatment to neutralize acid products, followed by several boilings in fresh water and finally a number of cold water washings.

Trinitrotoluene[13]—In the case of nitroglycerin and nitrocellulose, nitration is a one-step process, all the acid and the material for nitration being introduced during one operation. With trinitrotoluene (TNT), either a two-step or a three-step process is used, the former separating out the mono-nitro compound first, then going through the bi- and tri-stages in one step. The three-step process obtains in separate nitration stages, the mono-, di-, and trinitro-compounds, by successive action of one molecule of nitric acid on one molecule of toluene, or its nitration compounds, with simultaneous splitting off of water:



Toluene Mononitrotoluene



Dinitrotoluene Trinitrotoluene

The preparation of TNT is not as simple as the outline shown above indicates. Three isomeric forms of the mono-compound exist and all are formed in

[13] Smith, G. C., "Trinitrotoluenes and Mono- and Dinitrotoluenes," D. Van Nostrand Co. (1918); Colver, E. de W. S., "High Explosives," p. 170, D. Van Nostrand Co (1918); Marshall, A., "Explosives," second edition, p. 260, Blakiston (1917).

the mono-nitration, the ortho, meta- and para-compounds, having melting points of −10°, 16°, and 58° C., respectively. Six isomers are possible and known for the trinitro-compound. It is the formation of undesirable impurities, both isomeric and oxidation products, that makes the preparation of pure TNT a complicated operation. Commercial TNT consists principally of the 2-4-6-isomer, and the completely purified material melts at 80.8° C.

In the preparation of TNT in several nitration steps, stronger acids and higher temperatures are used during the contact of mixed acid and nitratable material as the higher stages of nitration are carried out. According to one process, the acid composition for the final nitration step is approximately 79.5% H_2SO_4, 17.8% HNO_3, and 2.7% H_2O.[14]

Other Nitration Procedures—In the three examples of nitration described, mixtures of sulfuric and nitric (mixed acids) have been employed as the nitration medium. While nitric acid is always the active reactant, various other procedures are frequently followed. In the preparation of picric acid from phenol,[15] the latter is commonly first treated with strong sulfuric acid to form phenol sulfonic acid, which is then converted to picric acid by treatment with strong nitric acid. In the case of pentaerythritol tetranitrate, Naoum [16] states that mixed acid is not suitable for the nitration, and he treats the pentaerythritol with acid having a content of around 99% HNO_3.

DYNAMITE

Dynamite may be defined as a commercial high explosive. This distinguishes it (1) from the solid organic high explosives which are used for military purposes and (2) from low velocity commercial explosives of the black powder type. There is no sharp line as to velocity which separates the high from the low explosives, but the distinction is often made between the two as detonating and deflagrating compositions. The dynamites or detonating explosives are exploded by means of the violent impulse from a blasting cap, while the deflagrating explosives are initiated by means of a flame. Sometimes the term dynamite has been limited to those commercial explosives which contain nitroglycerin, but this is not necessarily the distinguishing point in the United States. The relation between the various types of dynamite is shown by the diagram of Figure 1.

The invention of dynamite dates from 1866, when Alfred Nobel conceived the idea of mixing liquid explosive nitroglycerin with a highly absorbent material. In this way he obtained, in place of a liquid dangerous to transport and to handle, a solid composition relatively insensitive to ordinary shock, but capable of complete detonation by means of a blasting cap. Nitroglycerin had been discovered by Sobrero in 1846, twenty years earlier, but prior to Nobel had been of little practical value. The importance of Nobel's discovery to the advancement of civilized nations cannot be too strongly emphasized, and at the same time it should be realized that commercial dynamites are constructive tools. It

[14] "Thorpe's Dictionary of Applied Chemistry," Vol. 4, p. 468, Longmans, Green & Co. (1940).

[15] U. S. War Dept., "Military Explosives," Technical Manual No. 9—2900 (1940).

[16] Naoum, P., "Nitroglycerin and Nitroglycerin Explosives," American translation, p. 244, Williams & Wilkins (1928).

is this type of explosive which is the most important and the one to which the explosive companies devote the bulk of their equipment and efforts.

Ingredients of Dynamites—Unlike black powder, there is no standard composition for dynamite. Nitroglycerin, probably the most characteristic ingredient, may vary in percentage, for example, from 5 to 90%, and other ingredients may likewise vary widely, depending upon the properties desired in the finished explosive. Not only are there many ranges of composition, but also many types of dynamites, owing to the differing fields of application for such explosives where varied forms of blasting action are needed. A few of the most important ingredients of dynamite compositions will first be considered briefly.

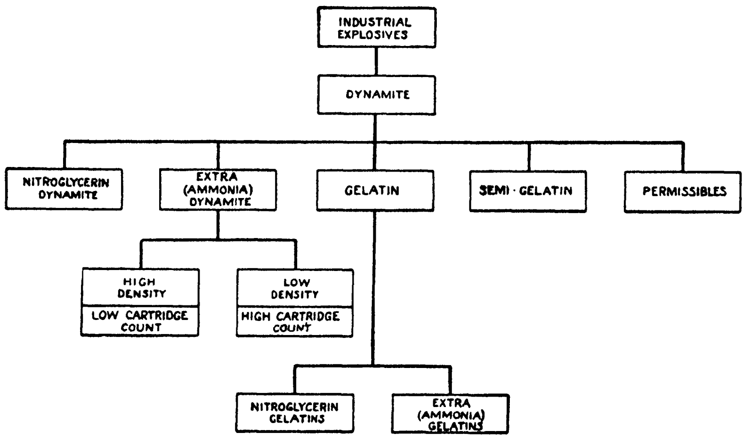


FIG. 1. General Classes of Industrial Explosives.

Nitroglycerin. This has long been the most important explosive ingredient of dynamite, though the trend for many years has been continuously toward a reduction of the nitroglycerin content. The preparation and properties of nitroglycerin have been discussed previously in connection with nitration processes.

Ammonium Nitrate. While nitroglycerin holds its place in popular estimation as the outstanding ingredient of dynamites, ammonium nitrate probably should be given first place. It does not possess the explosive properties of nitroglycerin, when used by itself and in small quantities, but it is a powerful explosive compound when once initiated by an external detonating impulse of sufficient magnitude and when used in considerable amounts. It has the advantages of being absolutely safe to handle under ordinary conditions, of being formed readily by the neutralization of nitric acid with ammonia, two universally available raw materials, and being low in cost. As will be seen in a later discussion of types of dynamites, ammonium nitrate has been increasingly used as an explosive salt to replace a portion of the nitroglycerin formerly used.

Combustible Absorbents. Nitroglycerin is retained in dynamite compositions by absorption by combustible ingredients. The absorbent first used by Nobel was kieselguhr, a siliceous material, which was excellently adapted for that purpose but which reduced the strength of the explosive, because it was itself inert in action and could not be converted into gaseous matter. Such combustible materials as wood pulp, starch, and various meals and low density fibers are now used. The choice of absorbent depends on various factors, such as nitroglycerin content of the dynamite, desired density, and sensitiveness, etc.

Sodium Nitrate. Sodium nitrate is used as an oxidizing agent in dynamite. It is desirable that the explosive be oxygen-balanced so that good fume properties and good blasting execution can be obtained. The combustible absorbents are very deficient in oxygen and the presence of sodium nitrate makes possible a balanced mixture, where all the carbon and hydrogen present will be burnt completely to carbon dioxide and water.

Freezing Point Depressants. Nitroglycerin has the disadvantage of a relatively high freezing point, about 55° F. (12.8° C.). Consequently dynamites containing it will freeze at comparatively mild winter temperatures. When in frozen condition, dynamite is unsatisfactory for use in blasting and must be thawed. Not only is the thawing operation time-consuming, but it is also extremely hazardous unless unusual precautions are taken.

The hazard of frozen dynamite has been removed by introduction into the nitroglycerin of materials which depress the freezing point sufficiently to ensure soft dynamite at the most extreme winter temperatures. At the same time the strength of the explosive is maintained, as the depressant used is itself a highly nitrated explosive compound. The usual procedure is not to dissolve the nitrated compound in nitroglycerin, but to nitrate the solution of the starting material in glycerin.

The introduction of ethylene glycol dinitrate or tetranitrodiglycerin as freezing point depressant has been discussed in connection with the nitration of glycerin. The co-nitration of glycerin with either ethylene glycol or diglycerin (polymerized glycerin) makes it possible to obtain a nitrated product of the desired extremely low-freezing properties. The amount of nitroglycol or tetranitrodiglycerin present in the nitroglycerin can be ascertained by determination of the nitrogen content of the product, as obtained on the nitrometer, together with the specific gravity.

Many other freezing point depressants have been proposed and used, for example, nitrochlorhydrins, nitrotoluenes, etc. No two such depressants are equivalents and, with a change of depressant, formulas must be adjusted so that the explosive properties of the finished explosive remain unaffected.

Ant-Acids (*Anti-Acids*). The presence of even a small amount of nitric acid has a slight decomposing effect on nitroglycerin. For this reason, it is the usual practice to include in the formulas of nitroglycerin dynamites a small amount of an acid-accepting material, or ant-acid. Calcium carbonate is commonly used for this purpose, in the amount of 0.5 to 1.0% of the total composition. The regulations of the Interstate Commerce Commission state that, for shipment by freight, explosives containing nitroglycerin or other liquid explosive ingredients, must contain an ant-acid material "in quantity sufficient to have the acid neutralizing power of an amount of magnesium carbonate equal to 1 per cent of the nitroglycerin."

Manufacture of Dynamite—The various types of dynamites require different treatments, but the general manufacturing procedure depends upon whether the explosive is (1) a gelatin dynamite or (2) a non-gelatinous dynamite. The operations will be described briefly under these two classifications, and are illustrated on the accompanying flow sheet, Figure 2.

Non-Gelatinous Dynamites—The manufacture of this class of pulverulent dynamites from the raw materials consists essentially of two operations, (1) mixing and (2) cartridging.

Mixing. The ingredients to be mixed come from two different sources. First, the nitroglycerin from the neutralizer is wheeled to the mixing house in rubber-tired, hand-operated "buggies," which have copper compartments adapted to hold weighed charges of nitroglycerin, in the amount desired for the dynamite mixing. The second ingredient comprises a mixture of material and is designated

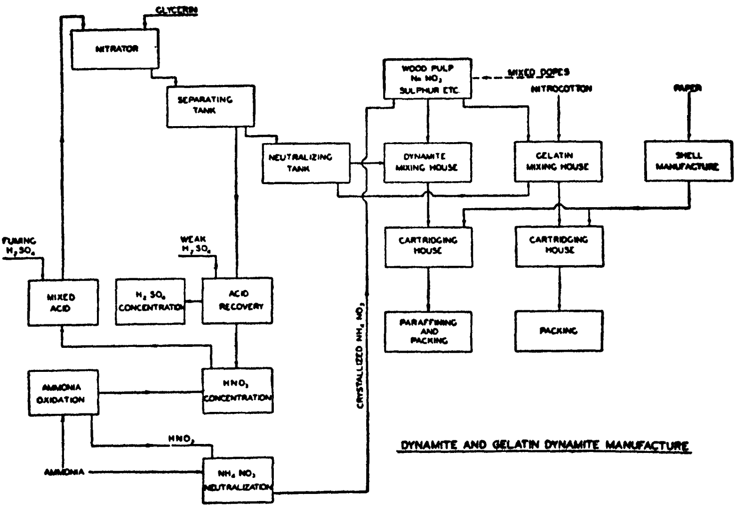


FIG. 2. Dynamite and Gelatin Dynamite Manufacture.

as "mixed dope." This mixture comes from what is known as the "dope house," where all the dry non-explosive ingredients, called for by the dynamite formula, have been mixed and screened. This mixture is likewise transported to the mixing houses in the required amount.

The mixing vessel ordinarily consists of a circular wooden bowl or trough about 7 feet in diameter and less than 2 feet deep. The bottom of the bowl may be covered with hard rubber. The mixing device consists of two large wooden wheels, preferably rubber-covered, which operate on the edge-runner principle.

When a mixing is to be made, the "dopes" are emptied into the mixing bowl and levelled, and the nitroglycerin is poured from the buggy over the top of the dopes by means of a rubber hose. The mixing wheels are then started, two hard rubber plows following the wheels, one serving to move material from the inside of the bowl under one wheel while the other plow throws the dynamite from the outside edge of the bowl under the other wheel. Between 5 and 10 minutes is ordinarily sufficient mixing time. Mixings of around 1,000 pounds of dynamite are commonly made at one time.

Cartridging. The mixed dynamite is usually of a dry, powdery nature and is transported in barrows to the cartridging or punching house. Here it is loaded into preformed, cylindrical paper shells, open at one end of any desired diameter from 7/8 inch up, and ordinarily about 8 inches in length. By means of special machines, the dynamite is packed to the desired density in the paper cartridge, and the open end of the cartridge is crimped down tightly. While a standard size of dynamite cartridge is 8 inches long by 1¼ inches in diameter, the cartridges may be as large as 7 inches in diameter by 24 inches in length. The sticks are packed in wooden boxes for shipment.

The cartridged dynamite may be protected from moisture penetration, if necessary, by coating with paraffin.

Gelatin Dynamites—The manufacture of gelatin dynamites includes both operations described under the non-gelatinous dynamites, but with different types of equipment, and one additional operation: gelatinization.

Gelatinization. The essential difference between gelatin dynamites and the non-gelatinous comes in the introduction of nitrocotton into the nitroglycerin in the gelatins. This forms a viscous liquid which gives a plastic rather than powdery product when mixed with the dry, non-explosive ingredients.

The gelatinization often takes place in what is known as a figure 8 bowl, the shape of which inside is evident from its name. Two sets of bronze paddles rotate at opposite ends of the vessel so that thorough incorporation of ingredients will take place. After introduction of the nitroglycerin into the bowl, the weighed amount of nitrocotton is added to the nitroglycerin. Dynamite nitrocotton ordinarily has a nitrogen content of around 12.25%. With the nitroglycerin and nitrocotton in the bowl, the agitation is started, while the bowl is maintained at a slightly elevated temperature by water-jacketing control. Five to eight minutes will ordinarily give a satisfactorily gelatinized product.

Mixing. The mixing operation follows gelatinization immediately in the same vessel. The "mixed dope," or mixture of dry non-explosive ingredients, is introduced into the bowl with the liquid mixture. After mixing for perhaps another five minutes, the gelatin is removed from the bowl. Instead of a powdery mixture, it is now a plastic putty-like product, incapable of free flow, but capable of being pressed into any desired form.

Cartridging Gelatin dynamite, like the non-gelatinous product, is packed into preformed cylindrical paper cartridges. Instead of being pressed or tamped into the cartridges, however, it is packed in by means of a metal worm extruding device, operating under slight pressure. The open end of the shell is crimped down after the cartridging operation.

Types of Dynamites—There are two conditions which must be satisfied if a dynamite is to prove satisfactory in blasting service. First, it must have the safety properties that allow it to be used without hazard, and, secondly, it must be adapted to the type of blasting in question. Because of the many and varied kinds and hardnesses of material to be blasted and the different uses to which the explosives are put, a great number of types and brands of dynamite have been developed. See Figure 1.

Straight Dynamites. The straight dynamites are the simplest type of dynamite and may be defined as high explosives containing nitroglycerin as the sole explosive ingredient, a sufficient amount of absorbent material being present to prevent exudation of the nitroglycerin.

The straight dynamites are the basis of comparison, as to strength, for all other dynamites. They are made in a series from 15 to 60%, each grade being designated by its nitroglycerin content. For example, 40% straight dynamite contains 40% nitroglycerin. Other types of dynamites are designated as 40%, 60%, etc., when they have the same strength by ballistic mortar determination

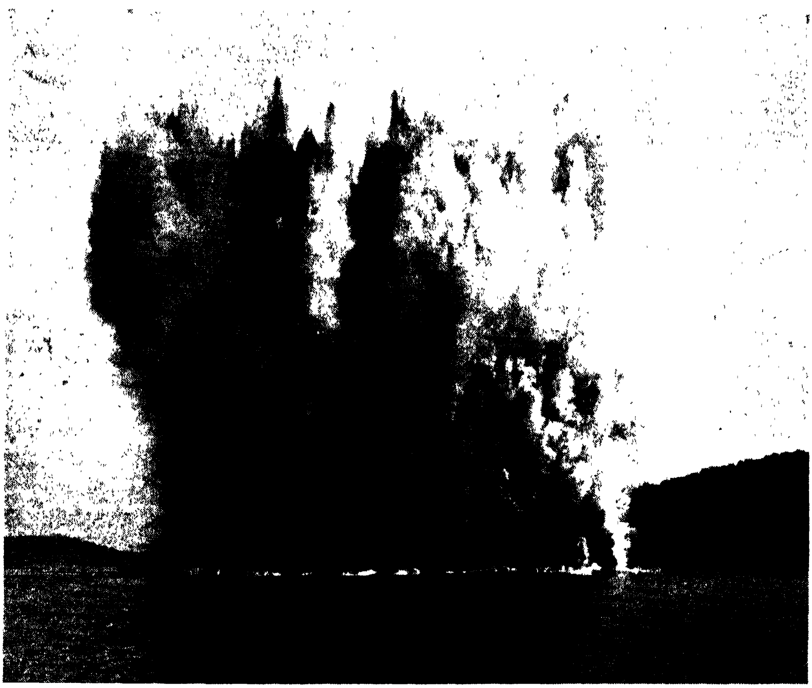


FIG. 3. Pipe Line Crossing Ditch Blast in Order to Lay Pipe Below Bed of River.

as the correspondingly named straight dynamite. The standard 40% straight dynamite used in tests by the U. S. Bureau of Mines has the following composition:

Nitroglycerin	40%
Sodium Nitrate	44
Wood Pulp	15
Calcium Carbonate	1

The straight dynamites are characterized by high velocity of detonation (over 13,000 feet per second for 40% straight, for example) and a high degree of sensitiveness to propagation. Because of this latter property, they are excellently adapted for use in submarine work and ditch blasting, where the explosion from one stick of dynamite is propagated successively to a large number of other sticks separated from one another by distances of perhaps 18 inches. See Figures 3 and 4. Because of the relatively high sensitiveness to friction, straight dynamites are not recommended for quarrying and general blasting work, where other types are suitable.

Ammonia Dynamites. The ammonia dynamites are dynamites in which a portion of the nitroglycerin of the straight dynamites has been replaced by ammonium nitrate. These dynamites are very widely used, because of their effectiveness and their relatively low price. They are put out in the same strength designations as the straight dynamite but are lower in velocity than the straights for a given grade. The ammonia dynamites are attractive for use because of

FIG. 4. Removing Temporary Dam in Hydroelectric Development.

their insensitiveness to shock and friction and their lack of inflammability in comparison to the straight dynamites. They have one drawback in that they are relatively low in water resistance so that they are not well adapted for use under very wet conditions.

Gelatin Dynamites. The gelatin dynamites are those in which the nitroglycerin has been at least partly gelatinized by means of nitrocotton. The highest strength gelatin is "blasting gelatin," which is considered the strongest industrial explosive known. It usually has the approximate composition: 91.5% nitroglycerin, 8% nitrocotton, 0.5% calcium carbonate. Blasting gelatin is a solid, light-colored, elastic material, too adherent for mixing with other materials.

The common gelatin dynamites are made by the use of a lower ratio of nitrocotton in nitroglycerin, so that a thick, viscous liquid is obtained rather than a solid mass. The other usual ingredients of dynamites are mixed with this viscous liquid or gel. Both straight and ammonia gelatins are made, depending on whether nitroglycerin alone is the explosive ingredient or ammonium nitrate has replaced a part of the nitroglycerin.

The gelatin dynamites are designated by strength markings also, as 40%, 60%, etc. They are outstandingly excellent with respect to four properties: (1) they possess high bulk density; (2) they are the most water-resistant of all dynamites; (3) they excel from the point of view of fumes; and (4) they do not flow, but stick well in holes into which they have been loaded because of their plastic nature. These properties, in addition to their relative insensitiveness to shock, make the gelatin dynamites the preferred explosive for use under wet conditions where a high loading density is desired, as in hard rock blasting, in blasting underground in confined workings where toxic fumes would be dangerous, and in boreholes directed upwardly in hard rock. Because of their relatively high price, the gelatin dynamites are replaced frequently by other explosives of slightly less efficiency.

Semi-Gelatins. The so-called semi-gelatins are ammonia dynamites which are intermediate between the ammonia dynamites and the gelatins in the properties of density, plasticity, and water resistance.

Permissibles. The "permissible" dynamites are high explosives adapted to a special use, namely, in gassy coal mines, where black powder and the regular dynamites are not considered safe in the presence of the inflammable gases. A "permissible" may be defined as an explosive similar in all respects to a sample passing certain prescribed tests of the U. S. Bureau of Mines, when the explosive is used under the conditions and in the amounts prescribed by the Bureau. The Bureau of Mines issues periodically a list of active permissible explosives, all of which have passed the official tests. The Bureau has no authority to enforce the sale and use of "permissibles," but its stamp of permissibility carries great weight.

The first permissible list was issued in 1909 by the technologic branch of the U. S. Geological Survey, subsequently the Bureau of Mines. This list included 17 authorized explosives. The list of active permissible explosives published in December 1937 included 196 different explosives sold by 15 different explosive companies.

The permissibility tests of the Bureau of Mines[17] include several special determinations of properties which affect the suitability of the explosive for use in coal mines. One such test is the determination of the "unit deflective charge," that is, the weight of the explosive under test which will give a deflection of the ballistic mortar equal to that produced by ½ pound of the standard 40% straight dynamite. Tests are also made in their special testing gallery to determine the degree of safety of the explosive when fired in the presence of inflammable gases and of coal dust respectively. A special test is made for fumes also, and permissibles are classified according to the content of toxic gases (carbon monoxide and hydrogen sulfide) in their gaseous detonation products.

The most generally used permissibles today contain (1) a high percentage of ammonium nitrate, in the neighborhood of 80%; (2) a relatively low percentage of nitroglycerin as sensitizing agent; and (3) fibrous combustible material for utilizing the excess oxygen of the ammonium nitrate and absorbing the nitroglycerin. Black powder is admirably adapted for use in blasting down coal as far as its blasting action is concerned, but it is not safe in gassy mines. Its blasting action characteristically brings down coal in large lumps rather than shattering it

[17] Munroe, C. E. and Tiffany, J. E., "Physical Testing of Explosives at the Bureau of Mines Explosives Experiment Station," U. S. Bureau of Mines, Bulletin 346 (1931).

into fine fragments, and detonating permissibles have been developed which approach black powder in its heaving action by attainment of very low velocities and very low density by various expedients.

A gelatinous type of permissible has been introduced which is more suitable for use under wet conditions of blasting. This type contains a higher nitroglycerin content than the usual permissible, a small percentage of nitrocotton, and a lower content of ammonium nitrate.

Miscellaneous Dynamites—In addition to the important general types of dynamites, a great many special kinds have been developed, intended particularly for special kinds of work. The types of dynamite are similar to those already described. No attempt has been made here to describe the methods of use of commercial blasting explosives, as this is adequately covered in the published literature.[17a]

COMMERCIAL HIGH EXPLOSIVES CONTAINING NO NITROGLYCERIN

Ammonium Nitrate Explosives—The logical extension of the trend toward the replacement of nitroglycerin dynamites by ammonium nitrate would be to replace the nitroglycerin entirely. This idea is not new in the explosives industry; many formulas have been prepared over a long period of years embodying the combination of ammonium nitrate having an excess of oxygen, with an oxygen deficient but non-explosive sensitizing agent. However, ammonium nitrate is a highly deliquescent salt, and mixtures containing it tend to become hard and insensitive, and incapable of propagating the explosion after exposure to moisture.

A new type of blasting agent of this nature was introduced in 1935 designated "Nitramon," which possesses a degree of insensitiveness such that it is incapable of detonating under the influence of a blasting cap. When once initiated by a sufficiently strong booster charge, however, the material is capable of propagating the explosion indefinitely at high and undiminishing velocity when used in large diameters. The disadvantages of moisture effect are overcome by having the material enclosed in a waterproof metal container. A number of such cans of the material, for example, 7 inches in diameter by 24 inches long, are loaded into large-diameter vertical quarry holes. (See Figure 5.) The explosion propagates through the metal ends of the cans at velocities around 16,000 feet per second. Because of its insensitiveness to impact, friction, and shock, it is the safest high velocity agent yet introduced.

Nitrostarch Explosives—Nitrostarch is a solid, white explosive material obtained by nitration of cornstarch or cassava starch by means of practically anhydrous mixed acid. The nitrated product is drowned in an excess of water, washed thoroughly, neutralized with dilute sodium carbonate solution, and dried, first by wringing, then in hot-air driers. The commercial nitrostarch is mainly starch trinitrate and ordinarily contains slightly below 13.0% nitrogen, as against a theoretical content of about 13.3%.

Nitrostarch is used in commercial high explosives in America to a limited extent. Since it is a solid explosive material, no freezing can take place. Am-

[17a] LaMotte, A., editor, "Blasters' Handbook," describing practical methods of using explosives for various purposes, E. I. du Pont de Nemours & Co. (1939).

monium nitrate is commonly included in considerable amounts in nitrostarch explosive compositions. Nitrostarch has had some application in military explosives.

Chlorate Explosives—Explosives containing sodium or potassium chlorate have been made for well over a century and periodically attract renewed attention. The earlier chlorate powders were dry mixtures of chlorate with oxidizable materials such as sugar, charcoal, sulfur, etc. These mixtures were all highly inflammable and sensitive to frictional impact. Sooner or later their manufacture usually led to disastrous results. More recently, chlorate explosives have in-

FIG. 5. Quarry Blast at Instant of Explosion of a Charge of Nitramon.

cluded a liquid ingredient, or a desensitizing material, and such mixtures are less sensitive. In spite of the cheapness of raw materials, however, chlorate explosives have not proved very attractive.

Liquid Oxygen Explosives[18]—Liquid oxygen explosives comprise carbonaceous absorbent materials saturated with liquid oxygen. Theoretically, such explosives appear very attractive, as carbon burns to carbon dioxide completely, if sufficient oxygen for combustion be present, and the explosive is entirely gasified. In making liquid oxygen explosives, the cartridge, consisting usually of lampblack or other carbon black packed in a porous container, is first prepared. This cartridge is dipped into a bath of liquid oxygen and allowed to become saturated.

Potentially, liquid oxygen explosives are of high strength and velocity because of the composition, and this is actually the case under favorable conditions. There is the disadvantage that liquid oxygen evaporates very rapidly, so that

[18] Perrott, G. St. J. and Tolch, N. A., "Liquid Oxygen Explosives," U. S. Bureau of Mines, Bulletin 349 (1932).

the life of an explosive cartridge is relatively short. Also, the strength is not constant because of the steady loss of oxygen. A further disadvantage comes in the high sensitiveness to shock of liquid oxygen explosives, a serious consideration in quarrying operations.

Miscellaneous Explosive Devices—Mention should be made of a type of blasting device which has had some popularity, and which does not depend primarily for its effectiveness on the oxidation of combustible materials to gaseous products. One such device, which has been applied in the mining of coal, is based on the use of a confined supply of liquid carbon dioxide,[19] together with a heating composition, adapted to be ignited at the proper time and to exert the desired blasting effect by converting the carbon dioxide to the gaseous state. The real novelty comes in the use of a specially designed cartridge constructed with a closing disc which will rupture when the pressure exceeds a predetermined amount. A later development uses the same general type cartridge, but brings about the rupture of the disc and the release of pressure by the use of compressed air from a portable compressor.

A blasting device for use in coal has also been introduced, consisting of an expansible tube of particular design operating under hydraulic pressure.[20]

All these mechanical devices yield a good grade of lump coal, but their ultimate value must still be determined.

INITIATING DEVICES

After nitroglycerin became available as an explosive compound, its high explosive energy could not be utilized satisfactorily until Nobel had devised and introduced into practice a form of blasting cap. It was then realized that, whereas a simple flame was sufficient to initiate the explosion of black powder, the efficient development of the strength of nitroglycerin explosives resulted only when initiation was from the powerful influence of a detonating material.

A group of compounds has been developed which are peculiarly adapted for use in initiating detonating explosives of the dynamite type. Such materials are designated as primary detonating compounds. The secret of their effectiveness comes not in their high temperature of explosion, or the volume of gas produced, but in the fact that they attain their high velocity of explosion with extreme rapidity after initiation by a flame. As a matter of fact, the most effective primary detonating compounds are characterized by small volume of gas formation, and are not nitrates or nitrated compounds, as are most of the explosive materials.

Mercury Fulminate—Mercury fulminate, $(CNO)_2Hg$, has long been a very satisfactory primary detonating compound. It is commonly used with a smaller amount of an oxidizing agent such as potassium chlorate. It is made by dissolving mercury in a large excess of 68% nitric acid and adding the solution to 95% alcohol, with arrangements for controlling the temperature. The reaction soon causes the solution to boil spontaneously and vigorously and mercury fulminate precipitates in the boiling flask as a fine white powder of high density.

[19] Tiffany, J. E., "A New Permissible Blasting Device," U. S. Bureau of Mines, Report of Investigations 2920 (1929); Hart, E., Colliery Eng. *15*, 373-377 (1938).
[20] Mining Congr. J. *26*, 39-41 (1940).

One economic disadvantage of mercury fulminate comes in the high price of mercury and the fluctuations in price because of the uncertain supplies. Spain is the principal source of mercury ores.

Lead Azide—This compound, PbN_6, has become fully as important as mercury fulminate as a primary detonating compound in the last few years. It has the disadvantage of requiring a small ignition top charge because of its relative insensitiveness to flame, in contrast to mercury fulminate. However, it picks up to its maximum high velocity more rapidly than fulminate, hence a smaller weight charge will have the detonating effect of a heavier fulminate charge. An additional advantage lies in the ready availability of the raw materials. It is made by

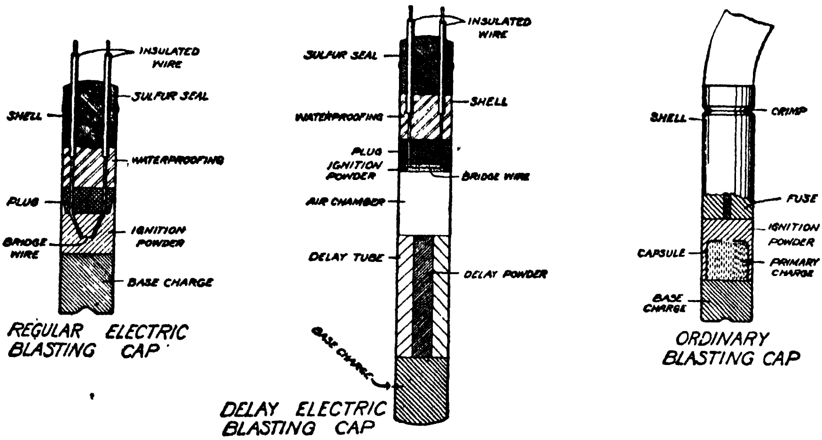


FIG. 6. Three Types of Blasting Caps.

the reaction of sodium azide with a soluble lead salt. Sodium azide in turn is derived from sodamide (from metallic sodium and ammonia) and nitrous oxide.

Other Primary Detonating Compounds—While mercury fulminate and lead azide are the two most widely used compounds of this nature, other materials are also employed; for example, diazodinitrophenol, obtained by reacting concentrated nitric acid with picramic acid or a picramate in the presence of alcohol, and mannitol hexanitrate, a nitration product of the polyhydric alcohol, mannitol (see compound 106, Chapter 27).

Blasting Caps—Blasting caps are small cylindrical metal shells, usually about ¼ inch in diameter by 2 inches long. These shells are of copper or aluminum and contain a detonating charge of explosive. Most blasting caps are of the compound type and contain a fraction of a gram of a base charge at the closed end of the shell, a charge of a primary detonating explosive upon the base charge, followed by a more readily ignitable top charge if necessary. Mercury fulminate and lead azide are the most commonly used primary detonating charges, while tetranitromethylaniline (tetryl) is an excellent base charge. Blasting caps are used for initiating the explosion of dynamites and are inserted into the explosive at the time of use.

Three types of blasting caps are employed, the first two differing by the method of firing. See Figure 6. In the case of ordinary or fuse caps, a length of safety fuse is inserted into the open end of the cap and the metal wall is crimped about the fuse. In use, the end of fuse away from the cap is lighted, and the spit of flame from the fuse within the cap fires the ignition charge and brings about detonation. The second type of cap is fired electrically,[21] the two leading wires being connected within the cap by a fine wire of high electrical resistance. When an electric current passes through the wires, the fine bridge wire becomes heated to incandescence and fires the ignition charge. A third type, designated as a delay cap, is ordinarily fired electrically, but contains a delay charge of a slow burning composition which is inserted in the cap so that the detonation of the cap charge will take place after a definite time interval. By the use of delays, the time interval before a cap will fire, after application of the current, can be varied from 0 to 15 or 20 seconds. Recently, delays have been improved by the use as delay compositions of charges which give off practically no gas on combustion; for example, mixtures of a combustible metal with an oxidizing agent. This permits the employment of ventless caps, so that moisture penetration is prevented, as well as excessive gas pressure variation in the cap previous to firing.

Squibs—When deflagrating explosives such as black powder are used, the simple application of flame is sufficient for firing. This is done by using devices similar to blasting caps, except that they contain no detonating explosive, hence explode less violently. Preferably, electric squibs are used and the construction of these is similar to that of electric blasting caps, except for the nature of the explosive charge. Squibs may be in metal or cardboard tubes, and may be either open or closed at the firing ends.

Fuse—Two types of fuse are in general use in blasting. Safety fuse is employed for initiating caps or squibs where electrical firing is not used. Safety fuse consists of a small-diameter core of black powder, enclosed in a covering wrapper of various waterproofed fabrics. It is made to have an approximate burning speed of 30 or 40 seconds per foot. When fuse is used to fire a shot in blasting, a sufficient length is used so that ample time is allowed for the shot firer to reach a point of safety.

Detonating fuse, on the other hand, has a velocity of detonation of over 5000 meters per second (16,500 feet). It is used principally for exploding charges of explosives in deep holes. The usual detonating fuse, called Cordeau, consists of a charge of high velocity explosive such as trinitrotoluene contained in a small-diameter lead tube. The line of Cordeau is in contact with the charge throughout its length, and thus causes practically instantaneous detonation of the whole charge, regardless of its velocity. A more recent type of detonating fuse comprises pentaerythritol tetranitrate contained in a non-metallic wrapping. The velocity of this fuse is about 7000 meters per second (23,000 ft.).

SPORTING AND MILITARY EXPLOSIVES

The explosives discussed in the preceding paragraphs have been almost entirely those intended for use in commercial blasting. In addition to such explosives, the explosives utilized for sporting and military purposes constitute a

[21] Ilsley, I. C. and Hooker, A. B., "Electric Shot-Firing in Mines. Quarries, and Tunnels." U. S. Bureau of Mines, Bulletin 240 (1926).

group which is of very great interest chemically, though normally of less importance than the blasting explosives.

Propellent Explosives—By propellent explosives are meant the explosives used in firearms, both rifle and shotgun powders, as well as propellants for military use. The term gunpowder might well be used in designating such propellants, but this word has been too long identified with black powder to be given any other meaning. The propellants here discussed will be what are commonly known as smokeless powders having a nitrocellulose base.

Smokeless powder has had a gradual development. Nitrocellulose was suggested for use in explosives at an early date, but not until the work of Vieille in France, about 1886, when he showed that the formation of nitrocellulose into dense colloidal form allowed control of the rate of burning, was there any marked success in its promotion. Two reasons existed for displacing the older black powder by a propellant such as a nitrocellulose powder. First, the dense cloud of smoke resulting from the explosion of black powder was very objectionable, particularly in military use. Secondly, there was a demand for increased energy per unit volume of propellant. The utilization of nitrocellulose in simple fibrous or compressed form was impractical, however, because the high rate of pressure development would burst the gun. Nitrocellulose has the advantage of raw materials that are of wide distribution and high availability. Cotton is the most suitable source of cellulose for use, and the ordinary form employed is cotton linters, obtained from the cotton seeds as a second cut, after removal of the long-fibered cotton and the first cut of lint. Wood pulp is another possible source of cellulose for nitration, and has been widely used for military purposes by countries shut off from cotton supplies. The nitration procedure for nitrocellulose has been outlined previously.

Smokeless Powder[22]—Nitrocellulose may vary rather widely in composition, as shown by the nitrogen content. This in turn means a variation in potential, which is an important consideration in smokeless powder manufacture.

Assuming the simplified, but hypothetical formula $C_6H_{10}O_5$ for cellulose, the trinitrate would contain 14.14% nitrogen. The nitrocottons of interest in connection with smokeless powder contain between 12 and 13.4% nitrogen. Pyrocellulose or pyrocotton, an important type for smokeless powder, contains between 12.5 and 12.7% nitrogen and is soluble in a 2 to 1 ether-alcohol solution; guncotton, with a nitrogen content of 13.0 to 13.4%, is insoluble in the ether-alcohol mixture; dynamite nitrocotton, with a 12.25% content, is used in gelatin dynamites where it is gelatinized by nitroglycerin; nitrocellulose of nitrogen contents below 12.3% is used for non-explosive outlets such as lacquers, plastics, fabrics, etc.

Manufacture of Single-Base Powders—The term "single-base powder" designates a type of smokeless powder in which nitrocellulose is the sole nitric ester. This is the type of powder used by the United States Army and Navy. The process involved in the manufacture of single-base nitrocellulose powders may be considered under (1) dehydration, (2) mixing and colloiding, (3) pressing and graining, and (4) solvent recovery and drying.

[22] Marshall, A., "Explosives," second edition, Vol. 1, p. 289, Blakiston (1917); U. S. War Dept., "Military Explosives," Technical Manual No. 9—2900 (1940); Storm C. G., "Smokeless Powder," in Alexander, J., "Colloid Chemistry," Vol. 4, p. 101 Chemical Catalog Co. (1932).

Dehydration. After the wringing of the purified nitrocotton, the material still has a water content of 25 to 30%, in which wet condition it is entirely safe to handle. The drying of this material by warm air currents on trays would be hazardous on a large scale, because of the static susceptibility of dry nitrocotton. In practice, therefore, dehydration takes place by displacing the water with alcohol. Since the following step in the process involves treating the nitrocotton with an ether-alcohol solution, the presence of the alcohol brings in no difficulties. Approximately 1.25 pounds of 95% alcohol are used per pound of dry nitrocotton, the introduction of the alcohol being by means of a hydraulic press.

Mixing and Colloiding. The dehydration operation leaves the nitrocotton in the form of a compressed block wet with alcohol. This is broken up and introduced into a mixing machine, where the material is kneaded by two sets of agitation blades rotating in opposite directions. The nitrocotton here is to be colloided by the ether-alcohol solution containing two parts of ether to one of alcohol, the total weight of solvent being approximately equal to the weight of the dry nitrocotton. Before addition of the ether, diphenylamine is dissolved therein in an amount such that about 1% will be present in the finished powder. The ether is quickly poured into the mixer, where it blends with the alcohol present and the contents are agitated for about an hour.

The diphenylamine is added to the ether during the mixing operation in order that it may be intimately distributed throughout the blend, so that any nitrogen oxide decomposition products which may be developed during years of storage will react with this stabilizer and thus be removed.

Pressing and Graining. The colloidal smokeless powder is now ready for its final treatment. A dense cylindrical mass is formed first by compression of the material in a cylinder by means of a hydraulic press exerting a pressure of around 3000 pounds per square inch. The blocks are then grained by forcing the material through dies provided with pins under a pressure of several tons per square inch. The strands of powder are perforated as they pass through the die and then are guided to mechanical cutters. Cannon powders in the United States have seven longitudinal perforations, one in the center surrounded by six others. Powders for small arms have only one small center perforation. The object of the perforations in the powder is to obtain a progressive increase in the area of burning surface during combustion. The smokeless powder in its final form is actually a cylinder of variable size, depending on the type of weapon in which it is to be used. Cannon powders in the United States have a length about 2½ times their diameter and are of considerable size, while various powders for small arms are of very small diameter.

Solvent Recovery and Drying. The solvent recovery process is adapted for partial drying of the "green" powder, with recovery of whatever alcohol and ether are given off. The drying is a continuation of the solvent recovery step except that in the second step, solvent is removed beyond the point where its recovery is justified. Precautions are taken that the removal of solvent is not rapid enough to cause distortion of the powder grains.

Recent Improvements in Nitrocellulose—The last few years have seen the improvement of the nitrocellulose type of propellent powder as used by the United States, particularly in two respects. First, the hygroscopicity of the powder has been reduced by using nitrocellulose of higher nitrogen content and replacing a portion of the nitrocellulose by non-volatile and non-hygroscopic solvents. Secondly, flashlessness has been obtained in many guns by the use of compositions of suitable potential which are in themselves flashless or by the use of supplemental flash suppressing salts. This means that muzzle flash, due to the secondary ignition of highly combustible gaseous products issuing from the gun, has been prevented from taking place, thus eliminating the usual large luminous muzzle flash which is visible for many miles. This is an important consideration in military operations.

Manufacture of Double-Base Powders—These powders differ because of the fact that, instead of containing nitrocellulose alone as explosive ester, they contain both nitrocellulose and nitroglycerin. A well-known example of this type powder is the British Cordite. M. D. Cordite contains 30% nitroglycerin, 65% guncotton, and 5% vaseline. The nitrocotton has a nitrogen content of at least 13%, hence is difficultly soluble in an ether-alcohol mixture. Consequently, acetone is used as solvent. The vaseline acts as stabilizer and cooling agent in the powder, as it has a tendency to lower the temperature of explosion.

The Italian Ballistite is another powder of this double-base type, but contains a nitrocellulose of about 12% nitrogen content, soluble not only in an ether-alcohol solvent, but also in nitroglycerin. This type of powder, which contains equal parts of nitrocellulose and nitroglycerin plus 1% of diphenylamine (see compound 239, Chapter 27), is made on rolls without the use of acetone or any other volatile solvent.

The nitrocellulose type of smokeless powder propellant has been used by the United States, Russia, England, and France. The nitroglycerin type of propellant is used by Great Britain and Italy. Germany is said to have used to a large extent the nitrocellulose type in their army and the nitroglycerin type in their navy.

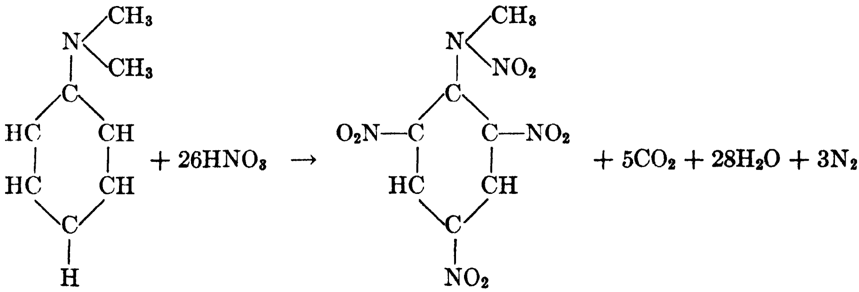
DISRUPTIVE EXPLOSIVES FOR MILITARY USE

The explosive compounds up to this point have been mainly nitric esters of aliphatic alcohols and carbohydrates. These compounds are not ordinarily suitable as bursting charges for firing shells and other military devices because of too great a sensitiveness to shock. The aromatic nitro-compounds are generally better adapted for this purpose.

Trinitrotoluene—This explosive compound is prepared by the nitration of toluene, an aromatic hydrocarbon derived from coal tar, or obtained synthetically from petroleum products. The nitration procedure has been discussed previously. TNT, as it is called, is the most widely used shell-firing explosive, and is well suited for loading into containers because of its low melting point of 80.8° C. Its importance for military use comes from its comparative excellence in the following respects: (1) it is a safe explosive in manufacture, transportation, and storage, (2) it is non-hygroscopic, (3) it has no tendency to form unstable compounds with metals, yet (4) it is a violent, disruptive explosive.

Amatol—Amatol is an explosive mixture of TNT with ammonium nitrate, developed during the First World War. A 50-50 mixture of the respective ingredients is sufficiently fluid to allow casting, but an 80-20 ammonium nitrate-TNT mixture was subsequently found suitable for loading into shells by an extrusion process. It was developed because of the imminent shortage of toluene for nitration during the early years of the war. Actually, such mixtures are, in some respects, an improvement on TNT by itself. TNT is deficient in oxygen so that combustion is not complete on explosion and black smoke always results. The detonation products may include carbon, carbon monoxide, hydrogen and methane, all capable of further combustion. The presence of 80% ammonium nitrate with 20% TNT assures almost an evenly balanced composition with respect to oxygen with resulting increased strength and improved fumes. Compared to TNT, amatol has the disadvantage of being hygroscopic.

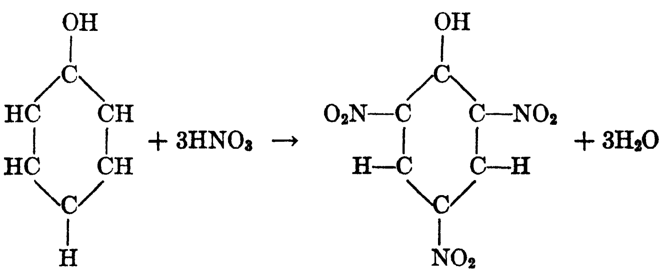
Tetryl—Tetryl is the name commonly applied to tetranitromethylaniline (see compound 328, Chapter 27), or more properly, trinitrophenylmethylnitramine. It is made by the nitration of dimethylaniline (see compound 231, Chapter 27), and has a melting point of around 130° C.



Dimethylaniline (5 mols) — Tetryl (5 mols)

Tetryl has a very important use in commercial explosives as a base charge for blasting caps. In military explosives, it is too sensitive for use as a main shell filling charge, but is well suited for use as a booster charge, intermediate between the sensitive ignition charge and the main bursting charge.

Picric Acid—Chemically, picric acid is trinitrophenol (see compound 330, Chapter 27). It has had considerable use as a shell-filling explosive.

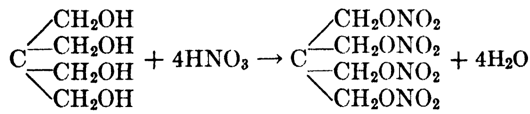


Phenol — Picric Acid

It has a melting point of about 122° C. One objectionable characteristic of picric acid is its tendency, as an acid, to form metallic salts or picrates, which salts are unfortunately dangerously sensitive.

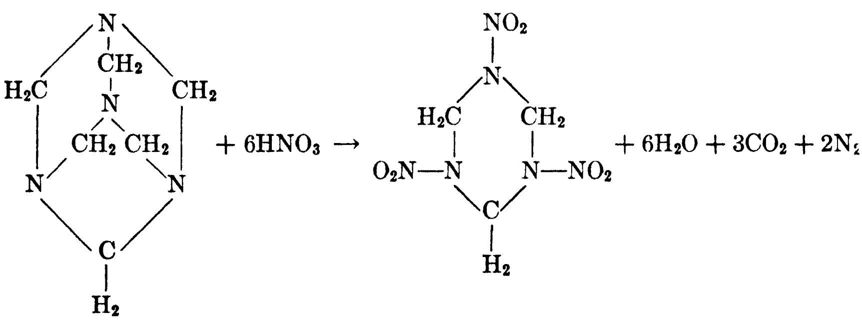
Ammonium Picrate—Ammonium picrate is the salt formed by neutralizing picric acid with ammonia. Its relative lack of marked tendency to form sensitive metallic picrates when in contact with metals gives it an advantage over picric acid. It is not altogether free from this tendency, however. Ammonium picrate is claimed to be the least sensitive to shock of all explosives used as shell bursting charges. However, it is inferior to TNT in strength.

Pentaerythritol Tetranitrate—This explosive compound has come to be important since the First World War, and owes its attractiveness partly to the fact that it is obtained from raw materials of almost universal occurrence. This makes the compound of particular interest to those nations which wish to become self-contained. Pentaerythritol tetranitrate, or PETN, melts at around 141° C. It is obtained by the nitration of the irregular tetrahydric alcohol, pentaerythritol, which in turn is prepared by the condensation of formaldehyde with acetaldehyde. (For a description of such condensation reactions see Chapter 2, The Unit Operations.)



Pentaerythritol   Pentaerythritol Tetranitrate

Trimethylene Trinitramine—This is another post-war high explosive compound, frequently designated Hexogen in the literature. Like the preceding explosive, it is attractive because of the widely-occurring raw materials. In this case, the explosive is obtained by the nitration of hexamethylenetetramine, a compound obtained from formaldehyde and ammonia. The raw materials in this case give Hexogen greater promise than PETN, but the yields obtained are said to be sufficiently low to offset that apparent advantage. Hexogen has a melting point of 200-201° C.



Hexamethylene Tetramine   Hexogen

HANDLING AND STORAGE OF EXPLOSIVES

Because of the potential hazard when explosives are present, some generally accepted rules are observed in their handling and storage. The basic principles underlying these rules are that (1) explosives should be treated with respect, (2) they should be handled only by those experienced or properly instructed in their use, and (3) they should be stored under favorable conditions and at positions sufficiently isolated that accidental or malicious explosion will not endanger persons not directly concerned with their use.

In the case of nitroglycerin explosives, the unwrapped explosive should not be handled unnecessarily, since the well-known nitroglycerin headache may result from bodily contact with nitroglycerin or other liquid nitric esters, or from breathing their vapors. This does not occur with ammonium nitrate, nitrocellulose, nitrostarch, or other solid explosive nitrates. The aromatic nitrocompounds possess a certain degree of toxicity and continued contact with them should be avoided, either in handling or inhaling their vapors or dust.[23]

For the storage of explosives in magazines there are definite laws and regulations in the various states. A so-called "American Table of Distances"[24] has been prepared which specifies minimum distances at which magazines containing explosives should be spaced from inhabited buildings, railroads, and public highways, the distances increasing with increased amount of explosives stored.

Because of the care exercised in the observance of safety rules, it was stated in 1937 that "during the last 14 years more than three billion pounds of dynamite have been shipped over millions of miles of American railroads," and "this movement of dynamite has been accomplished without injury to a person, and with no practical damage to property."

ECONOMIC TREND OF COMMERCIAL EXPLOSIVES

The accompanying graph shows the annual production figures for dynamite and black powder, along with those for coal and iron ore. From this it will be

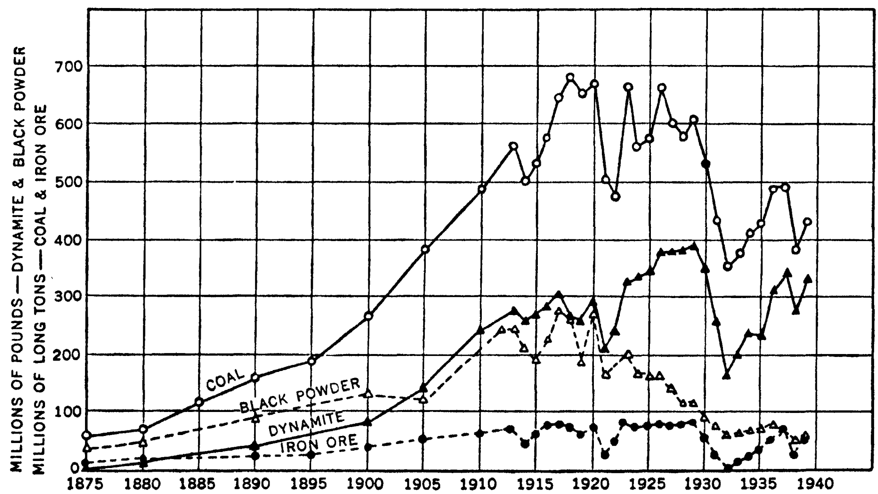


FIG. 7. Production of Dynamite, Black Powder, Coal, and Iron Ore in the U. S. A. from 1875-1939.

seen that the dynamite industry is a rather reliable index to the prosperity of the country. The curve for dynamite production follows closely that of coal and

[23] Hamilton, A., "Industrial Poisons in the United States," p. 497, Macmillan (1925).

[24] LaMotte, A., "Blasters' Handbook," p. 34, E. I. du Pont de Nemours & Co. (1939).

TABLE 2—STATISTICAL SUMMARY

The magnitude of the commercial explosives industry can best be realized from actual production figures, and these are given below for recent years. It will be noted that nearly 400,000,000 pounds of commercial blasting explosives were produced in the United States in 1939, of which over 325,000,000 pounds were of the dynamite type.

Production of Blasting Explosives in the United States—Pounds[25]

	1929	*1935*	*1936*	*1937*	*1938*	*1939*[26]
Dynamite						
1. Permissibles	62,669,434	39,170,016	47,859,019	49,579,441	41,859,281	49,950,415
2. High explosives other than permissibles	326,993,276	200,323,559	262,047,106	288,924,253	238,576,242	280,000,000
3. Total dynamite (1 + 2)	389,662,710	239,493,575	309,906,125	338,503,694	280,435,523	329,950,415
Black Powder						
4. Granular	86,818,225	34,222,625	40,420,250	29,836,650	23,552,075	28,322,250
5. Pellet	33,227,425	34,665,050	41,278,125	36,403,950	28,142,900	29,914,575
6. Total black powder (4 + 5)	120,045,650	68,887,675	81,698,375	66,240,600	51,694,975	58,236,825
7. Total blasting explosives (3 + 6)	509,708,360	308,381,250	391,604,500	404,744,294	332,130,498	388,187,240

No statistical figures are available for the production of sporting and military explosives. For the latter, the amount produced is relatively small ordinarily, but will increase greatly in times of national emergency. The dollar magnitude of the commercial explosives industry is shown by U. S. Census figures, which give the value of the products in 1929 and 1935 respectively as $72,539,724 and $40,667,200.

[25] U. S. Bureau of Mines—Report of Investigations 3350 (July, 1937) and Technical Paper 606 (1939).
[26] Final official figures not available.

is quick to register the pulse of business activity; more so than iron ore. The explanation of this fact comes in the varied uses of dynamite in connection with nearly all construction activities.

The proportion of production of the different commercial explosives is given in more detail in Table 2.

READING LIST

GENERAL WORKS

Marshall, A., "Explosives," second edition, 3 vols., Blakiston (1917-1932).

Brunswig, H., "Explosives," American translation by Munroe and Kibler, Wiley (1912) (Second German edition, 1923).

"Thorpe's Dictionary of Applied Chemistry," fourth edition, Vol. 4, "Explosives," pp. 453-562, Longmans, Green & Co. (1940).

Marshall, A., "Dictionary of Explosives," Blakiston (1920).

Taylor, C. A. and Rinkenbach, "Explosives: Their Materials, Constitution and Analysis," U. S. Bureau of Mines, Bulletin 219 (1923).

Beyling, C. and Drekopf, K., "Sprengstoffe und Zundmittel," Julius Springer (1936).

Stettbacher, A., "Schiess- und Sprengstoffe," second edition, Barth, Leipzig (1932).

DYNAMITES

Naoum, P., "Nitroglycerin and Nitroglycerin Explosives," American translation by E. M. Symmes, Williams and Wilkins Co. (1928).

LaMotte, A., editor, "Blasters' Handbook," describing practical methods of using explosives for various purposes, E. I. du Pont de Nemours & Co. (1939).

Sohlman, R. and Schuck, H., "Nobel: Dynamite and Peace," translation, Cosmopolitan Book Corp. (1929).

BLACK POWDER

Guttmann, O., "Manufacture of Explosives," 2 vols., Whittaker & Co. (1895).

MILITARY EXPLOSIVES

United States War Dept., "Military Explosives," Technical Manual No. 9—2900 (1940).

Colver, E. de W. S., "High Explosives," D. Van Nostrand Co. (1918).

Storm, C. G., "Smokeless Powder," in Alexander, J., "Colloid Chemistry, Theoretical and Applied," Vol. 4, pp. 101-116, Chemical Catalog Co. (1932).

HISTORICAL

Van Gelder, A. P. and Schlatter, H., "History of the Explosives Industry in America," Columbia University Press (1927).

TESTING

Munroe, C. E. and Tiffany, J. E., "Physical Testing of Explosives at the Bureau of Mines Explosives Experiment Station," U. S. Bureau of Mines, Bulletin 346 (1931).

CHAPTER 33

MILITARY GASES[1]

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DEFINITION OF MILITARY GASES

In military parlance, a "gas" is any chemical substance, whether solid, liquid or true gas, which is employed in combat for producing incapacitating effects on the human body by direct chemical action. Military gases are often called chemical agents and are sometimes referred to as combat substances.

FUNCTION OF MILITARY GASES IN WARFARE

General—When the Germans first employed toxic gas in battle in April, 1915, a new principle of combat was introduced, namely, chemical action, as contrasted with physical force. Unlike impact weapons previously used in warfare, gas produces its incapacitating effects by pervading the surrounding atmosphere and reacting chemically with the surfaces of the living bodies with which it comes in contact. Accordingly a chemical projectile does not have to strike a specific object in order to be effective, but only sufficiently close to enable its gaseous contents to envelop the object. With this radical change in the basic principle of combat, many new possibilities in the tactics and technique of battle were presented, the full implications of which have so far been only dimly foreshadowed.

Mode of Action of Gas—The action of gas differs from that of impact weapons in the following important particulars:

(1) It does not follow a narrow trajectory, but pervades the atmosphere over an area.
(2) It may be instantaneous in action, or persist for periods of from a few minutes to as many weeks, depending upon the type of gas used.
(3) It readily turns corners, flows into depressions in the ground and penetrates into every nook and cranny in the area covered. It thus searches out and reaches defiladed and protected target areas, such as deep trenches, field fortifications and dense woods which cannot be reached with impact weapons.

[1] In general, the matters outlined in this chapter are based upon world-wide developments and do not reflect the situation in any particular country.
The author does not presume to set forth the official views of his government upon any of the matters discussed, and he alone is responsible for the statements made herein. The views expressed are, therefore, solely those of the author and are in no sense official.

(4) It affects *equally* all persons in the area covered, whereas impact weapons may kill or wound one person and not harm another standing next to him. With gas, *all* within reach will be equally affected, depending upon the strength of the gas and time of exposure.
(5) It produces a great variety of effects, depending upon the particular kind of gas employed. Thus, the effect produced by gas may be varied all the way from simple lacrimation to almost instant death. This permits a wide latitude in adjusting the blow to conform to the objective sought. With impact weapons, no such control of the resulting effects is possible.
(6) It has a far greater coverage than any impact weapon and, pound for pound, produces from four to five times the number of casualties; however, the fatalities are only about one-twelfth of those produced by impact weapons.[2]
(7) It exerts a profound psychological effect, often far greater than its actual physiological effect, especially upon those who do not understand its mode of operation. This is an important factor in battle and adds greatly to the power of gas as a weapon.

Because of its peculiar properties, as indicated above, gas is used against military forces:

(1) To produce widespread (but non-fatal) casualties, thus reducing the enemy's effective strength and increasing his burden of maintenance by forcing him to take care of large numbers of non-effective troops.
(2) To reduce the enemy's mobility and fighting power by forcing his troops to wear masks, which retards their rate of march, diminishes their marksmanship, and lowers their physical stamina.
(3) To force the evacuation of strong points and to deny critical ground to the enemy by contaminating it with persistent gas.
(4) To produce a psychology of fear and anxiety, by constant uncertainty as to the possible appearance of a new and more powerful gas, against which existing protective measures are ineffective.

When skilfully used, gas enables a military commander to accomplish his mission with a minimum loss in men and material.

Gas may also be employed behind the battle front: (1) to retard or arrest industrial production and commercial activities; (2) to render unfit for use, food and other supplies necessary to the conduct of the war; and (3) to terrorize the civil population by causing widespread disablement, discomfort and fear, with a view of lowering the morale of the people and thus bring about a will to compromise or surrender.

TYPES OF MILITARY GASES

Classification—Military gases used to date may be divided into five general classes, according to their principal physiological effect as follows:

I. Lacrimators, which produce lacrimation and temporary inability to see; effects last only a few minutes after removal from presence of gas.

[2] Prentiss, A. M., "Chemicals in War," pp. 658 and 670, McGraw-Hill Book Co, New York (1937).

Examples: Bromacetone (CH_3COCH_2Br)
Ethyliodoacetate ($CH_2ICOOC_2H_5$)
Brombenzylcyanide ($C_2H_5CHBrCN$)
Chloracetophenone ($C_6H_5COCH_2Cl$)

II. Lung Injurants, which produce serious disability by damage to the lungs and pulmonary system; in severe cases, death from edema of the lungs results.

Examples: Phosgene ($COCl_2$)
Diphosgene ($ClCOOCCl_3$)
Chlorpicrin (CCl_3NO_2)
Ethyldichlorarsine ($C_2H_5AsCl_2$)

III. Systemic Toxics, which exert a general systemic poisoning action, usually resulting in death from paralysis of the central nervous system.

Examples: Hydrocyanic acid (HCN)
Cyanogen chloride ($CNCl$)
Cyanogen bromide ($CNBr$)
Hydrogen sulfide (H_2S)

IV. Vesicants, which produce blisters and burns on any surface of the body with which they come in contact; serious disability and occasional deaths (2 to 3 per cent) result from inhalation of the vapor.

Examples: Mustard gas ($S(CH_2CH_2)_2Cl_2$)
Lewisite ($ClCHCHAsCl_2$)
Phenyldichlorarsine ($C_6H_5AsCl_2$)
Methyldichlorarsine (CH_3AsCl_2)

V. Respiratory Irritants, which produce an irritation of the respiratory passages and cause coughing and vomiting; effect is temporary.

Examples: Diphenylchlorarsine ($(C_6H_5)_2AsCl$)
Diphenylcyanarsine ($(C_6H_5)_2AsCN$)
Diphenylamine chlorarsine ($(C_6H_4)_2NHAsCl$)
Ethylcarbazol ($(C_6H_4)_2NC_2H_5$)

In addition to the above classifications with respect to physiological effects, **military gases** are also divided into two general categories with respect to their persistence or duration of action in the field as follows:

(1) *Non-persistent gases,* which are generally volatile liquids that are rapidly converted into gases and smokes and continue to be effective only until dissipated by dilution with the surrounding air.
(2) *Persistent gases,* which are generally non-volatile liquids or solids that continue to give off vapors for a considerable period until completely vaporized.

As a rule, chemical agents which remain in effective concentrations in the field for less than 10 minutes after release are classed as non-persistent, while those which persist for more than 10 minutes are classed as persistent.

Examples:

Non-persistent Gases	*Persistent Gases*
Chloracetophenone	Bromacetone
Phosgene	Ethyliodo acetate
Diphosgene	Brombenzyl cyanide
Hydrocyanic acid	Chlorpicrin
Cyanogen chloride	Mustard gas
Diphenylchlorarsine	Lewisite
Diphenylcyanarsine	Methyldichlorarsine

Properties of Military Gases—Table 1 shows the principal properties of the more important military gases that have been used to date.

REQUIREMENTS FOR MILITARY GASES

Characteristics of Military Gases—Before a chemical substance can qualify as a military gas it must meet a large number of exacting, and often conflicting, requirements. These requirements may be conveniently grouped into two general categories, as follows: (1) *Technical Requirements*, or the essential qualities which chemical agents must possess in order that they may be manufactured in the form of chemical munitions in sufficient quantities to meet the vast demands of modern war; and (2) *Tactical Requirements*, or those properties which chemical agents must have in order to exert the effects desired in battle.

TECHNICAL REQUIREMENTS

Raw Materials—Since military gases, to be effective, must be used in enormous quantities, the question of availability of the *raw materials* from which these gases are made should receive first consideration. Thus, it is obvious that no matter how militarily effective a chemical substance may be, it should not be adopted as a military gas unless it can be made in sufficient quantities from raw materials that are available under war conditions. If one or more ingredients required for the manufacture of a war gas cannot be procured in sufficient quantities from domestic sources, dependence must be placed on importation from foreign countries, since it is seldom possible for a government to acquire in time of peace a sufficient stock of raw materials to last throughout the duration of a war, except for certain critical materials which are needed in relatively small quantities and are stable in long storage.

In connection with imported raw materials, there must always be borne in mind the all important question of the control of the seas in time of war. If a nation at war does not have control of the seas over which its imports are borne, it cannot count upon being able to secure raw materials from other countries. And so, while foreign raw materials may be feasible for the manufacture of commercial products in time of peace, they cannot safely be used as a basis for the production of military munitions in time of war. We may, therefore, lay down as a first requirement that the raw materials for a military gas must be available from domestic sources. This at once rules out a vast number of possible chemical agents, depending upon the extent of the domestic resources of the country.

Ease of Manufacture—The next most important technical requirement is ease of manufacture. Most military gases are relatively complex organic compounds, the synthesis of which is a highly specialized and sometimes difficult operation. The more complicated the chemical process, the more highly skilled is the personnel required, and the more complex and specialized is the equipment needed, for production. Such personnel and equipment is extremely difficult to obtain in time of war when the whole industrial machinery is in high gear to meet mobilization demands. Moreover, simple syntheses can be completely performed in one plant, thus avoiding transfer of intermediates from one place to another, with the attendant confusion and difficulty of coordinating production. Hence, ease of production is one of the most important factors in selecting a war gas.

Chemical Stability—Another important requirement which a successful military gas must meet is chemical stability under all conditions of storage. Compounds which react with iron cannot be stored in steel tanks nor loaded into steel shells, bombs, or other projectiles, without providing special protective linings for all such containers. Such substances are, therefore, generally unsuitable as war gases, no matter how excellent their other properties may be. Compounds which decompose on long standing, or which polymerize into forms having unsuitable physical and physiological properties, are also obviously unsatisfactory as military gases.

Another form of chemical instability which militates against the effectiveness of chemical substances for combat purposes is hydrolysis. Compounds which react readily with water quickly break down when released in a moist atmosphere and thus become largely ineffective. Also hydrolysis on contact with water seriously complicates the process of loading into munitions and storage, since special precautions have to be taken to exclude moisture during the loading operation and while in storage.

Resistance to Dissociation—Of hardly less importance than chemical stability is the capacity of a compound to withstand the heat and pressure of explosion without dissociation, when dispersed from artillery shells, aircraft bombs and other projectiles. To the extent that a chemical agent is dissociated by the heat and pressure of explosion, to the same extent is its efficiency as a war gas reduced; while substances that are seriously so decomposed are wholly unsuitable for military purposes. The same is true of decomposition by inflammability, since if a chemical filling ignites when the shell explodes, it is largely consumed by the flames and its toxic effect is lost. So a chemical agent must be able to withstand the high temperatures and pressures of explosion without dissociation by burning.

Other factors affecting the suitability of a chemical substance as a military gas are:

(1) Physical state, i.e., solid, liquid, or true gas
(2) Boiling point
(3) Melting point
(4) Specific gravity

Physical State—Of the three physical states, solids are preferred for those chemical agents that are used in shells and bombs, since the complete cavity of the projectile can be filled with a solid while a void must be left for expansion with a liquid. Also, solid filled gas projectiles have the same ballistic characteristics as high explosive shells, whereas liquid filled shells do not. Chemicals which are most effective in the form of cloud gas, or are best distributed by spraying, should be liquids at ordinary temperatures. Chemical substances in a gaseous state at ordinary temperatures are the most difficult to handle as they must be loaded into containers under high pressures or low temperatures, necessitating heavy wall containers and high pressure joints.

Boiling and Melting Points—From a manufacturing and loading viewpoint, chemical substances that are liquids with boiling points well above maximum summer temperatures are far less difficult to handle, and in general the higher the boiling point the better. Similarly the melting point of a solid substance should be above ordinary summer temperature so that the substance will not change its physical state with changes of atmospheric temperature. This not only makes for uniformity of ballistic effects and dispersion in artillery shell, but also renders the shell filling operation less complicated.

Finally, the specific gravity of a chemical is important, in that the heavier the substance the greater the mass that can be loaded into a given space (as in a shell). In general, therefore, the heavier the substance the better as a chemical agent.

TACTICAL REQUIREMENTS

Persistency—Unlike the technical requirements which are the same for all types of gases, the tactical requirements differ in some properties, depending upon the tactical use for which they are to be employed. Thus, when gas is to be used on the tactical offensive, where friendly troops expect to move forward on ground held by the enemy, it should be non-persistent, so that it may be employed in aid of the advancing infantry and dissipated before friendly troops reach the gassed area. On the other hand, when gas is to be used on the tactical defensive, it should be as persistent as possible, so that it may be laid down in heavy concentrations in critical areas over which the enemy must advance to the attack and serve as effective barriers for as long a time as possible. Likewise harassing gases, used to force enemy troops to mask and thus reduce their combat efficiency, should be as persistent as possible, for maximum effectiveness.

And so, while the requirement as to persistency varies with the tactical situation in which gas is to be used, it may be said that in general offensive war gases should be non-persistent, while defensive and harassing war gases should be as persistent as possible.

Toxicity—Probably the most important requisite of a casualty-producing gas is high toxicity. Since the casualty effects of such gases are in direct proportion to their toxicities, it follows that the more toxic the gas, the more effective it is as a chemical agent. Stated in another way, we may say that in proportion as its toxicity increases, the same casualty results can be secured with decreasing quantities of a gas and with shorter periods of exposure. As toxicity is the most important tactical requirement of a military gas, the search for a new and more powerful gas usually begins by an investigation of its toxic power.

Vapor Density—Of almost equal importance with toxicity is the vapor density, or weight of a gas as compared to air. Since military gases act on personnel which are generally on the surface of the ground, only the layer of gas extending not above the heads of standing men (i.e., about 6 feet high) is effective in producing casualties. If a military gas does not have a vapor density greater than air, it will immediately rise from the surface of the ground upon release from its container and become largely ineffective. Hence, it is imperative that all non-persistent gases be heavier than air, and it is almost as important that persistent gases also have vapor densities greater than air, as otherwise excessive loss of vapor into the upper air will largely nullify the effectiveness of the gas.

In general, the heavier the gas, the better it clings to the ground and rolls into depressions, thus exerting a more extensive and lasting effect upon troops taking shelter in such places. Hence, we may say, the heavier the gas the better.

Multiple Effects—Another important consideration in selecting a war gas is the manner in which it acts upon the human body. Many gases have only a single effect, as for example the lacrimators, which act only on the eyes and have no other effect. Other gases have dual effects. Thus, chlorpicrin is both a lung injurant gas and a lacrimator, so that both the eyes and lungs must be protected from this agent. Still other gases, such as mustard, have a triple effect, being a vesicant, lung injurant and lacrimator combined. It is obvious that as the number of effects of a chemical agent increases, the difficulty of providing adequate protection against it correspondingly increases, and its value as a war weapon is similarly enhanced. So we may say that multiple effects are one of the most important properties of a war gas.

Duration of Effects—Hardly less important than multiplicity of action is the duration of the effects produced by a war gas. Since the primary object of modern warfare is to inflict upon the enemy the maximum number of serious, but non-fatal casualties, it follows that those chemical agents that produce the most lasting effects are the most efficient, other things being equal.

Speed of Action—The next most important tactical requirement is speed of action. Some chemical agents act with great rapidity in producing effects upon the human body, while others act very slowly and their effects are not felt until several hours after exposure. It is obvious that the quicker a military gas produces its effect, the sooner it secures the desired results in battle. In modern combat, attacks are launched with great rapidity and may last only a few minutes, hence gases intended for casualty effects on the offensive must necessarily be quick acting. For defensive situations, slower acting gases may be used, but even so, rapidity of action in producing incapacitating effects is advantageous.

Insidiousness—If a gas produces its incapacitating effects with no warning discomfort during the necessary period of exposure, it will exert its full casualty effect before protective measures can be taken. Hence, insidiousness of action is a valuable attribute of a military gas, and the slower acting the gas, the greater is the need for insidiousness in action.

Volatility—The volatility of a chemical agent determines the maximum concentration that can exist in the open air at a given temperature; it also largely measures the persistency of the agent. Hence, volatility is an important requirement of a war gas. In general, liquids with low boiling points and high vapor pressures build up much heavier concentrations in a given volume of air than liquids with high boiling points and low vapor pressures It is imperative that the volatility of a gas be such that it can develop a concentration in the open air, at ordinary temperatures, at least above the minimum lethal dose (i.e., the minimum concentration required to produce death or serious casualties); otherwise the gas in practical effect is non-toxic from a military viewpoint.

Penetration—The degree to which gas penetrates masks, protective clothing and other means of chemical defense, often measures its effectiveness in battle, therefore the penetrability of a gas is an important factor in its tactical value.

Invisibility and Odorlessness—Akin to insidiousness in action are the properties of invisibility and odorlessness, since gases possessing these properties are far more difficult to detect when present and are more apt to take the enemy by surprise. Hence, the more nearly a gas is invisible and odorless, the more valuable it is as a chemical agent.

REQUIREMENTS FOR IDEAL MILITARY GAS

Having now reviewed the principal properties and characteristics of military gases, we may summarize this subject by stating the requirements of an ideal war gas, as follows:

Technical Requirements

1. Availability of raw materials (from domestic sources).
2. Ease of manufacture.
3. Chemical stability.
4. Nonhydrolyzability.
5. Ability to withstand explosion without decomposition.
6. A solid or liquid at ordinary temperatures.
7. Melting point above ordinary atmospheric temperature.
8. Boiling point as low as possible.
9. High vapor pressure.
10. Specific gravity approximately 1.5.

Tactical Requirements

1. High toxicity.
2. Vapor density heavier than air.
3. Non-persistency, or persistency, depending upon use.
4. Multiple effects.
5. Durability of effects.
6. Speed of action.
7. Insidiousness in action.
8. Volatility (maximum field concentration).
9. Penetrability.
10. Invisibility.
11. Odorlessness.

WORLD WAR EXPERIENCE

Because of the many exacting requirements mentioned above, only a few of the many thousands of toxic substances possess the necessary properties to qualify them as successful chemical agents. The number of chemical compounds which have been studied to the extent that their principal properties are known, are well over 200,000 and it is safe to say that there are many thousands of compounds that exert sufficient deleterious effect upon the human body to be classified as toxic substances. From this vast field, the great majority of compounds can be eliminated as possible military gases by an inspection of their known properties in comparison with those required to qualify them as chemical agents. The field of search is thus greatly delimited but is still vast. From this field, over 3,000 compounds were selected and investigated by the Allies for use as chemical agents during the World War. Of this group, only about 30 were found suitable for actual use in the field; about 12 were finally adopted and used to any extent in battle; and not over 6 proved to be notably successful.

German research and development added considerably to the number of compounds investigated, and again not over 8 or 10 proved to be really worth while on the field of battle. However, those gases that were successful achieved a truly remarkable record, notwithstanding lack of prior development, and very crude weapons and methods of use. Gas caused nearly one-third of the non-fatal American casualties in the World War, and on the basis of ratio of casualties to military effort, *gas was from four to five times more effective* than the average of the military weapons used in the war.[3]

FUTURE DEVELOPMENT OF CHEMICAL WARFARE

Despite its proven effectiveness in the World War, chemical warfare was not developed to a point where it realized more than an infinitesimal part of its possible powers. Thus, it is known that 20 milligrams of mustard gas, when inhaled into the lungs, is sufficient to cause death. On this basis, one ton of mustard gas has enough inherent toxic power to kill 45,000,000 men, yet actually there was only an average of 33 casualties from each ton of mustard gas used in the World War, and of these only about 2 per cent died. From this, it is obvious that much great effectiveness may be expected from the use of chemicals in war, especially in view of the vast improvement that has been achieved during the past twenty years in chemical weapons, tactics and technique. Nor is it improbable that new and more powerful gases will be discovered and more efficient methods developed for utilizing them in war.

MANUFACTURE OF MILITARY GASES

General—With the single exception of chlorine, all gases that have heretofore been used, or are likely to be used, in chemical warfare are organic compounds. The manufacture of military gases is, therefore, essentially a problem of applied organic chemistry. It is, moreover, a highly specialized field in which the paramount considerations differ to a marked degree from those underlying the manufacture of commercial organic chemicals. Thus, in the commercial manufacture of chemical products, economic considerations are of primary importance in that they directly affect the cost of production and largely control the success or failure of the business from the competitive viewpoint.

On the contrary, cost of manufacture is very definitely not a primary consideration in the production of war munitions, and hence, does not enter very seriously into the problem of manufacturing military gases.

The paramount considerations in the production of munitions in time of war are speed, simplicity and safety of operation and certainty of output. Speed in processing is essential to rapid production of the enormous quantities of materials

[3] See Prentiss, A. M., "Chemicals in War," p. 658, McGraw-Hill Book Co., New York (1937).

required in war, and simplicity of operation is desirable to enable production to be organized and quickly expanded by those having ordinary skill in the art, so that highly specialized personnel, difficult to procure on short notice and requiring long training, are unnecessary.

Most war gases are very dangerous to work with and the safety of those employed in these operations demands that every possible step be taken to guard against the leakage of gas and the occurrence of accidents during the processes of manufacture. As between two processes having the same general efficiency, one being less dangerous but more expensive to install and operate, as compared to another more dangerous but less expensive, there is no question of choice. The safety of the plant personnel demands the less dangerous, regardless of its greater cost.

Finally, certainty of output is imperative and this demands uninterrupted flow of raw materials and the constant availability of equipment required in the processes of production.

Manufacturing Processes—Space does not permit a consideration of the methods used in manufacturing all of the well-known war gases, but the process of manufacture of one gas typical of each group mentioned on page 1260 is described below, as illustrative of the problems involved and the methods used.[4]

Manufacture of Chloracetophenone (Tear Gas)—The manufacture of chloracetophenone is a commercial application of the Friedel and Crafts synthesis[5] of an aromatic ketone. This synthesis consists of the reaction between an aromatic hydrocarbon and an aliphatic acid chloride in the presence of anhydrous aluminum chloride. Acetophenone, for example, is made by treating benzene with acetyl chloride which is formed from acetic acid. To make chloracetophenone, a halogen derivative of acetophenone, it is necessary to use a chlorinated acid chloride, i.e., chloracetylchloride, which is obtained from chloracetic acid.

The raw materials required are: (1) glacial acetic acid (CH_3COOH); (2) commercial chlorine; (3) sulfur; (4) benzene (C_6H_6); and (5) steam. In addition, two catalysts are necessary: (1) zinc chloride ($ZnCl_2$); and (2) anhydrous aluminum chloride ($AlCl_3$).

The steps in the process for the manufacture of chloracetophenone are four in number, as follows:

1. The chlorination of sulfur to obtain sulfur monochloride:

$$2S + Cl_2 = S_2Cl_2$$

2. The chlorination of acetic acid to obtain monochloracetic acid:

$$CH_3COOH + Cl_2 \rightarrow CH_2Cl \cdot COOH + H \cdot Cl$$

3. The treatment of monochloracetic acid with sulfur monochloride, in the presence of zinc chloride catalyst, to obtain chloracetylchloride:

$$4CH_2Cl \cdot COOH + S_2Cl_2 + 3Cl_2 \xrightarrow{(Zn \cdot Cl_2)} 4CH_2Cl \cdot COO \cdot Cl + 2SO_2 + 4HCl$$

[4] Book II of the texts of The Chemical Warfare School, U. S. Army, Sec. V, Chapter III.
[5] For an outline of this type of reaction see Chapter 27.

4. The treatment of chloracetylchloride with benzene, in the presence of aluminum chloride (catalyst) which gives chloracetophenone:

$$C_6H_6 + CH_2Cl \cdot COO \cdot Cl \xrightarrow{(Al \cdot Cl_3)} C_6H_5COCH_2Cl + HCl$$

(See Figure 1)

The first step, the formation of sulfur monochloride, is carried out by dissolving the sulfur in a quantity of sulfur monochloride, previously prepared by the

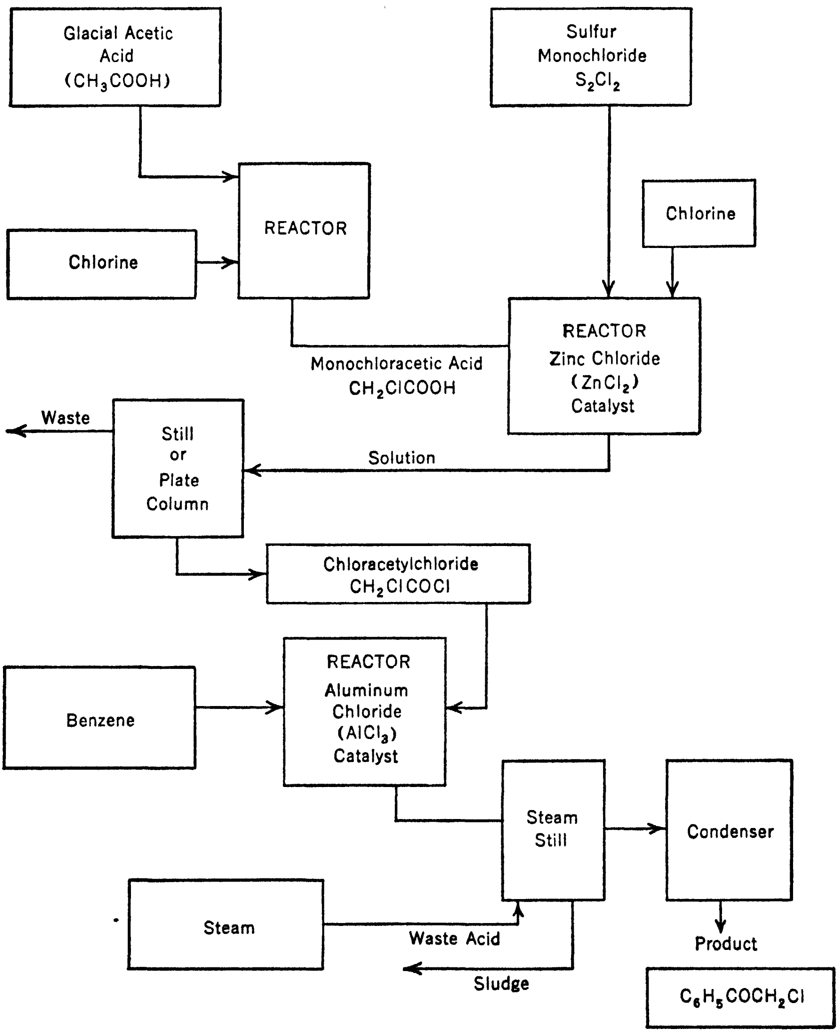

FIG. 1. Flow Sheet for the Manufacture of Chloracetophenone.

direct union of its elements, and then passing the chlorine into this solution at a temperature between 10° and 58° C. The operation is continuous, but must be carefully controlled, since, if the sulfur and chlorine are not added in the proper proportions, either some sulfur dichloride is formed (S_2Cl_4), if chlorine is in excess, or the liquid may contain unchanged (dissolved) sulfur, if not enough chlorine is used.

The second step, the manufacture of monochloracetic acid, is carried out in a lead-lined jacketed still. The pot is charged with glacial acetic acid; steam is allowed to enter the jacket and the contents of the still heated up to 98° C.; and the chlorine let in for three hours.[6] This is sufficient time for the completion of the reaction. Whatever liquor distillate has passed over and through the condenser runs back to the still so that nothing actually has left the charge except the hydrochloric acid formed during the reaction.

From this first still the chloracetic acid is blown to a second of similar design. Into this is charged also known weights of sulfur monochloride (S_2Cl_2). The mixture is heated to 45° C. and the further chlorine added in exactly the same manner as in the first still. The gases of this reaction, sulfur dioxide and hydrogen chloride, are absorbed in a tower. Following the completion of chlorination, the charge, consisting now of chloracetylchloride, sulfur chloride, zinc chloride (used as a catalyst) and some unchanged monochloracetic acid are blown to a third still, for separation by fractional distillation.

The final step in the formation of chloracetophenone is the treatment of benzene with chloracetylchloride in the presence of anhydrous aluminum chloride. A known quantity of benzene is put into an enamel-lined reactor together with the aluminum chloride and to it is added a known weight of chloracetylchloride, maintaining the temperature at 25° C. during the addition which takes about one and one-half hours. The whole mass is agitated during the mixing. Following the addition of the latter, the mass is heated up to 60° C. for about two hours, which suffices for the completion of the reaction. A valve in the bottom of the apparatus is now opened and the material is quenched in water. When this is done, the mixture is run into a separator, where two layers form. One of these, the lower, consists of an aqueous solution of aluminum chloride, while that above is a solution of chloracetophenone in benzene. By means of sight glasses, it is possible to effect a separation, the water solution being run into the sewer while the other is sent to an enamel-lined still for purification and separation of the benzene. The benzene is simply distilled off, dried by means of calcium chloride tubes and returned to storage tanks for further use. Chloracetophenone was formerly distilled in vacuo but the vacuum distillation has now been replaced by steam distillation.

Manufacture of Phosgene (Lung Injurant)—The simplest and most direct method of producing phosgene, and the one chiefly employed during the First World War, consists of the direct union of carbon monoxide (CO) and chlorine gas in equimolecular proportions, thus:

$$CO + Cl_2 = COCl_2$$

The new materials required for this process are: (1) air; (2) coke; and (3) chlorine. In addition, animal charcoal is used as a catalyst, while potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4) are

[6] For a discussion of the principles of chlorination see Chapter 3.

needed for absorbing CO_2, for scrubbing and drying oxygen, and for drying phosgene.

The principal steps in the process of manufacturing phosgene are as follows:

1. The oxidation of carbon to form carbon dioxide: [7]

$$C + O_2 \rightarrow CO_2$$

2. The liquefaction and distillation of air to separate out the oxygen:

$$\text{Air} \rightarrow O_2 + N_2$$

3. The reduction of carbon dioxide to carbon monoxide by combining with carbon: [7]

$$CO_2 + C = 2CO$$

4. The combining of carbon monoxide with chlorine, in the presence of animal charcoal as a catalyst:

$$CO + Cl_2 = COCl_2 \text{ (See Figure 2)}$$

At high temperatures, phosgene dissociates into chlorine and carbon monoxide, and since the reaction is reversible, it is clear that the combination of the two gases under the conditions given is incomplete. Hence, the gases coming from the first series of reaction chambers (called "hot catalyzers") and containing about 85 per cent phosgene, are cooled and then led into a second series of reaction chambers. These are constructed like the first series, and also contain "Filtchar" but are made of lead instead of iron, since they are cooled by being immersed in tanks of cold brine, and lead resists corrosion better than iron. These boxes are called the "cold catalyzers" and the temperature at which they operate is about 95° C.

The resulting gas mixture, containing about 93-94 per cent of phosgene, is dried by means of sulfuric acid. After drying, the gases are cooled to −20° C. At this temperature the phosgene vapor is largely condensed to liquid which is run from the condensers directly to steel containers.

Manufacture of Mustard Gas (Vesicant)—Two general methods for the manufacture of mustard gas were used during the World War.

The Germans manufactured it by the original method by which it was first developed in the laboratory. This consisted of the treatment of ethylene chlorhydrin (ClC_2H_4OH) with sodium sulfide (Na_2S) which formed sodium chloride and thiodiglycol, $S(CH_2CH_2OH)_2$ and the latter was then heated with hydrochloric acid which formed water and mustard gas.

This method was rather complicated and, furthermore, involved the manufacture of the rather unstable ethylene chlorhydrin. Hence, the Allies set out to develop a better method, and found that mustard gas can be obtained by the direct interaction of ethylene with sulfur monochloride, S_2Cl_2, thus:

$$2C_2H4 + S_2Cl_2 = S(CH_2CH_2Cl)_2 + S$$

The only raw materials required for this process are ethyl alcohol, sulfur and chlorine.

[7] For the apparatus and methods used to produce CO, see Chapter 19.

Both of the intermediates necessary for this reaction (ethylene and sulfur monochloride) can be made quite easily with good yield, and are stable. The ethylene is a colorless, inflammable gas, having a faint, rather pleasant odor,

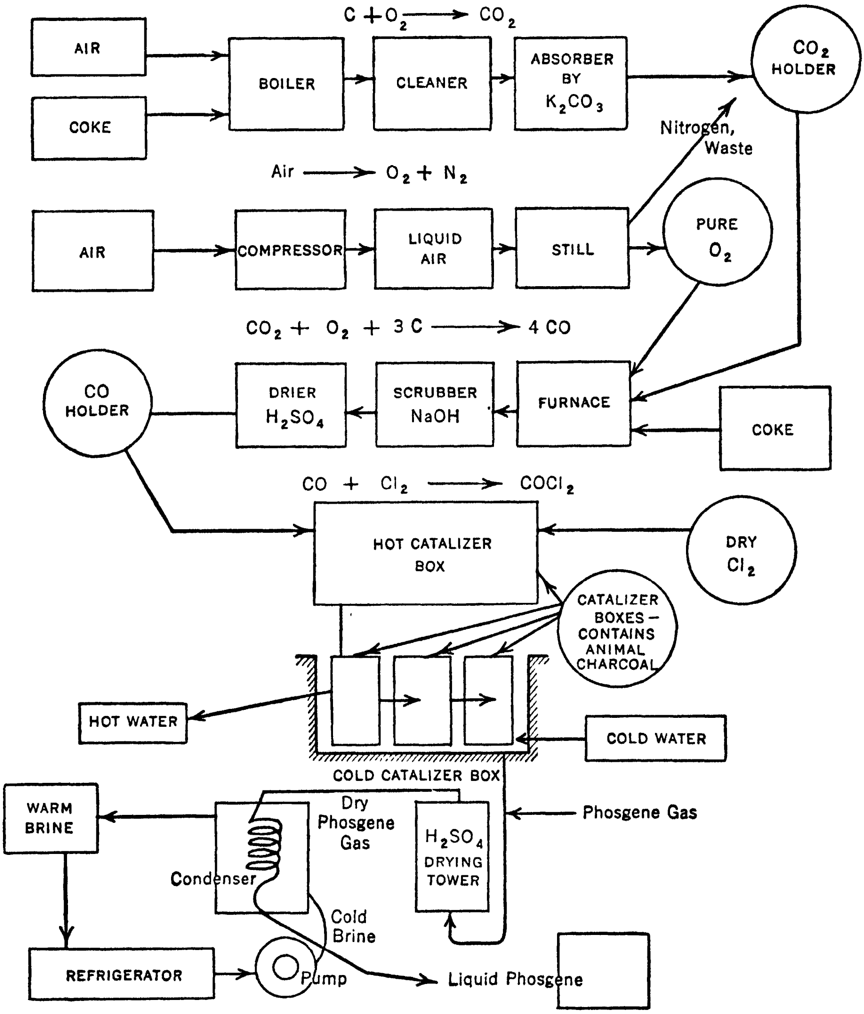

FIG. 2. Flow Sheet for the Catalytic Manufacture of Phosgene.

while the sulfur monochloride is a rather heavy (sp. gr. = 1.705) dark yellow, oily liquid, having a penetrating, disagreeable odor, and boiling at 138° C.

We will first consider, briefly, the manufacture of these materials.

Ethylene, C_2H_4, is obtained from ordinary grain alcohol by splitting off water, thus:

$$C_2H_5OH = C_2H_4 + H_2O$$

This is accomplished by merely heating the alcohol in the presence of some dehydrating agent, such as sulfuric acid or phosphoric acid, but it has been found that the same change occurs, at elevated temperatures, in the presence of a catalyst, such as "Kaolin" or china clay.

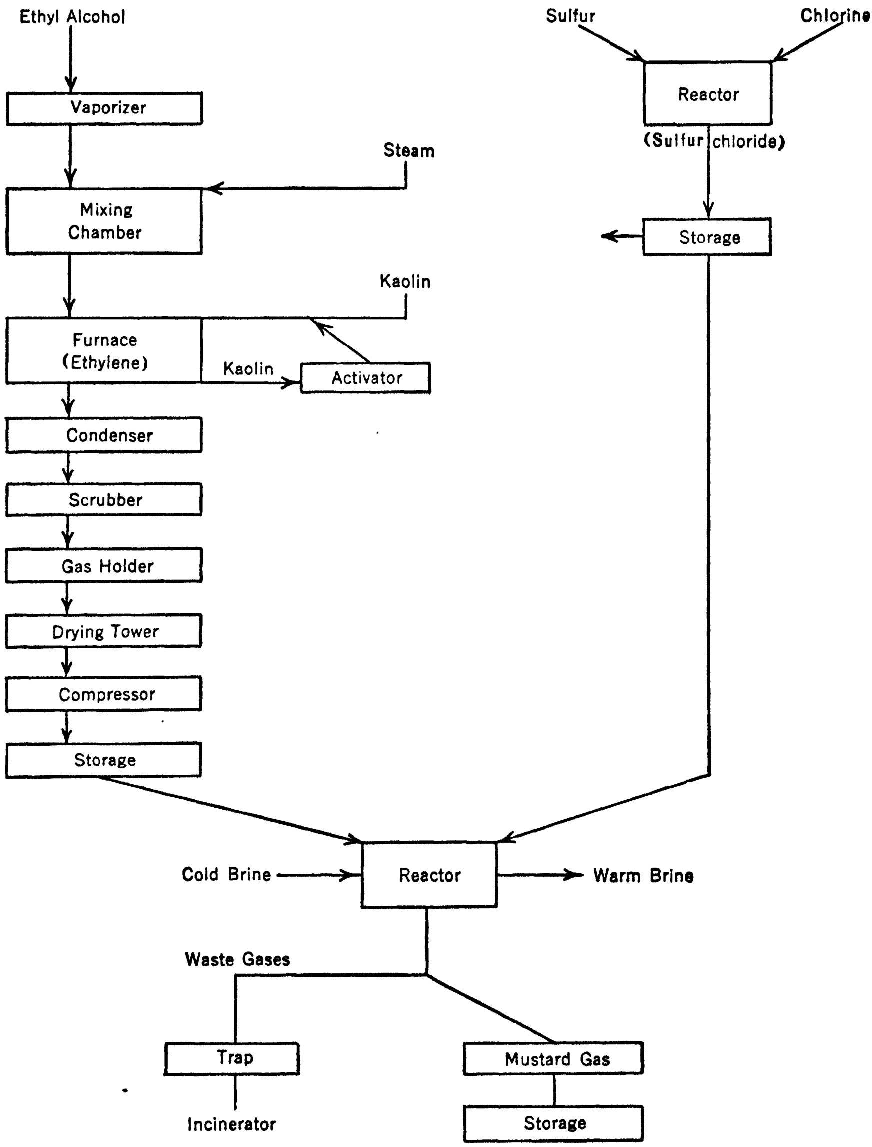

FIG. 3. Flow Sheet for the Manufacture of Mustard Gas. Levinstein Process.

The kaolin, in the form of cylindrical pellets, is placed in the annular space between an upright iron pipe and a central core and the whole is heated by a gas or oil burner, to a temperature of about 550° C. The alcohol, in the form of vapor mixed with an equal volume of steam, is introduced at the bottom of this apparatus and the products, including some unchanged alcohol, leave at the top. The pellets of kaolin gradually become coated with carbon, due to the charring of some of the alcohol, and thus gradually lose their power to catalyze the above reaction. The steam helps to increase the "life" of the catalyst (and hence its use) but it does not entirely prevent the charring of the alcohol. Consequently, the kaolin must be renewed from time to time. The carbonized kaolin is removed at the bottom of the furnace while fresh kaolin is added at the top, the two operations being carried out without interrupting the operation of the furnace. The carbonized kaolin can be decarbonized or "revivified" by heating it in a kiln in a stream of air or oxygen to a temperature of about 800° C.

The mixture of ethylene gas, steam and alcohol which comes from the upper part of the furnace is cooled to condense the steam and alcohol, the latter being recovered and used in another operation. The ethylene gas is then passed through a scrubbing tower where it is washed with water, after which it is dried by contact with concentrated sulfuric acid. After this the ethylene, which should have a purity of about 95 per cent or more, is ready to be used for the manufacture of mustard gas. (See Figure 3.)

Ethylene may also be obtained by fractional distillation under pressure of waste oil refinery gases which normally contain about 20 per cent ethylene.[8]

Sulfur monochloride is obtained by the same process as previously described under the manufacture of chloracetophenone.[9]

The reaction between the sulfur monochloride and ethylene can be carried out in different kinds of apparatus and under varying conditions. The method generally used is known as the "Levinstein Process."

In the Levinstein process a small amount of a mixture of 75 per cent of crude mustard gas and 25 per cent of sulfur monochloride is run into a lead-lined, jacketed kettle of special design, provided with a stirring device and two sets of cooling coils within it to insure very thorough control of the temperature. In this process the temperature is not permitted to rise above 35° C. but is kept between this point and 30° C. Ethylene is then passed in, and as the sulfur monochloride is converted into mustard gas, more sulfur chloride is added from time to time. Since the best absorption of ethylene is obtained when the liquid in the reaction vessel contains about 20-30 per cent sulfur monochloride, the latter is added in such amounts as to maintain approximately this concentration. When the size of the total charge has reached the capacity of the kettle, the addition of sulfur chloride is discontinued but the ethylene is passed in until there is no further absorption.

The purity of the product usually ranges from 74 per cent to 89 per cent, the melting point varying from 5° C. to 10° C.

In all this work, of course, all equipment, instruments, etc., which have to be handled by the workmen engaged in the manufacture or handling, must be kept clean and free from mustard gas to prevent casualties. This can generally be accomplished by washing with a solution of bleaching powder.

Manufacture of Diphenylaminechlorarsine (Respiratory Irritant)—The manufacture of this chemical agent is comparatively a very simple process. The

[8] See Chapter 14.
[9] See p. 1268.

fundamental reaction for the manufacture of this agent is the interaction of diphenylamine and arsenic trichloride, according to the equation:

$$(C_6H_5)_2NH + AsCl_3 \rightarrow NH(C_6H_4)_2AsCl + 2HCl$$

Diphenylamine [10] is a common intermediate widely used in the dye industry and is obtained from commercial sources.

Arsenic trichloride is made by the action of hydrochloric acid on arsenic trioxide according to the equation:

$$As_2O_3 + 6HCl \rightarrow 2AsCl_3 + 3H_2O$$

This reaction is reversible and it is, therefore, necessary to displace the equilibrium by removing the water formed during the reaction. This is done by adding concentrated sulfuric acid in appropriate amounts.

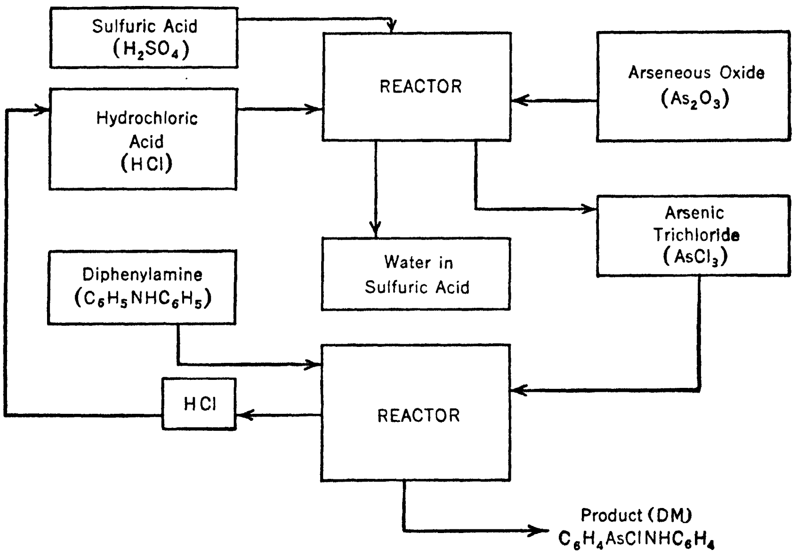

FIG. 4. Flow Sheet for the Manufacture of Diphenylaminechlorarsine.

The raw materials are: (1) diphenylamine; (2) sulfuric acid; (3) arseneous oxide; and (4) hydrochloric acid.

The plant process is as follows: 81 pounds of arsenic trioxide and 300 pounds of hydrochloric acid are heated for one hour in a jacketed reaction kettle equipped with a reflux condenser. The mixture is then blown into another kettle fitted with brine coils and is cooled to 0°. Concentrated sulfuric acid is cautiously added and the mixture agitated by blowing air through it. The arsenic trichloride is drawn off as a nearly colorless liquid. The yield is about 80 per cent.

The arsenic trichloride and diphenylamine are heated together in a jacketed kettle, which is equipped with a reflux condenser and an agitator. (See Figure 4.)

The diphenylamine is put in first and heated to a temperature of 160° C. at which temperature it is melted. The arsenic trichloride is then added and the

[10] See compound 239, Chapter 27 and Chapter 28.

heating is continued for five hours, during which time the temperature gradually rises to 250° C. During the course of the reaction, large amounts of hydrochloric acid gas are evolved, which pass through the reflux condenser and are absorbed by water in an absorption tower. When the reaction is finished, this agent is blown into a vat of water in which it is insoluble. It is washed twice with water, centrifuged and finally dried at 30° C. The yield is about 80 per cent.

A modification of the above method of manufacturing diphenylaminechlorarsine, which considerably shortens the process, was recently worked out by Professor Contardi, an Italian chemist. In this modification, the preparation of diphenylamine is carried only halfway to the formation of diphenylaminehydrochloride. Contardi discovered that diphenylaminehydrochloride is almost completely dissociated at temperatures above 100° C. into diphenylamine and hydrochloric acid. If arsenic trioxide is added, it reacts with the dissociated hydrochloric acid forming arsenic trichloride which then reacts with the dissociated diphenylamine forming diphenylaminechlorarsine, according to the following equation:

$$2(C_6H_5)NH \cdot HCl + As_2O_3 \rightarrow 3H_2O + 2C_6H_4\left\langle\begin{matrix} NH \\ AsCl \end{matrix}\right\rangle C_6H_4$$

The preparation of arsenic trichloride is therefore omitted.

The Contardi method consists of two steps only: (1) the preparation of diphenylaminehydrochloride by heating together a mixture of aniline and aniline hydrochloride; and (2) heating the product with arsenic trioxide, forming diphenylaminechlorarsine.

METHODS OF DISSEMINATING MILITARY GASES

General—When used in combat, military gases must be distributed in an effective form over a suitable target area. This distribution is termed "*Dissemination*" and comprises two processes: the delivering of the chemical agents to the target area, which is accomplished by "*projection*"; and the spreading of the chemicals over the target area in an effective state, which is accomplished by "*dispersion.*"

Means of Projection—The simplest means of projecting gas was that used in the beginning of gas warfare, namely, the cloud method, which consists of merely releasing a military gas, in true gaseous state, from a point as close as possible to the target area and letting the wind blow it over the target area in the form of a large gas cloud. Only chemical agents that are true gases or smokes, at ordinary atmospheric temperatures, such as phosgene and diphenylchlorarsine, can be employed in this method. With such agents, the cloud gas method of attack is simple and effective, but is wasteful of chemicals, since much of the gas is lost through diffusion and dilution before reaching the target area.

The next most simple means of projection is by the use of hand or rifle gas grenades. These are small missiles, holding a few ounces of gas, and are thrown, either by hand to a distance of about 30 yards, or by rifle to a distance of about 250 yards. As the amount of gas which can be projected by grenades is small, this method has only a limited use, and is employed chiefly by infantry for "mopping up" operations in trench warfare.

For projecting gases at longer ranges, a variety of mortars and guns are used. The most effective means of projection to a distance of 2500 yards is the chemical mortar. This is a light, mobile weapon employed by special chemical troops for putting heavy gas concentrations on favorable targets within its range. It fires a shell, weighing 25 pounds and holding about 7 pounds of gas, at a maximum rate of 20 rounds per minute. With its high mobility and great gas delivering capacity, it is one of the most efficient chemical weapons yet devised.

For longer ranges, gas is projected by artillery shell of all calibers from the light 75-mm. field gun to the heavy 155-mm. gun and 240-mm. howitzer. Owing to its small cubic capacity, the 75-mm. shell is generally used only for persistent gases such as mustard, as too many of these shells are required to establish effective concentrations with non-persistent gas. The larger calibers of artillery may be used for any type of gas, but here again, the long range guns are seldom employed for projecting non-persistent gas, as persistent gases are more effective for their normal missions of counter-battery and interdiction fires.

The most recently developed and generally effective means of projecting gas is the airplane. For this purpose two weapons are employed: the gas bomb and the gas spray. A gas bomb is very similar to a high explosive bomb, except it has a thinner casing and is opened by a small explosive charge. As a rule, small bombs (i.e., up to 100 pounds) are used for projecting persistent gas (mustard), since the object is maximum distribution over the target area, while large bombs (e.g., 300 pounds) are used for non-persistent gas (phosgene), since the object is maximum gas concentration. Because of their high carrying capacity and the almost unlimited range of aircraft, gas bombs are a most efficient and effective means of projecting gas.

The gas spray consists of one or two chemical tanks attached to the fuselage or wings of a plane and adapted to rapidly discharge their contents at the will of the pilot or operator. As there is a considerable evaporation loss while the liquid chemical is falling to the ground, only persistent liquid or solid gases can be effectively sprayed and then only at very low altitudes (50 to 100 feet). As a rule, low flying "attack" planes and light bombers are used to spray gas, and when properly employed, are capable of rapidly contaminating large areas. Thus, a single attack plane, carrying two 22½-gallon tanks, can, with one flight, spray an area about 1000 yards long by 200 to 300 yards wide, and the resulting concentration may cause as high as 90 per cent casualties among all unprotected personnel in the area. While not yet used in war, there seems little room for doubt that the gas spray is destined to become one of the most formidable methods of attack in modern warfare.

After chemicals have been delivered to the target area by any of the means of projection mentioned above, they are dispersed over the area by either a physical process, or a chemical process. The physical means of dispersion are: (1) mechanical force, as when a toxic dust is sprayed from an airplane; (2) heat, as when a chemical substance is distilled into the air from toxic smoke candles; and (3) a combination of force and heat, as when the contents of a gas shell are scattered by the explosion of its bursting charge.

The chemical means of dispersion consists of the reaction of two substances simultaneously discharged into the air in the presence of each other and which, by reaction, yield a liquid or solid compound in the dispersed state. Thus, gaseous hydrochloric acid and ammonia yield ammonium chloride in the form of a dense white fume. So far, chemical dispersion has been employed only in the distribution of non-toxic screening smokes, but there is no inherent reason why it cannot be also used for the dispersion of toxic chemicals and thus further enlarge the already formidable "materia chemica" of war.

READING LIST

AMERICAN

Prentiss, A. M., "Chemicals in War," McGraw-Hill Book Co., New York (1937).

Prentiss, A. M., "Civil Air Defense," McGraw-Hill Book Co., New York (1941).

Texts of the Chemical Warfare School, U. S. Army, Edgewood Arsenal, Md., Books I to VI.

"The Medical Department of the United States Army in the World War," Vols. XIV and XV, Government Printing Office, Washington (1926).

Gilchrist, H. L., "The Residual Effects of Warfare Gases": I, "Chlorine"; II, "Mustard"; III, "Phosgene"; IV, "Arsenical Compounds"; Government Printing Office, Washington (1933).

Underhill, F. P., "The Lethal War Gases," Yale University Press, New Haven (1920).

BRITISH

Foulkes, C. H., "Gas, The Story of the Special Brigade," Wm. Blockwood & Sons, Ltd., London (1934).

Thuillier, H. E., "Gas in the Next War," Geoffrey Bles, London (1939).

Air Raid Precautions Handbooks, Nos. 1, 2, 3, and 4, A. R. P. D. Home Office, H. M. Stationery Office, London (1938, 1939).

FRENCH

Hederer, C. and Istin, M., "L'Arme Chimique et ses Blessures," J. B. Bailliere et Fils, Paris (1935).

Meyer, A., "Les Gas de Combat," Chas. Lavauzelle & Cie, Paris (1936).

GERMAN

Hanslian, R., "Der Chemische Krieg," Dritten Auflage (Zweiten Banden), E. S. Mittlin & Soher, Berlin (1937).

CHAPTER 34

THE MANUFACTURE OF PHARMACEUTICALS

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From the early dawn of history, man has sought to relieve or cure himself of the ailments which befall him. The earliest medicine makers were the priests and the magicians who prescribed charms and spells and concocted brews from vile tasting plants. Occasionally the patient was cured, and knowledge of the efficacy of the charm used was handed down to the next generation. Man early knew the most fatal arrow-poisons as well as the beneficial effect of cinchona, opium, sarsaparilla, copaiba, etc. From out of the centuries of trial and error treatment, there grew a folklore which contained a knowledge of the medical value of various naturally occurring substances, which was far from contemptible. It was not until the nineteenth century that the scientific advancement of modern medicine occurred, paralleling the development of chemistry, physics and biology, and it did not attain its full stride until well after the middle of the century. We can appreciate how far we have advanced since the 1840's when ether and chloroform were first used for anesthesia, and since 1865 when Lister first used a chemical antiseptic, phenol.

OUTLINING THE FIELD

The twentieth century has seen the development and use of so many organic chemical compounds in the field of medicine that it would require a large volume to describe them. In order to depict the different processes employed to produce the varied list of drugs and medicine used by modern man, one is compelled to select representative compounds. It should be borne in mind that while the general outline of many processes has been published, information concerning the specific variations used in different establishments is not available. In many instances the only information concerning manufacturing processes is that contained in scientific papers or in the patent literature.

Pharmaceutical chemistry covers an exceedingly broad field. Naturally occurring substances, both of an inorganic and organic nature, are employed, as well as many synthetic organic materials. In addition to the chemical problem of isolation, identification and synthesis, there is the "art and science" of compounding the various chemicals or drugs in such a way that they can exert the maximum effect by the desired mode of administration. Due to the lack of space, it will not be possible to include a discussion of this phase of pharmaceutical chemistry.

The inorganic chemicals employed for medicinal use are purified to a degree which meets the specific medicinal requirement and in the main, therefore, their preparation does not depend upon many unique procedures.

The preparation of the organic compounds of plant origin involves varying procedures of extraction, followed by concentration steps which result in a crude extract, a partially purified extract, or the isolation of the pure components. The organic materials of animal origin range from crude dried tissues, or their extracts, to the isolated pure hormone. The methods of extracting hormones from animal tissues differ in many respects from the methods used in extracting active principles from plant tissues. At the present time, many preparations which previously were available only from plant and animal origins, are made more economically by synthetic procedures, as, for example, *l*-ephedrine, vitamin B_1, and vitamin C.

Few products used solely for medicinal purposes are produced in large amounts. However, acetylsalicylic acid and *p*-aminobenzenesulfonamide (now called sulfanilamide) are examples of synthetic organic chemicals employed solely for medicinal use whose yearly output is over half a million pounds. In order to get a clearer picture of pharmaceutical manufacture, therefore, one should consider pharmaceutical production in terms of the amount required for clinical treatment rather than the number of pounds produced. There is not so much of a chemical engineering problem involved in the production of neoarsphenamine or vitamin B_6 as there is in making acetanilid or sulfanilamide, yet the former are of equal importance and their production must be given equal consideration. There are many products such as vitamins and hormones of which one gram is worth much more than ten pounds or even a hundred pounds of many organic or inorganic chemicals. Extremely large scale production of drugs whose dosage is measured in grains or milligrams cannot be expected, since the very minuteness of the dose precludes the use of great quantities.

Most synthetic medicinal products are made in batches, and the equipment must be so planned, if possible, to permit its being used for several different processes. Due to the high standards of purity required, corrosion-resistant equipment is generally used. In some instances stainless steel, Monel, Inconel, or rubber lined stills, kettles, and pots can advantageously be used in place of enamel-lined equipment. Many of the syntheses involved in the manufacture of medicinal products represent but an enlarged laboratory experiment, where the one hundred-gallon still takes the place of the five-liter flask.

THE ECONOMIC PICTURE

While the various surveys available give somewhat different pictures of the pharmaceutical industry due to the use of different bases, the relative dollar volume of the several groups of drugs is of great significance in showing the present trend or use. During the past few years, for example, the vitamins have forged ahead to become by far the leading group among all the medicinal products.

Value of Products—The amount of synthetic coal-tar medicinals produced and sold has shown a steady increase since 1921, as shown in Table 1. The bulk of this group consists of salicylic acid and its derivatives, acetanilid and sulfanilamide. The non-coal-tar medicinals, data for which are available only for recent years, represent fewer pounds, but they have a higher value per pound, due in part to the inclusion of synthetic vitamins and hormones.

TABLE 1—UNITED STATES PRODUCTION OF SYNTHETIC MEDICINALS

	Coal-Tar		*Non-Coal-Tar*	
Year	*Pounds Produced*	*Value per Pound in Dollars*	*Pounds Produced*	*Value per Pound in Dollars*
1921	1,545,917	$1.56	......	...
1922	2,946,347	1.37	......	...
1923	3,273,085	1.58	......	...
1924	2,967.944	1.93	......	...
1925	3,237,796	1.92	......	...
1926	3,696,196	1.88	......	...
1927	3,598,839	1.95	......	...
1928	4,008,393	2.16	......	...
1929	5,000,205	1.76	......	...
1930	5,449,954	1.45	......	...
1931	....	...	......	...
1932	....	...	......	...
1933	8,715,027	0.85	421,734	2.58
1934	10,023,626	0.96	464,839	2.55
1935	10,022,667	0.94	751,225	2.36
1936	12,033,857	0.97	1,216,147	1.56
1937	14,799,821	0.96	1,814,035	1.67
1938	11,097,000	1.07	1,379,174	2.00
1939	13,910,001	1.10	1,444,670	4.84

[a] Pounds sold.
From United States Tariff Commission reports for the years indicated.

The synthetic pharmaceuticals show the usual pattern of greatly increased use following the lowering of price.[1] For instance in contrast to the 1921 production of 733,510 pounds of acetylsalicylic acid at $0.73 a pound, the 1939 production was 5,371,682 pounds valued at $0.47 a pound. Sulfanilamide came into general medicinal use in 1937, when the 355,369 pounds produced were valued at $4.95 a pound. In 1939, this amount was doubled with the cost per pound reduced to $1.28. In the non-coal-tar group, 78,645 pounds of barbituric acids produced in 1933 were valued at $8.05 a pound, while in 1939 the 167,393 pounds produced were valued at $7.71 a pound. The production of vitamin C, first reported in 1939, was 15,654 pounds, valued at $43.15 a pound.

The volume of synthetics listed in Table 1, represents only a fraction of the production of pharmaceuticals. The total value for drugs and medicine reported by the manufacturers for 1939 was $364,985,404.[2] This is a 25 per cent greater volume of business than that reported by E. I. du Pont de Nemours and Company for the same year. Of the total amount of drugs and medicines sold, slightly less than half belong to that class not sold to the general public, that is, compounds sold to or prescribed by physicians.

[1] See Chapter 1.
[2] Dept. of Commerce, Census of Manufactures, 1939, Preliminary Report (Nov. 12, 1940).

Vitamins now represent as big a dollar volume as do alkaloids, synthetic medicinals, and gland products combined. Biologicals are almost as large an item as synthetic medicinals, and gland products surpass either.

In these data, which are the manufacturers' values and not the retail values, the cost of supplies, fuel, power, etc., was a little less than a third of the total reported value.

Although no data are available on the net sales of all drugs and medicinals, prescription sales in drug stores were reported to have been $253,629,956 for 1939.[3] It was estimated that in 1929, the annual national expenditure for all medicines, prescriptions, home remedy, and "patent," was $715,000,000.[4] This value is about half of the total sales volume for General Motors for the same year.

Exports and Imports—Though the bulk of United States production is consumed domestically, this country has a significant international business in this field. While exports and imports of medicinal products have varied considerably in the last decade, during this period the exports were approximately three times the imports. See Table 2.

TABLE 2—UNITED STATES EXPORTS AND IMPORTS OF MEDICINALS[a]

Year	*Exports*	*Imports*
1929	$21,282,411	$6,422,034
1930	17,800,996	4,947,534
1931	15,103,936	3,973,072
1932	10,026,617	2,530,072
1933	9,816,253	3,605,089
1934	10,973,153	4,234,072
1935	12,239,340	4,127,588
1936	14,393,487	4,890,232
1937	17,979,326	4,893,994
1938	17,079,099	4,328,207
1939	22,317,000	5,507,000
1940 (11 mo.)	26,707,000	4,370,000

[a] Chem. & Met. Eng. *47*, 93 (1940). Ibid., *48*, 89 (Feb., 1941).

Out of a total of 3,246 chemical industries, which employ 489,439 wage earners, 548 are listed as drug and medicinal manufacturers with 21,336 wage earners.[5] It has not been possible to ascertain how many of the 129 chemical research laboratories reported in 1934 (the latest report) are engaged in drug and medicinal research.

PLANT PRODUCTS

A great many plants and roots are still employed in pharmaceutical chemistry. In some instances, there is little scientific justification for their use, and they are merely hang-overs from the days when all of the medicinal products were substances found, as such, in nature. In other instances extracts of plant tissue are employed for a specific effect, due to the fact that we have as yet been unable to isolate, identify, or, as it is in many cases, economically synthesize the active

[3] Drug Trade News *15*, 1 (1940).
[4] Rorem, C. R. and Fischelis, R. P., "The Costs of Medicine," p. 18, University of Chicago Press, Chicago (1932).
[5] Monthly Labor Review, U. S. Department of Labor, *50*, 1473 (1940).

component contained in the plant, and so must depend on the plant as the source of the medicament.

Of the plants still employed, one might mention squill, aconite root, aloe, althea, asafetida, aspidium, Peruvian balsam, tolu balsam, belladonna, benzoin, cannabis, cayenne pepper, cardamom and caraway seeds, cloves, cascara sagrada,

FIG. 1. Crude Drug Percolators Mounted on an Endless Track.

chrysarobin, cinchona bark, cinnamon, colchicum seed, balsam copaiba, digitalis, ergot, eriodictyon, nut gall, gentian root, hyoscyamus, ipecac, kino, lycopodium, peppermint and spearmint, nutmeg, gum myrrh, nux vomica, oleoresin of aspidium, gum opium, juniper and pine tars, podophyllum, wild cherry, rhubarb, red saunders, sarsaparilla, senna, serpentaria, black mustard, stramonium, storax, gum tragacanth, valerian, veratrum viride, and ginger.

Extraction—The active principles of plant tissue are obtained by extraction or percolation of the ground drug. In some instances it is necessary to defat the material before extraction. Because of the moderate amounts used of most of these drugs, it is not economical to employ continuous automatic percolators, except in the case of alkaloids, so that the conventional batch extractor with the percolator set above the receiver, is used for most of the drugs. The inconvenience in the handling of the batch type of percolators can be minimized by mounting both percolator and receiving tank on an endless track which can be revolved so that each percolator can be moved at will to the filling and dis-

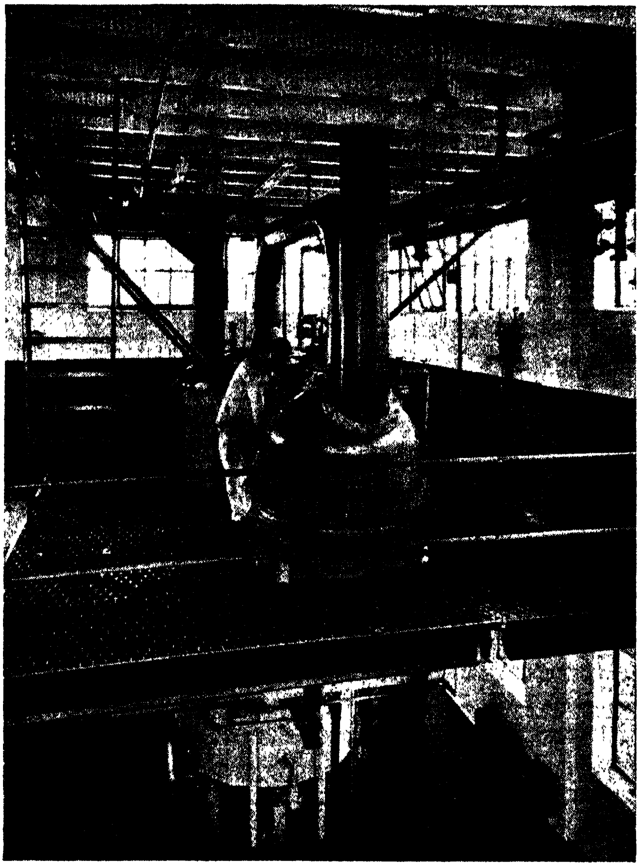


FIG. 2. Jacketed Enameled Stills Used to Remove Solvent from Drug Extracts.

charging platform. See Figure 1. From this platform the operator is able to handle several hundred percolators, remove the percolate, discard the spent drug, recharge the percolator with new drug, and add the extracting solvent.

The solvents used to extract crude drugs are neutral, acid, or alkaline alcohol, dilute alcohol, or water. The solvent is in most instances removed from the extract *in vacuo* in jacketed stills. See Figure 2. The residue left in the still may in some instances be used as it is. In other instances, it is subjected to a chemical procedure in order to separate the active chemical component in pure form.

ALKALOIDS

The term alkaloid,[6] generally speaking, is applied to basic organic compounds of plant origin, many of which show marked physiologic action. This definition excludes some compounds commonly regarded as alkaloids and includes some not usually regarded as such.

The procedures for obtaining the alkaloids depend on macerating the drug in an alkalinized solvent, followed by extraction with an immiscible solvent, or extracting the drug with an acidified aqueous or alcoholic solution. Purification procedures vary greatly and are for the most part dependent on solubility relationships of the free base and its salts in water and various immiscible organic solvents.

Those alkaloids which are readily hydrolyzed require low boiling solvents such as ether, while the more stable alkaloids, such as strychnine and quinine, can be extracted by boiling solvent naphtha or benzene. The details of the extraction and separation vary with the alkaloid, and different factories often use different procedures for the same alkaloid. The main purpose, however, is to obtain the crude alkaloid as free as possible from sugar, protein, chlorophyll, etc., using as inexpensive procedures and solvents as possible. The commercial extraction equipment which uses volatile solvents for the extraction of heat stable alkaloids, is constructed on the principle of the Soxhlet extractor. Such equipment can be run under partial pressure to lessen the danger of overheating the alkaloidal residue.

The alkaloid is removed from the solvent by churning it with a weak acid. The dilute acid extract may or may not be concentrated *in vacuo* before being neutralized, a step which causes the free alkaloid to precipitate. Fat has to be removed at some stage by extraction with a suitable solvent. The final purification of alkaloids is usually tedious, and must be varied, not only for each alkaloid, but often with each batch.

Products from Opium—Opium, the dried juice or latex of the unripe capsules of the opium poppy, yields about twenty-five bases which can be separated by difficult, tedious procedures. Morphine, a complex phenanthrene derivative, is the most important of these alkaloids. When opium is extracted with a calcium chloride solution, some of the alkaloids, including morphine, are taken into solution in the form of their hydrochlorides, while the organic acids are removed as insoluble calcium salts. The solution, after filtering, is evaporated *in vacuo* and is then neutralized with sodium acetate to the point where narcotine and papaverine precipitate. The addition of a small amount of alkali to the filtrate precipitates the crude morphine. The latter is freed from codeine by extracting with benzene or ether and is converted to the hydrochloride.[7]

Codeine, which is methylmorphine, may be prepared from morphine by methylating the phenolic hydroxyl group. It is also obtained from the filtrate

[6] Schwyzer, J., "Die Fabrikation der Alkaloide," Julius Springer, Berlin (1927); Henry, T. A., "The Plant Alkaloids," third edition, J. & A. Churchill, Ltd., London (1939).

[7] (a) Evers, N., "The Chemistry of Drugs," p. 70, D. Van Nostrand Co., New York (1926). (b) Barrowcliff, M. and Carr, F. H., "Organic Medicinal Chemicals," p. 52, D. Van Nostrand Co., New York (1920). (c) Schwyzer, J., "Die Fabrikation pharmazeutischer und chemisch-technischer Produkte," p. 376, Julius Springer, Berlin (1931).

of the precipitated morphine by extraction with chloroform. Ethylmorphine is prepared by ethylating the phenolic hydroxyl group of morphine.

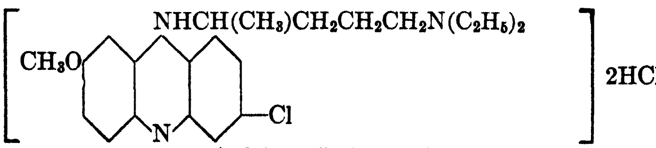
When a molecule of water is removed from morphine by heating with hydrochloric acid in an autoclave, apomorphine is formed.

Diacetylmorphine, heroin, is prepared by heating morphine with an excess of acetic anhydride. Dihydromorphinone hydrochloride, 'Dilaudid'[8] hydrochloride, differs from morphine hydrochloride in that one of the hydroxyl groups of morphine has been replaced by a ketone group, and the adjacent double bond has been hydrogenated.[9]

Quinine—Quinine is the most important of the alkaloids obtained from cinchona bark. While the cinchona species is indigenous to South America, it has been cultivated so extensively in Java that the bulk of the cinchona bark now used comes from Java. The dried bark is powdered, mixed with lime and caustic soda solution, and then extracted with hot solvent naphtha, usually in a steam heated ball mill, until no further alkaloid can be extracted. The alkaloid is removed from the solvent by extracting with hot dilute sulfuric acid solution in a lead lined vessel equipped with a stirrer. This acid extract is partially neutralized and concentrated if necessary, so that on cooling, crude quinine sulfate, contaminated by several other alkaloids, crystallizes out. The quinine sulfate is repeatedly crystallized until it is substantially free from the other alkaloids.[10]

Hydroquinine, one of the chief impurities in commercial quinine, is prepared by the hydrogenation of quinine.[11] When hydroquinine is boiled with hydrochloric acid, a methyl group is removed, yielding hydrocupreine. When hydrocupreine is ethylated, it forms ethyl hydrocupreine, the hydrochloride of which is called 'Optochin'[8] hydrochloride.

While synthetic products having some effect against malaria are not rare, few have been found to be effective enough for actual clinical use. One of these is 3-chloro-7-methoxy-9-(4-diethylamino-1-methylbutyl)-aminoacridine dihydrochloride, 'Atabrine'[8] dihydrochloride.



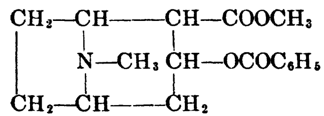
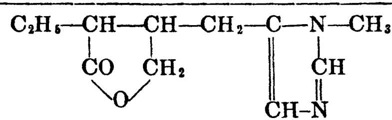
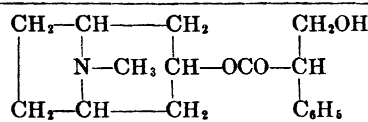
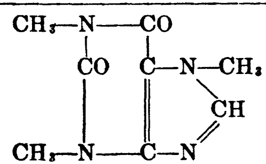
'Atabrine' Dihydrochloride

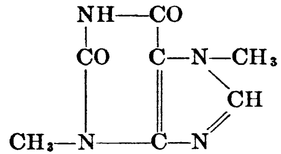
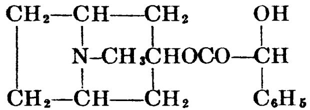
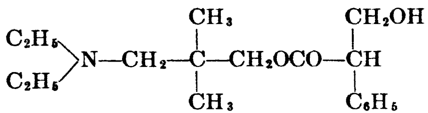
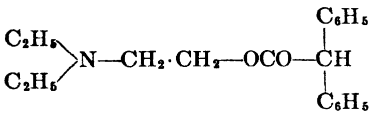
This is said to act only on the asexual forms of the malaria parasite and is complementary to 'Plasmochin,'[8] which acts mainly on the sexual form. 'Plasmochin' is 8-(δ-diethylamino-α-methylbutylamino)-6-methoxyquinoline dihydrochloride, and has the same side chain attached to the methoxyquinoline nucleus as is contained in 'Atabrine' dihydrochloride.[12]

[8] Trade-mark. See trade-mark explanation at the end of the chapter.
[9] German Patent 380,919 (Sept. 13, 1923).
[10] See reference 7a, p. 85; 7b, p. 75, and 7c, p. 300.
[11] British Patent 3948 (1912).
[12] Schulemann, W., Schönhöfer, F. and Wingler, A., U. S. Patent 1,747,531 (Feb. 18, 1930); Mietzsch, F. and Mauss, H., U. S. Patent 2,113,357 (Apr. 5, 1938). Formula used for 'Atabrine' is that given in J. Am. Med. Assoc. *115*, 1886 (1940); Chemical Abstracts use the name "Atebrin."

TABLE 3—MISCELLANEOUS ALKALOIDS

Including Synthetic Products Derived from or Having Action Similar to Alkaloids

Name	*Structure*	*Source*	*Extractant*	*Use*
Cocaine		Coca leaves	Leaves, after macerating with water and soda ash, are extracted with benzene or toluene.[a]	Local anesthetic; mydriatic.
Strychnine	$C_{21}H_{22}O_2N_2$[b]	Seeds of strychnos nux-vomica	Ground seeds, macerated with water and slaked lime, are extracted with benzene or toluene.[c]	"Tonic"; respiratory stimulant.
Pilocarpine		Leaves of Pilocarpus Jaborandi	Leaves are extracted with alcohol acidified with HCl.[d]	Miotic; diaphoretic.
Atropine		Belladonna root	The powdered root is alkalinized and extracted with ether.[e]	Mydriatic; antispasmodic, control of enuresis.
Caffeine		Tea, coffee, kola nuts	Hot water extraction of tea and coffee waste,[f] or by methylation of theobromine.	Cerebral stimulant; respiratory stimulant.

Theobromine		Cacao beans	Whole ground seeds mixed with slaked lime and extracted with alcohol. Cacao bean shells and press cake extracted with excess lime water.[g]	Diuretic; coronary dilator.
Emetine	$C_{29}H_{40}O_4N_2$	Ipecacuanha root	Ground root extracted with alcohol or benzene.[h]	Amebicide.
Homatropine		Synthetic	Mandelic acid is condensed with tropine obtained by hydrolyzing alkaloidal residue left from the preparation of atropine.[i]	Mydriatic.
'Syntropan'[j] *dl*-3-Diethylamino-2,2-dimethylpropyl tropate		Synthetic	*dl*-Tropic acid is condensed with 3-diethylamino, 2, 2-diethyl-1-propanol.[k] (This amino alkanol is used in the synthesis of the local anesthetic 'Larocaine.'[j])	Antispasmodic.
'Trasentin'[j] 2-Diethylaminoethyl diphenyl acetate		Synthetic	Diethylamino ethanol is condensed with diphenyl acetic acid.[l] (When condensed with *p*-amino benzoic acid, procaine is obtained.)	Antispasmodic.

[a] Schwyzer, J., "Die Fabrikation pharmazeutischer und chemisch-technischer Produkte," p. 327, Julius Springer, Berlin (1931).
[b] Henry, T. A., "The Plant Alkaloids," p. 511, J. and A. Churchill, Ltd., London, 3rd Ed. (1939).
[c] See p. 402, reference a.
[d] Barrowcliff, M. and Carr, F. H., "Organic Medicinal Chemicals," p. 82, D. Van Nostrand Co., New York (1920).
[e] See p. 290, reference a, and p. 68, reference d.
[f] See p. 230, reference d.
[g] See p. 407, reference a, and p. 244, reference d.
[h] See p. 65, reference d.
[i] See p. 72, reference d.
[j] Trade-mark. See trade-mark explanation at the end of the chapter.
[k] Guggenheim, M., U. S. Patent 1,932,341 (Oct. 24, 1933).
[l] Miescher, K., U. S. Patent 2,079,962 (May 11, 1937).

There is need for effective synthetic products in combating malaria, since quinine is too often unable to destroy all the parasites, although it produces a rapid alleviation of the clinical symptoms.

Ergot—Ergot, the dried sclerotium of *Claviceps purpurea,* a fungus growing chiefly on rye, contains a number of alkaloids to which it owes its therapeutic effect—a stimulating action on the muscles of the uterus.

While many alkaloids had been isolated from ergot and some were of clinical value, it was long recognized that the crude fluid extract of ergot had clinical properties not possessed by any of the isolated compounds. About 1935, four

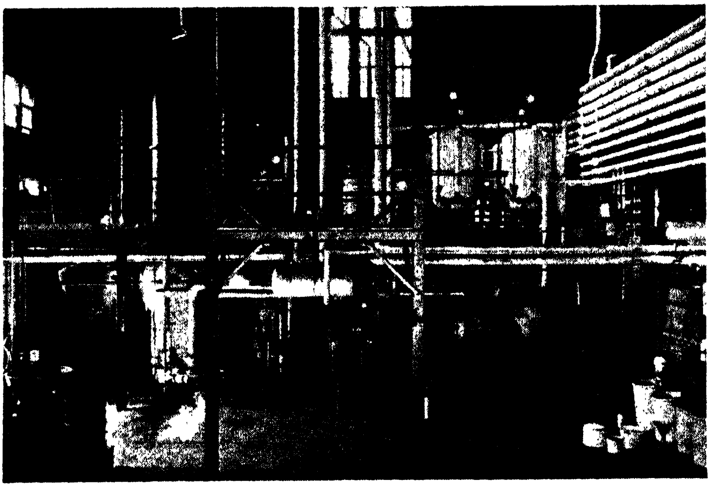


FIG. 3. Equipment Used for the Sulfur Dioxide Extraction of Ergot.

groups [13] of investigators reported on the isolation of a hitherto undetected constituent of ergot which was responsible for the desirable effects of the crude extract. Because this alkaloid is present in lesser quantity than the other alkaloids and because it is appreciably soluble in water and insoluble in chloroform, it had escaped detection. Not all ergots contain this alkaloid, called ergonovine. Used as its maleate salt, it is called 'Ergotrate.' [8]

Ergot, which contains less than 0.2 mg. ergonovine per gram, is exhaustively extracted with alcohol. The alcohol is removed, and the ergonovine is separated from the other alkaloids and the readily water-soluble extractives. It is purified by crystallization from benzene.[14]

Liquid ammonia can be used as a solvent for removing the alkaloids of ergot. After evaporating the liquid ammonia extract to a small volume, ether is added, which extracts the alkaloids. The ether solution is extracted with acidulated water. This aqueous extract is partially neutralized to a point where it is

[13] Kharasch, M. S. and Legault, R. R,, Science *81*, 388 and 614 (1935); Dudley, H. W. and Moir, C., Brit. Med. J. *1*, 520 (1935); Stoll, A. and Burkhardt, E., Compt. rend. *200*, 1680 (1935), and Thompson, M., J. Am. Pharm. Assoc. *24*, 24 and 185 (1935). See also Stuart, E. H., U. S. Patent 2,067,866 (Jan. 12, 1937).

[14] Dudley, H. W., Pharm. J. *134*, 709 (1935).

possible to extract the ergonovine with ether while the rest of the bases are left in the aqueous phase.[15]

Ergonovine has been extracted commercially from ergot by the use of liquid sulfur dioxide.[16] See Figure 3. The amorphous brown powder, obtained from the sulfur dioxide extract, can be purified rather readily to yield ergonovine.

These brief descriptions give the principal points involved in the extraction and preparation of the various natural alkaloids. The operations and equipment are, in general, the same as those used on a variety of other materials. The pertinent information on several other commonly used alkaloids is assembled in Table 3.

GLUCOSIDES

There are a number of drugs of plant origin termed glucosides. They are substances which yield a sugar and one or more other products on acid hydrolysis. The glucoside drugs consist of crude drugs, extracts, and approximate principles. The disadvantage resulting from the use of these has served to stimulate the search for the pure principles. As yet there is much of the chemistry of the glucosides which is not known.

Digitalis—The digitalis group, which exerts a specific action on the heart, is one of the more important of the glucosidic groups. Since the glucosides of this group form no definite compounds with ordinary reagents, they are difficult to separate and purify. One has to resort to variations in solubility in different solvents; an imperfect method. Even the digitalin which is available is a mixture of two or more substances, and the different digitalins vary somewhat in their action, due to differences in the process of separating them.[17] Digitoxin and gitalin together represent the effect of the crude drug digitalis, the former being the chief active principle of digitalis. Other glucosides present in the medicinal preparations are digitonin and gitonin.

It is of interest to note that toad poison, used for medicinal purposes in China, contains toxic principles, cinobufagin and cinobufotoxin, which are chemically related to digitalis glucosides.

Strophanthin—Strophanthus seeds have a high content of the glucoside, strophanthin, also used for its action on the heart. The seeds are crushed, defatted, and exhaustively extracted with absolute alcohol. After the evaporation of the alcohol, the residual crude extract is dissolved in water, and the solution is clarified with lead acetate treatment. The excess lead is removed from the filtrate with hydrogen sulfide. The filtrate is partially evaporated, and ammonium sulfate is added in an amount sufficient to effect the crystallization of the strophanthin. Further purification is effected by crystallization from dilute alcohol.[18]

[15] Stuart, E. H., U. S. Patent 2,067,866 (Jan. 12, 1937).
[16] Kharasch, M. S. and Legault, R. R., U. S. Patents 2,082,342 (June 1, 1937) and 2,082,343 (June 1, 1937).
[17] Cleotta, M., Arch. exp. Path. Pharmakol. *88*, 113 (1920); Mameli, E., Giorn. chim. ind. applicata *4*, 355 (1922); and Kraft, F., Schweiz. Woch. Chem. Pharm. *49*, 161 (1911).
[18] Heffter, A. and Sachs, F., Biochem. Zeit. *40*, 83 (1912).

HORMONES

A hormone is a chemical substance—a chemical messenger—produced by an organ, which, being carried to another organ by the blood stream, excites a functional activity in the latter.

Most of the chemical problems concerning hormones have to do with the isolation of these hormones from the animal tissues which either elaborate, or yield on extraction, the desired active principle. Such animal tissues are the liver, stomach, and the ductless glands. There are five ductless glands used; the thyroid, which lies in front of the trachea at the base of the neck; the parathyroid, found near the thyroid; the adrenal, which sits on top of the kidney; the pituitary, a small gland within the skull at the base of the brain, and the pancreas, a large gland in the abdomen, situated below and behind the stomach,—the sweetbread of animals. While the ovaries and testes function as glands for internal secretion, the hormones which they elaborate are obtained commercially from other sources.

It is very fortunate that the warm-blooded animals produce essentially the same hormones that man does. Thus, the glands of animals slaughtered for food serve as the raw materials for the production of these essential chemical messengers. In the larger packing houses, most of the ductless glands and part of the livers and stomachs are now utilized for the preparation of hormones.

Of the hormones obtained from the above sources, two have been synthesized: epinephrine and thyroxin. In the field of sex hormones, several have been made by partial synthesis, through the utilization of naturally occurring steroid structures. The chemical nature of the active principles produced by the pituitary, parathyroid, pancreas, and the liver-stomach hormones is not known.

Insulin—Insulin[19] is obtained from the pancreas, a gland having two general functions: the secretion into the intestine of an enzymatic digestive juice and the secretion into the blood of a hormone, insulin, which regulates the process of carbohydrate metabolism. When the insulin secretion in man is deficient, diabetes occurs, which is evidenced by the inability of the body to utilize sugar. As a result, glucose accumulates in the blood stream and is excreted in the urine. This is followed by the breakdown of protein into sugar and the derangement of fat metabolism. The oxidation of fat is incomplete, and acetone bodies accumulate in the blood and are excreted in the urine.

The United States Census reports 31,037 individuals as having died from diabetes in 1938.[20] It is estimated that there are 660,000 diabetics in the United States.[21] Unless conditions change, it is probable that at least 2,000,000 more people, now free from diabetes, will develop it before they die.[20] Insulin obtained from animal pancreas, if administered subcutaneously, corrects this condition. It is ineffective on oral administration.

[19] Banting, F. G., Best, C. H. and Collip, J. B., U. S. Patent 1,469,994 (Oct. 9, 1923); Moloney, P. J. and Findlay, D. M., U. S. Patent 1,470,024 (Oct. 9, 1923); Walden, G. B., U. S. Patent 1,520,673 (Dec. 23, 1924), and Best, C. H. and Scott, D. A., J. Biol. Chem. 57, 717, et seq. (1923).

[20] Joslin, E. P., "Treatment of Diabetes Mellitus," seventh edition, p. 22, Lea & Febiger, Philadelphia (1940).

[21] Nat. Inst. Health, "Magnitude of the Chronic Disease Problem" (1935-6).

In insulin production it is necessary to prepare enzyme-free, non-toxic pancreatic extracts, hence a procedure had to be developed which would destroy the enzymes, extract the hormone fraction, and separate the hormone from the other protein material. The final step was the preparation of the hormone in pure form.

Extraction Process. Fresh pancreatic glands[19, 22] of cattle and hogs, from which fat and connective tissue have been removed, are immediately frozen at the slaughterhouse to stop enzymatic action. Figure 4 indicates the extraction operations. The frozen glands are ground and extracted with 1½ volumes of 95 per cent alcohol, containing about 12 cc. of hydrochloric acid per pound of

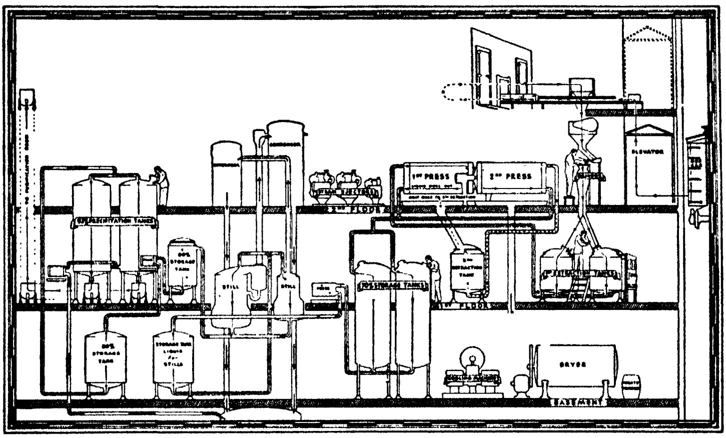


FIG. 4. Diagrammatic Flow Sheet of Insulin Production.

Pancreas from the refrigerator car is placed in cold storage until it is ground. The arrows indicate the successive steps up to the isoelectric purification.

pancreas in enameled pots which are equipped with stirrers. The mixture is agitated during two hours and then centrifuged in a rubber-lined basket centrifuge or filtered through a filter press. The residue is again extracted, using an equal volume of 60 to 70 per cent alcohol. This is filtered, and the second filtrate added to the first. The combined 70 per cent alcoholic filtrates are chilled, filtered, and concentrated in an enameled vacuum batch still, keeping the temperature of the contents below 30° C., to about one twenty-fifth its volume, and again filtered. See Figure 5. Sufficient alcohol is added to this filtrate to give it an alcoholic concentration of 80 per cent. This mixture is allowed to stand for several hours, and then filtered from the precipitated inactive protein. The filtrate is then made up to contain about 93 per cent alcohol. After standing several days, the precipitate formed, which contains the crude insulin, is collected and dissolved in distilled water. The alcohol from the last filtrate is brought up to 95 per cent strength in a standard rectification still. The size of the batch used varies with the different manufacturers and is dependent on the desired output of insulin.

[22] (a) Banting F. G., Can. Med. Assoc. J. *16*, 221 (1926) and Edinburgh Med. J. *1*, 1 (1929). (b) Somogyi, M., Doisy, E. A. and Shaffer, P. A., J. Biol. Chem. *60*, 31 (1924).

An alternative process is extraction of the pancreas with acidified 60 per cent alcohol. The extract after concentrating in a vacuum still to about one-twelfth its volume is freed from fat. Ammonium sulfate is then added in sufficient quantity to precipitate the active principle. This precipitate is dissolved in water, using dilute ammonium hydroxide if desired. Sufficient alcohol is then added to precipitate the active principle. Ether may be added to make the precipitation more complete. The precipitate thus obtained is collected and dissolved in distilled water.

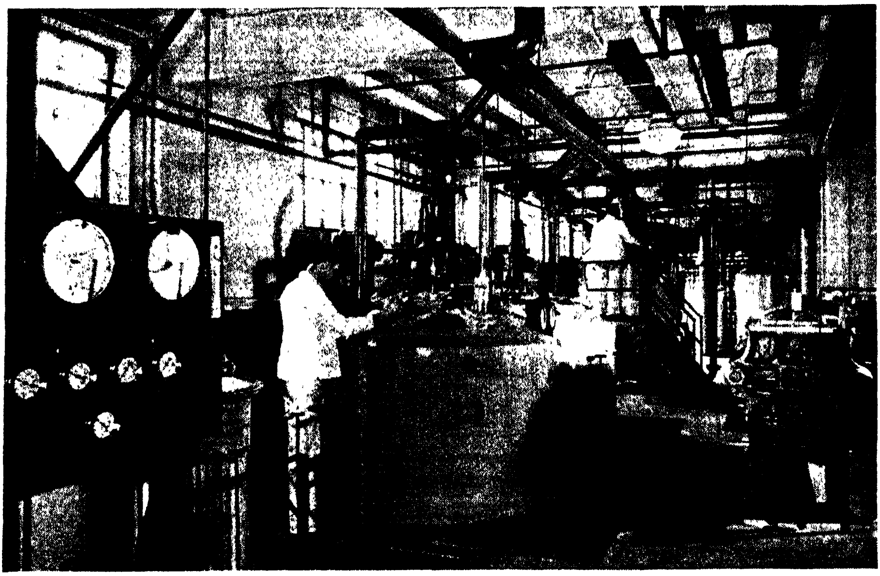


FIG. 5. Enameled Jacketed Stills Used to Concentrate the Alcoholic Insulin Extract.

Purification. The insulin preparation made by the above procedures is further purified by precipitation at the iso-electric point,[22b] the hydrogen ion concentration being adjusted to approximately pH 4.7 by the addition of dilute alkali, after which the solution is allowed to stand at a temperature of 5-10° C. until no more insulin precipitates. The precipitated insulin is separated and dissolved in acidified water (pH 2.5), filtered, reprecipitated, and redissolved if necessary for further purification. The insulin solution is then diluted to approximately the desired potency, filtered through a Berkefeld filter, and submitted for standardization and sterility tests. The insulin obtained by this procedure is in an amorphous form, one milligram of which contains about 20 to 22 clinical insulin units.

Standardization. Since chemical methods of assay have been found to be non-specific, biological methods of standardization depending on the lowering of the blood sugar level in normal animals have to be employed. The international unit of insulin is the smallest quantity which lowers the blood sugar of a two kilogram rabbit, starved for twenty-four hours, to a level of 0.045 per cent in the course of five hours. The clinical unit is one-third of this amount. Each lot of insulin must be assayed, and its concentration adjusted so that it equals the standard.

Yields. As the chemical nature of both insulin and the inert ingredients became better understood, it was possible to increase the yields from 15 to 40 units per kilogram of pancreas to as high as 4000 units.[23] The older the animal, the less is the insulin content of the pancreas.[24] Since pure insulin contains about 25 units per milligram, the highest reported yield is 160 milligrams per kilogram of pancreas.

Modifications. By the addition of a small quantity of zinc to amorphous insulin, it is possible to make zinc insulin crystals.[25] Procedures recently re-

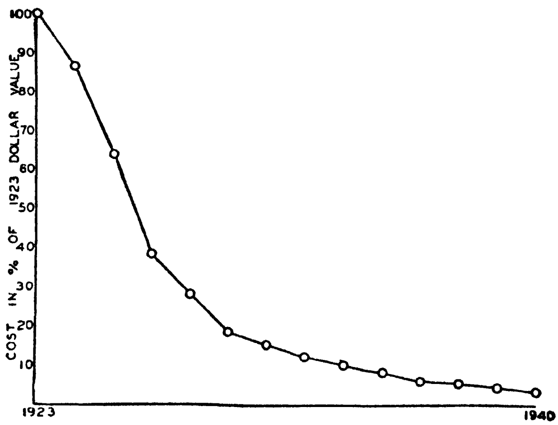


FIG. 6. Progressive Price Reductions of Insulin.

ported[26] yield crystalline insulin directly from the hydrochloric acid-alcohol extract of the pancreas glands. This process is based on the fractional precipitation of insulin by suitable concentrations of acetone and zinc acetate. Protamine zinc insulin is a slowly absorbed insulin preparation obtained by the addition of protamine and a zinc salt to insulin.[27] This permits the possibility of using fewer daily injections, because of the gradual and prolonged action. This product necessitates the preparation and purification of protamine, a basic protein obtained from fish sperm.

Chemical Structure. While insulin can be obtained in crystalline form, its structure is complex, and it appears to be of a protein-like nature having a molecular weight of approximately 35,000. Since it is a protein, it is readily broken down and its activity lost when it is digested with enzymes or hydrolyzed

[23] Jensen, H. F., "Insulin, Its Chemistry and Physiology," p. 31, Commonwealth Fund, New York (1938).

[24] Fisher, A. M. and Scott, D. A., J. Biol. Chem. *106*, 305 (1934).

[25] Abel, J. J., Proc. Nat. Acad. Sci. U. S. *12*, 132 (1926); Scott, D. A., Biochem. J. *28*, 1592 (1934).

[26] Romans, R. G., Scott, D. A. and Fisher, A. M., Ind. Eng. Chem., Ind. Ed. *32*, 908 (1940).

[27] Hagedorn, H. C., Jensen, B. N., Krarup, N. B. and Wodstrup, I., J. Am. Med. Assoc. *106*, 177 (1936).

with acids or alkalies. Complete breakdown has disclosed only known amino acids, in about the same proportion as occur in other proteins. There is no evidence as yet of any specific chemical group being responsible for its action.

Since degradation has not given any evidence of building stones other than amino acids, the probability of synthesis at the present time is remote.

Price Reductions. The remarkable decrease in the cost of insulin over a period of less than two decades, is shown in Figure 6. The progressive price reductions of insulin resulting from the economics of large scale production have been passed on to the consumer. In 1940, a unit of insulin cost only 3.5 per cent as much as it did in 1923.

The preparation of insulin was described in some detail because the processes involved well illustrate the principles and methods involved in the preparation of extracts from animal tissue. The preparation and functions of the other more important hormones will be given only briefly.

Liver and Stomach Extracts—Another hormone almost as important to mankind as insulin is the one obtained from liver, which is used to combat pernicious anemia and other anemias. The antianemia hormone, as yet unnamed, stimulates the formation of red blood cells. This hormone is present in the livers of edible animals. Fresh livers are ground directly into water and adjusted to an approximate pH of 5-6.

The aqueous suspension is then heated with stirring to about 80° C. for about 30 minutes, in order to coagulate and separate the inactive protein. After filtering, or centrifuging, the filtrate is concentrated in an enameled jacketed pot to a small volume under vacuum. To this residue is then added sufficient alcohol to give a concentration of approximately 70 per cent. This causes an additional precipitation of inactive material, which is filtered or centrifuged off and discarded. The filtrate is evaporated to dryness under vacuum in an enameled pot and used as such, or subjected to further purification procedures in order to obtain the active principle in a higher degree of concentration or for subcutaneous administration. Treatment with activated carbon, silicate of aluminum, ammonium sulfate, and zinc sulfate has been used to remove undesirable components. Liver hormone preparations are active when taken orally, whereas insulin is not.

Whole stomach tissue is likewise used for its antianemic activity. Fresh whole stomachs from healthy hogs are freed from extraneous fat, ground, and dried in a vacuum at a temperature not exceeding 65° C. The dried material is then defatted by extraction with petroleum ether. The defatted material is dried without further application of heat, ground, and milled to coarse powder.[28]

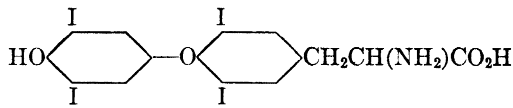
Pituitary—The small pituitary gland so securely protected at the base of the brain has many vital functions to perform. It contains a posterior and an anterior lobe, each having separate duties. The separation and clinical use of the several factors of the anterior lobe have not yet been accomplished.

The posterior lobe of the pituitary gland contains hormones which stimulate the contraction of the blood vessels and the uterus. This lobe may be dried and powdered and used as such, or extracts may be made from it. The oxytocic and

[28] Sharp, E. A., Sturgis, C. C. and Isaacs, R., U. S. Patent 1,937,133 (Nov. 28, 1933).

the pressor principles may be separated from this extract by involved extraction and fractionation procedures.[29]

Thyroid—The hormone of the thyroid gland has a profound influence on metabolism, so much so that 1 milligram of it increases the metabolic rate of adults approximately 2 per cent. It is active by oral or intravenous administration. The thyroid gland is used as such, in a dried powdered form, after being separated from connective tissue and fat, or the hormone may be used in a partially purified form. The active component of the thyroid gland, first isolated by Kendall,[30] is called thyroxin, and is β-[4-(4-hydroxy-3,5-diiodophenoxy)-3,5-diiodophenyl] alanine. It is a tetraiodo-derivative of *p*-hydroxyphenyl ether of tyrosine.



Thyroxin

The structure of thyroxin was established by Harington,[31] who first prepared it synthetically. The synthetic product is used when subcutaneous administration is desired.

Parathyroid—The parathyroid gland elaborates a principle which influences calcium metabolism, increasing the calcium content of the blood serum. The glands[32] after being freed from fat and connective tissue are ground and extracted with hot dilute hydrochloric acid. The filtrate after removal of the insoluble material is cooled, defatted, and concentrated, and is then ready for use. Nothing is known about the structure of this hormone other than that it must be of moderate molecular weight and is neither readily hydrolyzed by acid nor affected by heat.

Sex Hormones—There is a considerable group of naturally occurring substances which influence all sexual processes of mammals, and which are known as sex hormones.[33] In the short space of six years, three important types of sex hormones have been isolated and their structures elucidated. Both the male and female sex hormones are closely related chemically and are also similar in structure to the steroids of the adrenal cortex and other tissues of the body. While distinctly different in their main function, they do possess, however, physiologic properties common to each other.

Due to the complexity of their structure, they are obtained either from natural sources or by the chemical modification of naturally occurring sterols.

[29] Kamm, O., Aldrich, T. B. and Grote, I. W., U. S. Patent 1,960,493 (May 29, 1934); Kamm, O., Aldrich, T. B., Grote, I. W., Rowe, L. W. and Bugbee, E. P., J. Am. Chem. Soc. *50*, 573 (1928).

[30] Kendall, E. C., J. Biol. Chem. *39*, 125 (1919); Kendall, E. C. and Osterberg, A. E., J. Biol. Chem. *40*, 265 (1919); Kendall, E. C., "Thyroxin," Chemical Catalog Co., New York (1929); Harington, C. R., "The Thyroid Gland: Its Chemistry and Physiology," Oxford University Press, London (1933).

[31] Harington, C. R. and Barger, G., Biochem. J. *21*, 169 (1927); Harington, C. R. and McCartney, W., Biochem. J. *21*, 852 (1927).

[32] Hanson, A. M., U. S. Patent 1,890,851 (Dec. 13, 1932).

[33] Fieser, L. F., "Chemistry of Natural Products Related to Phenanthrene," p. 187 Reinhold Publishing Corp., New York (1936).

The urine of pregnant mares collected after the fifth month of pregnancy is the main source of the female sex hormone, estrone[34] (theelin), $C_{18}H_{22}O_2$, 3-hydroxy 17-keto-Δ-1,3,5-estratriene. This is present in the urine as the glucuronide. Urine in lots of 500 gallons or more is subjected to acid hydrolysis with mineral acid. The hormone which is separated by extraction with benzene is subsequently separated from contaminating impurities.

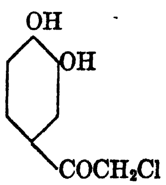
Estriol[34] (theelol), $C_{18}H_{24}O_3$, is 3,16,17-trihydroxy-Δ-1,3,5-estratriene and is obtained from human pregnancy urine. (See Addendum, page 1331.)

Progesterone, 3,20-Δ-4-pregnandione, is the hormone of the corpus luteum. Commercial preparations of progesterone are either extracts of animal ovaries or are the pure compounds prepared synthetically by the modification of naturally occurring sterols.[35] Sterols such as stigmasterol, obtained from soy beans, and cholesterol, obtained from the brain and spinal cord of animals, when oxidized by means of chromic oxide or potassium permanganate yield progesterone and substances having male hormone properties.

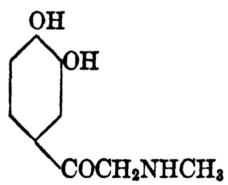
Testosterone, the most potent of the male hormones, has been isolated from testicular tissues.[36] However, it is commercially prepared from the oxidation of sterols which yield androstendione, which can be reduced to testosterone.[37] It is used in the form of the propionate ester.[38]

Pressors—The first hormone to be isolated was epinephrine, 'Adrenalin,'[8, 39] which is obtained from the adrenal gland. It is used for its constrictive action on blood vessels and for its relaxing action on the bronchial muscles. At present the glands of cattle are the chief source of this hormone, because it is more economical to isolate it than to synthesize it. Epinephrine is *l*-methylaminoethanolcatechol. The *l*-form can be separated laboriously by means of *d*-tartaric acid from the synthetic racemic mixture.

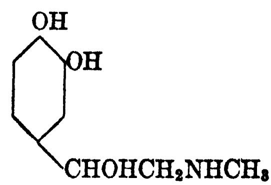
In the synthetic procedure, catechol is condensed with monochloroacetic acid by means of phosphorus oxychloride. The resulting chloroacetocatechol (I) is reacted with an alcoholic solution of methylamine to form methylaminoacetocatechol (II). This can be catalytically reduced to *dl*-epinephrine (III), which is then resolved.



I.



II.



III.

[34] Doisy, E. A., Thayer, S. A. and Veler, C. D., U. S. Patent 1,967,350 (July 24, 1934), and U. S. Patent 1,967,351 (July 24, 1934).

[35] Dirscherl, W. and Hanusch, F., U. S. Patents 2,152,625 (Apr. 4, 1939) and 2,152,626 (Apr. 4, 1939); Dirscherl, W., U. S. Patent 2,197,853 (Apr. 23, 1940).

[36] Laqueur, E., David, K. G., Dingemanse, E. and Freud, J., U. S. Patent 2,175,963 (Oct. 10, 1939).

[37] Ruzicka, L. and Wettstein, A., U. S. Patent 2,143,453 (Jan. 10, 1939).

[38] Miescher, K., Wettstein, A. and Scholz, C., U. S. Patent 2,109,400 (Feb. 22, 1938).

[39] Abel, J. J. and Crawford, A. C., Johns Hopkins Bulletin *8*, 151 (1897); Takamine, J., Amer. J. Pharm. *73*, 523 (1901).

BIOLOGICAL AGENTS

Biological agents used immunologically in connection with various phases of human diseases include both vaccines and antisera. The former are of value on account of their antigenic action; that is, they have the capacity to stimulate the formation of various antibodies or resistant conditions by which present or subsequently encountered infectious agents are combated. The antisera are of value on account of their antibody content, and when used, these agents confer rapid immunity in a passive way to the recipient patient.

Vaccines—Vaccines include first various bacteria, generally devitalized by some means; second, various products of bacterial action which if very toxic are preferably rendered sufficiently non-toxic to be tolerated well by patients; and third, various sub-microscopic viruses which may be used either active ("alive") or in an inactivated form. In general, the vaccines necessitate a period of time from a few days to several weeks in order to incite immunity, and the number of doses may vary from one to three, or even five or six, or more. The actual immune substances or conditions are, of course, produced by the patient or recipient of the vaccine, and the degree of success of such *active* immunization obviously depends greatly upon the patient and his capacity to produce immunity as well as upon the excellence of the vaccine. When classified broadly the vaccines include such agents as typhoid vaccine, diphtheria toxoid, and smallpox vaccine, and these illustrate the three categories mentioned above.

Preparation. In the preparation of bacterial vaccines pure cultures of an organism such as *B. typhosus* are planted in 16-ounce Blake bottles containing a shallow layer of agar media. After inoculation these bottles are incubated at 37.5° C. for approximately eighteen hours, then removed from the incubator, examined for purity, and the growth harvested from the surface of the agar with 0.85 per cent saline solution. The heavy suspension of organisms in saline is then heated at 50-53° C. for one hour in order to kill them. In some instances heat is not used for killing the organisms, death being brought about chemically by the use of an appropriate germicide. Appropriate sterility tests are carried out, and, if the suspension is sterile, further dilution with physiological saline is made so that each cubic centimeter contains one billion organisms.

Antisera—The antisera comprise blood sera drawn from animals after they have been injected with properly treated pathogenic organisms against which immunity is sought. Serum is the clear fluid portion of the blood.

Production. For the production of diphtheria or tetanus antitoxin, horses are injected with appropriate toxin. The first doses are small, but the amount is gradually increased for a period of time to the point where the horse is receiving as much as 500 cc. or even more toxin at one time. Injections are made subcutaneously. Trial bleedings are made from time to time, and these bleedings are tested for potency. Sufficiently high potency for practical purposes usually is reached by diphtheric horses in three to four months and by tetanus horses in from four to eight months. When the potency is sufficiently high to make the blood usable, the horses are placed on regular bleeding schedules, bleedings being made about once every third week. The amount of blood taken at any one bleeding depends upon the size and condition of the horse, but for the average horse 10 to 12 liters may be taken. The blood is either allowed to clot and the clear serum withdrawn from the clot, or the bleeding is made into an anticoagulant such as sodium citrate. In the latter case blood is allowed to stand overnight and the plasma siphoned for the red cells. Fractional precipitation with ammonium sulfate yields a final precipitate of pseudo-globulin in which most of the antitoxin is contained. See Figure 7. This material is dialyzed

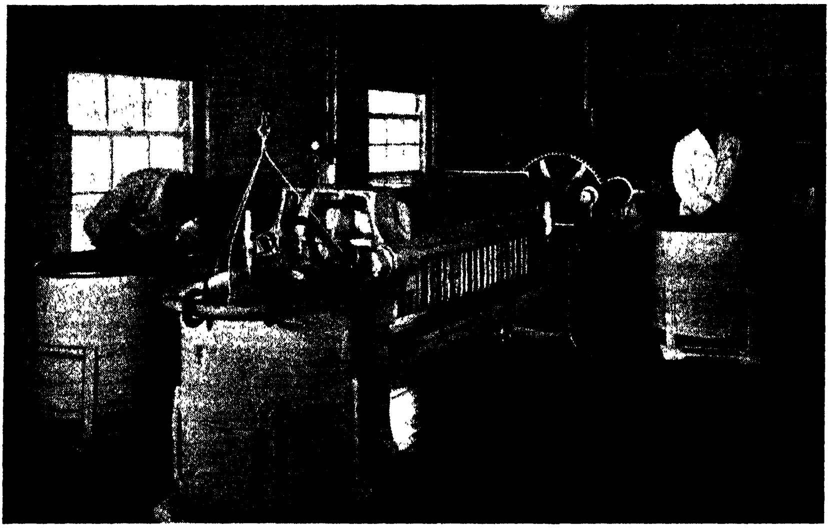


FIG. 7. Precipitation of Horse Serum by Means of Ammonium Sulfate.

and the dialysate rendered sterile by filtering through Seitz or Berkefeld filters.[40]

VITAMINS

It has long been known that man when deprived of fresh fruits and vegetables for long periods of time develops scurvy and that the eating of fruits and vegetables promptly relieves this condition. Other conditions of malnutrition related to diet were also recognized. Since it was thought that these naturally occurring substances, so essential to health, were amines, they were given the name vitamins—vital amines. They were further classified as oil-soluble and water-soluble. In the absence of any knowledge of their chemical structure they were designated as vitamin A, B, C, etc.

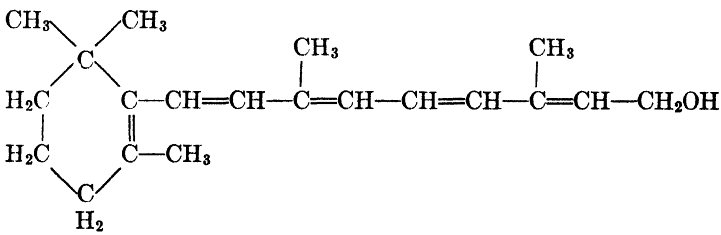
Concentrates were made of different foodstuffs which were rich in the desired vitamin. This was followed by the isolation, identification, and synthesis of many of the vitamins. At present, some nine of these essential food factors have been synthesized. However, it is not economical to produce all of these by synthetic procedures, for in some instances nature has been kind enough to furnish raw materials very rich in vitamins.

Vitamin Deficiencies in Our Nutrition—Recent studies of vitamin deficiencies show that our normally diversified diets may not afford us the needed

[40] Jamieson, W. A. and Powell, H. M., personal communication.

amounts of vitamins, because modern methods of processing foods tend to reduce their vitamin content. Sugar and wheat provide about half of the energy value of the food of the American people. Sugar is devoid of vitamins, and modern milling procedures produce a flour with about 5 per cent of the original vitamin content of the wheat. Our diet, for instance, contains about one-twelfth as much vitamin B_1 as it did a century ago.[41] Hence the use of vitamins either in pure form or as concentrates from natural sources may be expected to play an increasingly important role in our pattern of nutrition. Milk is now enriched with vitamin D, either through the irradiation of the milk or the addition of the synthetic product. Flour is being enriched by the addition of vitamins, especially B_1 and nicotinamide. If the necessary amount of B_1 were added to all of the flour produced, it would require 110,000 pounds annually of the pure vitamin. At current manufacturers' prices this quantity would be valued at almost $20,000,000.

Vitamin A—Vitamin A is necessary for the normal function of the skin and for the regeneration of visual purple and the promotion of normal vision. In the first instance, it affords resistance to infection and in the second, prevents the condition known as night blindness. It is a fat-soluble complex alcohol, present as an ester in the liver oils of many fishes, which has a β-ionone ring with a side chain containing four conjugated double bonds.



Vitamin A

If β-carotene were split at its central double bond, and a molecule of water were added to each half, we would have two molecules of vitamin A. Carotene has been called pro-vitamin A, since at least a portion of it can be converted in the liver into vitamin A. Carotene, prepared from carrots, is in clinical use.

Vitamin A, which has been reported synthesized, is readily obtained from fish liver oils. Both the ester and the free alcohol are equally effective. When fish liver oils are saponified by alcoholic sodium hydroxide, the non-saponifiable fraction is found to contain the alcohol form of vitamin A. Further concentration and purification of this fraction produces a concentrate of very high potency, one gram of which may contain as much as 2,000,000 units of vitamin A.

The recent commercial development of molecular distillation has made possible the concentration of the naturally occurring vitamin A ester.[42] When fish liver oils are fractionally distilled at a pressure of one to two microns, a fraction is obtained which is rich in vitamin A ester. This fraction has an activity of

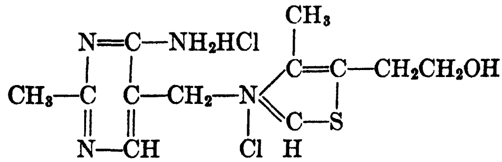
[41] Cowgill, G. R., J. Am. Med. Assoc. *113*, 2146 (1939).

[42] Hickman, K. C. D., Ind. Eng. Chem. *29*, 968, 1107 (1937); ibid. *32*, 1451 (1940); also U. S. Patents 1,925,559 (Sept. 5, 1933), 2,150.683-4-5 (Mar. 14, 1939), and others; Jewell, W., Mead, T. H. and Phipps, J. W., J. Soc. Chem. Ind. *58*, 56 (1939); Wittka, F., Angew. Chem. *53*, 557 (1940).

500,000 units per gram. Even though a daily dose of vitamin A may be 10,000 units, an ounce of this distillate would meet an individual's requirements for several years.

Vitamin B Complex—The term vitamin B was applied initially to water-soluble food essentials present in concentrates obtained from grain husks which were able to cure beri-beri and certain other nerve disorders. We now know that this concentrate consists of a number of chemically different compounds that exert different clinical effects and now designate this group as the vitamin B complex. These different factors are called B_1, B_2, etc.

Vitamin B_1—Vitamin B_1, also known as thiamin chloride and vitamin B_1 chloride hydrochloride, is 2-methyl-5-(4-methyl-5-β-hydroxyethyl-thiazolium chloride) methyl-6-aminopyrimidine hydrochloride.[43]



Vitamin B_1

This anti beri-beri vitamin is essential in the metabolism of carbohydrates and in cell respiration. It also plays an important part in promoting normal functions of the gastro-intestinal tract. It was originally obtained commercially from rice polishings, but now it is chiefly prepared synthetically.

In recovery from natural material, vitamin B_1 is removed from rice polishings by extraction with acidulated alcohol or water, and is separated from the solvent by adsorption on Fuller's earth or zeolites. It may be eluted by the use of aqueous alkali, acid, or ammonium salts and used as a concentrate or separated in its pure form. Many tons of rice polishings are required to produce a few grams of the vitamin. Yeast and wheat germ provide other sources of B_1.

The large extracting and concentrating units and the procedure of selective adsorption now have been superseded by enameled and stainless steel reaction kettles and stills, wherein the stepped-up laboratory procedures are being carried out for the commercial synthesis of thousands of pounds of vitamin B_1. See Figure 8. As might be anticipated, the large use of the synthetic product has resulted in a downward revision of the price. (See Addendum, page 1331.)

The commercial production is said to be based on modifications of the synthesis of Williams and his co-workers.[44] A large sequence of synthetic steps is necessary for the production of this complicated molecule. Ethyl formyl-β-ethoxypropionate, obtained from ethyl β-ethoxypropionate and ethyl formate, when reacted with acetamidine yields 2-methyl-5-ethoxymethyl-6-hydroxypyrimidine. When the latter is treated with phosphorus oxychloride, 2-methyl-5-ethoxymethyl-6-chloropyrimidine is obtained, which when treated with alcoholic ammonia gives 2-methyl-5-ethoxymethyl-6-aminopyrimidine. Treatment with

[43] Williams, R. R. and Spies, T. D., "Vitamin B_1 and Its Use in Medicine," The Macmillan Co., New York (1938).

[44] Williams, R. R. and Cline, J. K., J. Am. Chem. Soc. *58*, 1504 (1936), and Cline, J. K., Williams, R. R. and Finkelstein, J., ibid. *59*, 1052 (1937).

hydrobromic acid gives 2-methyl-5-bromomethyl-6-aminopyrimidine hydrobromide. When the latter is reacted with 4-methyl-5-β-(hydroxyethyl)thiazole, vitamin B_1 bromide hydrobromide is formed. By treatment with alcoholic silver chloride, vitamin B_1 chloride hydrochloride is obtained.

Variations in the method of synthesizing vitamin B_1 have been reported.[45]

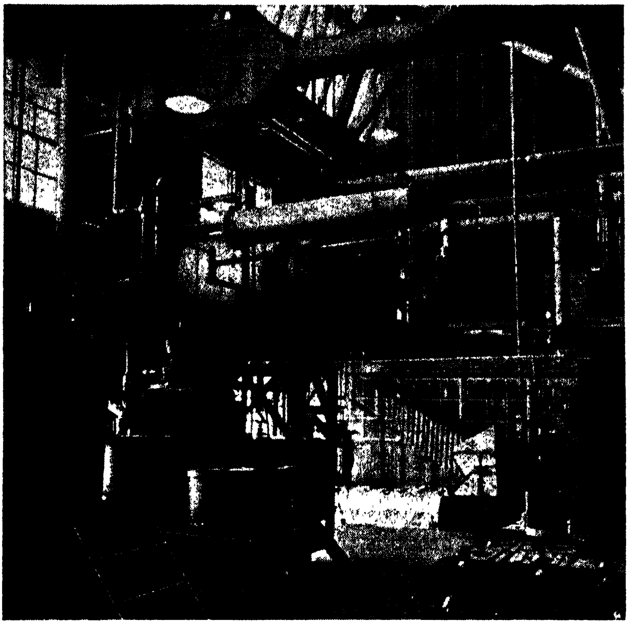
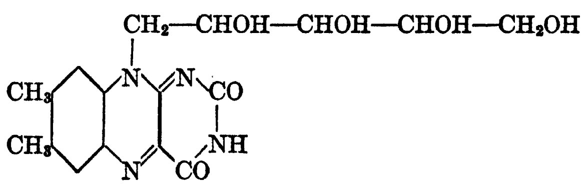


FIG. 8. Equipment Used for the Production of Synthetic Vitamin B_1.

Riboflavin—Another important component of the B complex is riboflavin, also called vitamin B_2, vitamin G, and lactoflavin. It is 6,7-dimethyl-9-(1'-*d*-ribityl) isoalloxazine.



Riboflavin

It is found in yeast, milk, kidney and liver tissue, and in many vegetables. Although a growth-promoting factor, its absence from the diet may cause cataract and certain skin diseases. The term B_2 is usually applied to the vitamin when it is obtained as a concentrate from natural sources. It may have an enhanced physiological effect due to traces of other factors. The term riboflavin is preferably applied to the synthetic product, which is identical in every respect

[45] Todd, A. R. and Bergel, F., J. Chem. Soc. *140*, 364 (1937), and Andersag, H. and Westphal, K., Ber. *70*, 2035 (1937).

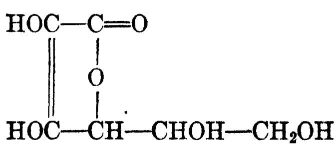
with the vitamin isolated from natural sources. A biological synthesis which uses the natural growth of certain bacteria is being industrially employed.[46]

Reference must be made to the scientific literature for the synthetic procedure, where it would appear that the chief problem is the limited availability of *d*-ribose. Of the several procedures described, one appears briefer and more direct than the others.[47] The first step is the condensation of *d*-ribose with 3,4-dimethylaniline and its simultaneous reduction to 3,4-dimethylphenyl-*d*-ribamine, with a 71 per cent yield. When coupled with benzenediazonium chloride, a 91 per cent theoretical yield of 2(*d*-ribitylamino)4,5-dimethylazobenzene is obtained, which can be reduced with sodium hydrosulfite, $Na_2S_2O_4$, to 1-amino 2-*d*-ribitylamino-4,5-dimethylbenzene. The latter is reacted with alloxantetrahydrate in an acetic acid solution containing boric acid to produce the desired riboflavin.

Vitamin B_6—Vitamin B_6, also called pyridoxine, is 2-methyl-3-hydroxy-4,5-di(hydroxymethyl) pyridine. It occurs in rice bran, liver, corn, and yeast, from which it may be extracted. Its specific clinical use is not quite clear at present. It is now produced synthetically by an involved method.[48] Ethoxyacetylacetone and cyanoacetamide are condensed to form 2-methyl-4-ethoxymethyl-5-cyano-6-pyridone, which is then nitrated at the 3 position. Reaction with phosphorus pentachloride yields 2-methyl-3-nitro-4-ethoxymethyl-5-cyano-6-chloropyridine. The nitro group is then reduced to the amino group and the cyano group to the aminomethyl group, forming 2-methyl-3-amino-4-ethoxymethyl-5-aminomethylpyridine, the chlorine having been eliminated in the reduction process. The amino group is replaced by a hydroxyl group by means of nitrous acid, and the ethyl group is then split off, giving at last vitamin B_6.

Other Members of the Vitamin B Complex—Other members of the B complex which have distinguishing characteristics, as shown from nutritional studies, are designated as vitamin B_3, B_4, and B_5. One is popularly called the anti-gray hair factor; another is called W, and another biotin, or vitamin H. There is still considerable work to do before the whole story of the vitamin B complex is unravelled. (See Addendum, page 1331.)

Vitamin C—Vitamin C, also called ascorbic acid, hexuronic acid, and cevitamic acid, is 2,3-enediol-1-gulono-1,4-lactone.



Vitamin C

This vitamin is present in citrus and many other fruits, in green vegetables and in paprika. It is a specific for the treatment and cure of scurvy and is an essential constituent of our diet. When its structure was established, it was found to be identical with hexuronic acid, which had been isolated previously in small amounts from the adrenal glands. While first obtained in quantity from

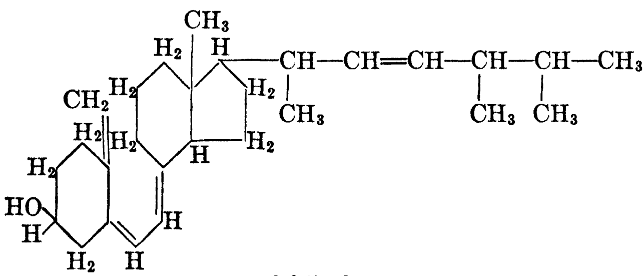
[46] Miner, C. S., U. S. Patent 2,202,161 (May 28, 1940).
[47] Karrer, P. and Meerwein, H. F., Helv. Chim. Acta. *19*, 264 (1936).
[48] Harris, S. A. and Folkers, K., J. Am. Chem. Soc. *61*, 1245 (1939). Chemical Abstracts calls B_6, Pyridoxin, 5-hydroxy-6-methyl-3,4-pyridine-dimethanol.

natural sources, it is now prepared far more economically by synthetic procedures. Many thousands of pounds are used annually in this country alone.

Several different methods for its synthesis have appeared in the scientific literature. The most direct process, which probably is the one used commercially, starts with *d*-sorbitol, a readily obtained reduction product of *d*-glucose. When *d*-sorbitol is subjected to the fermentive action of a bacteria (B. Xylinum Essigmutter), it is oxidized to *l*-sorbose. The *l*-sorbose is converted to diacetone sorbose, which is oxidized with permanganate to diacetone-2-ketogulonic acid. The acetone groups are removed, and the 2-ketogulonic acid lactonizes and enolizes in an acid medium, forming vitamin C.[49]

Vitamin D—The term vitamin D[50] is now used to designate a number of substances which function for the proper utilization of calcium and phosphorus and which prevent or cure rickets. These different vitamins have qualitatively the same effect on the animal body. The chief source of the natural vitamin D is fish liver oil, where it occurs in at least two forms. When ergosterol (from yeast) or 7-dehydrocholesterol (found with cholesterol) is irradiated with ultraviolet light, a structural change occurs and compounds are produced which are similar in function to vitamin D of fish liver oil.[51]

The irradiation of ergosterol has been the most carefully studied, and it is known that a progressive transformation occurs, with the formation of a series of products, each having the empirical structure of ergosterol. One of these products, which occurs about midway in this series, possesses antirachitic action. It has been called viosterol, or calciferol, and can be obtained in crystalline form.



Calciferol

The irradiated product of 7-dehydrocholesterol has also been obtained in crystalline form and is believed to be the same as the vitamin D obtained from natural sources. The properties of vitamin D are exhibited by at least ten different sterol derivatives.

It is possible to separate and concentrate vitamin D from fish liver oils by molecular distillation just as vitamin A is separated.[52]

The production of viosterol and the formation of vitamin D in foodstuffs by direct radiation has created a new industry of considerable size.

[49] Reichstein, T., Grüssner, A. and Oppenauer, R., Helv. Chim. Acta. *16*, 1019 (1933), and Reichstein, T. and Grüssner, A., ibid. *17*, 311 (1934).

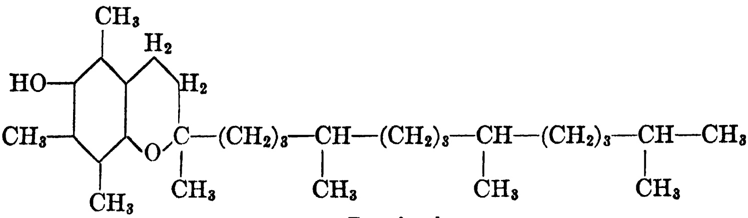
[50] American Medical Association, Council on Pharmacy and Chemistry and Council on Foods, "The Vitamins," p. 443, Chicago (1939).

[51] Steenbock, H., U. S. Patents 1,680,818 (Aug. 14, 1928) and 1,871,136 (Aug. 9, 1932); Milas, N. A., U. S. Patent 2,117,100 (May 10, 1938); and Sperti, G., Norris, R. J., Withrow, R. B. and Schneider, H., U. S. Patent 1,676,579 (July 10, 1928).

[52] Hickman, K. C. D. and Gray, E. L., Ind. Eng. Chem. *30*, 796 (1938).

Vitamin E—Vitamin E[53] is the term given to a naturally occurring group of closely related alcohols, the α- β- and γ-tocopherols. They appear to be a necessary factor in promoting normal reproduction. This group of vitamins is found in wheat germ and other oils.

α-Tocopherol has the greatest biologic activity and is, in most instances, referred to as vitamin E.



α-Tocopherol

The tocopherols may be obtained from the non-saponifiable residue of wheat germ oil or they may be separated from the oil itself by molecular distillation. α-Tocopherol can be synthesized from trimethylhydroquinone and phytyl bromide,[54] and the racemic form so obtained can be resolved into its isomers, of which the dextro-rotatory isomer is identical with the naturally occurring vitamin.

Vitamin K—Vitamin K, 2-methyl-3-phytyl-1,4-naphthoquinone, speeds up the clotting of the blood and thus decreases the danger of hemorrhage. It is found in various plant oils and in some animal fats. Alfalfa extracts which are rich in it provide its commercial source. It can be synthesized from 2-methylnaphthohydroquinone and phytol.[55] An extensive series of alkyl derivatives of 1,4-naphthoquinone have been prepared, many of which show a high degree of vitamin K activity. One of these, 2-methyl-1,4-naphthoquinone, is more active than the natural vitamin, and as it is more easily produced, it is the more widely used.

The necessary intermediate, 2-methylnaphthalene, can be obtained readily from coal tar. When an acetic acid solution of chromic acid is gradually added to an acetic acid solution of 2-methylnaphthalene, the latter is oxidized to 2-methyl-1,4-naphthoquinone, which separates on the addition of water. Final purification is obtained by recrystallization from methyl alcohol.

As is the case with nicotinic acid, we find vitamin activity in a compound which was previously known for many years.

Nicotinic Acid—Nicotinic acid, called vitamin P.P., was but recently found to be the specific curative agent for pellagra, a disease resembling leprosy in its external characteristics. It is a component of the vitamin B complex and is present in meat, liver, rice polishings, and yeast. The preparation of nicotinic acid is well known and simple as compared to most of the other vitamins. Nico-

[53] Evans, H. M. and Burr, G. O., "Antisterility Vitamine Fat Soluble E," University of California Press, Berkeley, Calif. (1927).

[54] Karrer, P., Fritzsche, H., Ringier, B. H. and Salomon, H., Helv. Chim. Acta. *21*, 520 and 820 (1938); Smith, L. I., Ungnade, H. E. and Prichard, W. W., Science *88*, 37 (1938); and Smith, L. I., Chem. Rev. *27*, 287 (1940).

[55] Fieser, L. F., J. Am. Chem. Soc. *61*, 3467 (1939), and J. Biol. Chem. *133*, 391 (1940).

tinic acid may be prepared by oxidizing nicotine, β-picoline or by oxidizing quinoline to quinolinic acid and heating the latter to remove CO_2.[56] The amide of this acid is also used for the same purpose and is prepared from ethyl nicotinate and ammonia. Its use in all flour would require an annual production of half a million pounds.

Pantothenic Acid—Pantothenic acid, α,γ-dihydroxy-β,β-dimethylbutyryl-β′-alanide, is also a member of the vitamin B complex.

$$
\begin{array}{ccccl}
 & CH_3 & & OH & \\
 & | & & | & \\
HOCH_2— & C & — & CH & —CONHCH_2—CH_2CO_2H \\
 & | & & & \\
 & CH_3 & & &
\end{array}
$$

Pantothenic Acid

It is found widely distributed in vegetables, in yeast, and in liver. It is believed to act in conjunction with riboflavin, although its exact physiological action is not known. While it can be obtained from natural sources, it is much more economical to prepare it by synthetic methods, in spite of the fact that it must be dextro-rotatory. The lactone of *d*,α,γ-dihydroxy-β,β-dimethylbutyric acid is condensed with ethyl-β-alanine, after which the ethyl group is removed by saponification.[57]

SYNTHETIC ORGANIC MEDICINALS

There are many synthetic organic drugs which do not duplicate naturally occurring products. In some instances, however, the naturally occurring product has furnished the chemist with the clue, as, for example, cocaine in the preparation of synthetic local anesthetics. In many other instances, the synthetic organic medicinal has no counterpart in nature.

Analgesics—There are a number of different synthetic organic compounds which have analgesic and antipyretic action; that is, they have the property of relieving pain in rheumatic conditions and in neuralgias, and also have the ability to lower the temperature in fevers. These compounds are derivatives of either phenol or aniline.

Salicylic Acid—Salicylic acid and its derivatives account for about half of the total amount of coal-tar medicinals produced in America. The use of acetylsalicylic acid has increased from slightly over 900,000 pounds in 1921 to over 5,000,000 pounds in 1939. To avoid the disagreeable taste and gastric symptoms produced by salicylic acid, esters and similar compounds have been introduced which are less soluble, so that the salicyl radical is liberated only in the intestine or after absorption into the blood stream.

The acyl derivatives (acetylsalicylic acid type) possess a greater degree of analgesic and antipyretic action than does the free acid and its salts. In addition

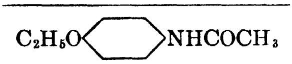
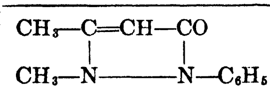
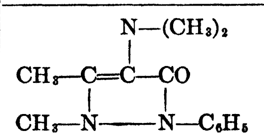
[56] Gilman, H., "Organic Syntheses," Coll. Vol. 1, p. 378, John Wiley & Sons, Inc., New York (1932); Adams, R. and Marvel, C. S., "Organic Chemical Reagents," IV, University of Illinois Bull. XX, No. 8, 37 and 39 (1922).

[57] Williams, R. J., Mitchell, H. K., Weinstock, H. H., Jr. and Snell, E. E., J. Am. Chem. Soc. *62*, 1784 (1940); Stiller, E. T., Harris, S. A., Finkelstein, J., Keresztesy, J. C. and Folkers, K., J. Am. Chem. Soc. *62*, 1785 (1940); Babcock, S H., Jr. and Jukes, T. H., J. Am. Chem. Soc. *62*, 1628 (1940).

to acetylsalicylic acid (the active material in aspirin tablets), there are methylenecitrylsalicylic acid[58] and salicylsalicylic acid.[59]

Manufacture—Salicylic acid is prepared from dry sodium phenate and carbon dioxide according to the Kolbe-Schmidt reaction. In this process, phenol is converted to sodium phenate by dissolving it in equimolar aqueous sodium hydroxide. The water from the aqueous solution is removed by evaporation with agitation, with final drying under reduced pressure at a temperature of about 150° C., since it is essential that every trace of water be removed from the sodium phenate. As evaporation proceeds the mass becomes gummy, and especially designed equipment, similar to a dough mixer, is required to finish the sodium phenate to a dry powder. The sodium phenate is then reacted with carbon dioxide under pressure in a jacketed autoclave. The carbon dioxide is finally forced in under about 100 pounds pressure. When the desired amount of carbon dioxide has been absorbed, the autoclave is heated at 150°-170° C. for several hours, after which the contents are cooled and dissolved in water. The solution of sodium salicylate is then conveyed to tanks, where it is acidified. The precipitated salicylic acid is then centrifuged, dried at a low temperature, and finally sublimed if a highly purified product is desired. Contamination with iron must be avoided.

TABLE 4—MANUFACTURE OF MISCELLANEOUS ANALGESICS

Name	*Structure*	*Method*
Acetophenetidin 4-ethoxyacetanilide		*p*-Phenetidine is refluxed in an enameled still with an excess of glacial acetic acid or acetic anhydride.[a, b]
Antipyrine 1,5-dimethyl-2-phenyl-3-pyrazolone		Phenylhydrazine is condensed with ethyl acetoacetate and the resulting phenylmethylpyrazolone is methylated.[c, d]
Aminopyrine 4-dimethylamino-1,5-dimethyl-2-phenyl-3-pyrazolone		Nitroso-antipyrine is reduced and methylated with methyl chloride or dimethyl sulfate.[d, e]

[a] Barrowcliff, M., and Carr, F. H., "Organic Medicinal Chemicals," p. 116, D. Van Nostrand Co., New York (1920).
[b] May, P., and Dyson, G. M., "May's Chemistry of Synthetic Drugs," p. 78, Longmans, Green and Co., London, 4th Ed. (1939).
[c] Knorr, L., Ann., *238*, 147 (1887), German Patent 26429, also p. 71, of reference b.
[d] Schwyzer, J., "Die Fabrikation pharmazeutischer und chemisch-technischer Produkte," p. 164, Julius Springer, Berlin (1931).
[e] Knorr, L., Ann. *238*, 212 (1887), also p. 73 of reference b.

Salicylic acid is preferably acetylated with acetic anhydride in the presence of a solvent, such as ethylene chloride, trichloroethylene, carbon tetrachloride, acetone, or Stoddard solvent. The reaction is fairly rapid, and the temperature

[58] Berendes, R. and Callsen, J., U. S. Patent 858,142 (June 25, 1907).
[59] Ach, L. and Sutter, T., U. S. Patent 922,995 (May 25, 1909).

should be kept around 40° C. to prevent undesirable side reactions. After the reaction is completed, the solvent is partially removed and the acetylsalicylic acid allowed to crystallize. After centrifuging, it still contains traces of acetic acid, acetic anhydride, and unreacted salicylic acid. To complete the purification it is recrystallized from a solvent, there being a choice of solvents or mixtures of solvents, as carbon tetrachloride and dioxane. The mother liquors are distilled to recover the solvent, and the acetylsalicylic acid which they contain is repurified. The by-product acetic acid may be recovered as such or converted to sodium acetate.

Acetanilid—Acetanilid is prepared by refluxing a benzene solution of one part of aniline and 1.4 parts of acetic anhydride in a jacketed, enameled still until all of the aniline has reacted. The reaction mixture is filtered and cooled, and the acetanilid which separates is recrystallized from hot water.

The essential points in the manufacture of the other important analgesics derived from aniline are contained in Table 4.

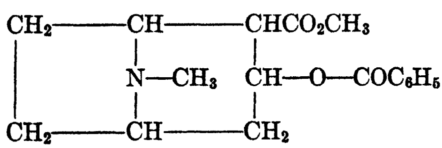
ANESTHETICS

Anesthetics may be divided into two groups, one having a general action, which consists chiefly of gases or volatile compounds, and the other group consisting of a very diversified series of organic substances, chiefly basic in nature, having a highly localized action which is centered at the point of administration.

General Anesthetics—In the field of general anesthetics, chloroform and ether are two well-known compounds which are widely used. Special methods must be employed for their purification and stabilization. Also ethylene, cyclopropane, and divinyl ether [60] are used for general anesthesia. 1-Chloro-2-dichloroethylene and tribromoethanol [61] are used for their general anesthetic effect.

Local Anesthetics—In addition to methyl and ethyl chloride, which cause local anesthesia by the production of low temperatures through evaporation, there are other compounds of far greater usefulness which produce local anesthetic effect either because they are protoplasmic poisons, such as quinine, or because they have a specific paralyzing effect when applied locally on sensory nerve ends, such as cocaine.

Cocaine, benzoylmethylecgonine, is an alkaloid obtained from coca leaves which possesses local anesthetic action. The elucidation of its structure initiated much chemical work, directed toward ascertaining the chemical basis for local anesthetic action.



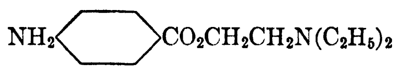
Cocaine

[60] Major, R. T. and Ruigh, W. L., U. S. Patents 2,021,872 (Nov. 19, 1935), 2,044,801 (June 23, 1936) and 2,099,695 (Nov. 23, 1937).

[61] Merwein, H., U. S. Patent 1,572,742 (Feb. 9, 1926); Callsen, J., U. S. Patent 1,725,054 (Aug. 20, 1929), and Schranz, K. and Jaeger, A. O., U. S. Patent 1,882,984 (Oct. 18, 1932).

Synthetic Local Anesthetics—One of the earliest of synthetic local anesthetics was β-eucaine hydrochloride, the benzoyl ester of 2,6,6-trimethyl-4-hydroxypiperidine.

Local anesthetic action is characteristic of a rather broad series of compounds which in general are alkylaminoalkanol esters of benzoic or *p*-aminobenzoic acid. The amino group may be secondary or tertiary, or may be part of a ring. The alcohol group may be primary, secondary, or tertiary, and separates the amino group and the acyl group by a chain of at least two carbon atoms. The most widely used member of this series is procaine hydrochloride, β-diethylaminoethyl *p*-aminobenzoate hydrochloride. It is readily prepared by heating diethylaminoethanol[62] with *p*-nitrobenzoyl chloride, which forms diethylaminoethyl *p*-nitrobenzoate. This latter compound may be reduced with tin and hydrochloric acid to give diethylaminoethyl *p*-aminobenzoate, procaine. After making alkaline, this base is separated, and converted into the hydrochloride.



Procaine

There are a number of other compounds having this general structure, which are used because they possess certain differences in the type and the intensity of local anesthetic action. Among these are γ-diethylaminopropyl cinnamate hydrochloride,[63] 'Apothesine'[8] hydrochloride; γ-dibutylaminopropyl *p*-aminobenzoate sulfate,[64] 'Butyn'[8] sulfate; γ-diethylamino-β-dimethylpropyl-*p*-aminobenzoate hydrochloride, 'Larocaine'[8] hydrochloride; γ-[2-methylpiperidino]propyl benzoate hydrochloride,[65] 'Metycaine';[8] β-di-methylaminoethyl *p*-butyl-aminobenzoate hydrochloride,[66] 'Pontocaine'[8] hydrochloride; γ-dimethylamino-amino-α,β-dimethylpropyl *p*-aminobenzoate hydrochloride, 'Tutocain';[8] 2-benzoxy-2-dimethylaminomethyl-1-dimethylaminobutane hydrochloride,[67] 'Alypin,'[8] and β-monoisobutylaminoethyl *p*-aminobenzoate hydrochloride,[68] 'Monocaine.'[8]

The following compounds differ in structure from the above, yet possess adequate local anesthetic action for clinical use: piperidinopropanediol-diphenylurethane hydrochloride,[69] 'Diothane'[8] hydrochloride; 2-butoxy-*N*-(β-diethylaminoethyl)-cinchoninamide hydrochloride,[70] 'Nupercaine'[8] hydrochloride, and ethenyl-*p*-diethoxydiphenylamidine hydrochloride, phenacaine hydrochloride.

This entire group of local anesthetics forms salts which are soluble in water and are in general less toxic than cocaine in proportion to anesthetic action. Procaine hydrochloride has no effect on intact mucous membrane, but a number of the other local anesthetics, particularly those having at least three carbon atoms

[62] Perkins, G. A. and Purse, J. H., U. S. Patent 2,090,485 (Aug. 17, 1937).
[63] Thorp, L., U. S. Patent 1,193,634 (Aug. 8, 1916); Wildman, E. A. and Thorp, L., U. S. Patents 1,193,649 (Aug. 8, 1916), 1,193,650 (Aug. 8, 1916) and 1,193,651 (Aug. 8, 1916).
[64] Kamm, O., Adams, R. and Volwiler, E. H., U. S. Patent 1,358,751 (Nov. 16, 1920)
[65] McElvain, S. M., U. S. Patent 1,784,903 (Dec. 16, 1930).
[66] Eisleb, O., U. S. Patent 1,889,645 (Nov. 29, 1932).
[67] Hofmann, F., U. S. Patent 808,748 (Jan. 2, 1906).
[68] Goldberg, S. D. and Whitmore, W. F., J. Am. Chem. Soc. *59*, 2280 (1937).
[69] Rider, T. H., U. S. Patent 2,004,132 (June 11, 1935).
[70] Miescher, K., U. S. Patent 1,825,623 (Sept. 29, 1931).

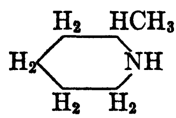
intervening between the alkyl amino group and the acyl group, are effective on mucous membrane.

Alkyl esters of *p*-aminobenzoic acid also have local anesthetic action, although they are such weak bases that their salts hydrolyze in water. The free bases are used in the form of ointments for topical application to painful areas.

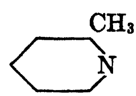
Synthesis of 'Metycaine'—Although no one process of manufacture may be said to be typical of the production of local anesthetics, the commercial preparation of one will be described to illustrate some of the methods commonly employed. The synthesis of 'Metycaine' consists of four steps: the preparation of trimethylene chlorohydrin, α-pipecoline, 2-methylpiperidinopropyl alcohol, and 2-methyl-piperidinopropyl benzoate hydrochloride.

Trimethylene chlorohydrin, $ClCH_2CH_2CH_2OH$, is prepared by the action of sulfur chloride on trimethylene glycol.[71] This reaction is preferably carried out in an enameled jacketed still, which can be heated with steam, or cooled with water should the reaction become too vigorous. This still has a side opening leading to a scrubber and a removable top, the latter containing peep-holes and an opening to admit the sulfur chloride. The desired amount of trimethylene glycol, $HOCH_2CH_2CH_2OH$, is added to the still and warmed. Sulfur chloride in the ratio of about 2.2 pounds to each pound of glycol is then added gradually, so that the reaction is not too vigorous, the evolved gases being absorbed by the scrubber. After the sulfur chloride has been added, the still is heated for several hours and then allowed to cool. The top is then removed and the contents scooped out. The precipitated sulfur is filtered from the crude trimethylene chlorohydrin, and the dissolved sulfur dioxide is removed from the filtrate by aeration. The crude trimethylene chlorohydrin is purified by fractional distillation *in vacuo,* in a separate fractionating unit. The yield is 60-65 per cent of theory. The size of the still is such that it has at least twice the volume of its contents.

α-Pipecoline

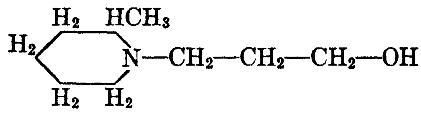


is prepared by the catalytic reduction of α-picoline,



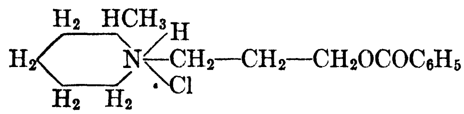
using hydrogen and the Rainey nickel catalyst. Care must be taken that complete reduction is secured. The α-pipecoline is converted into the corresponding piperidino alcohol in a jacketed enameled still, equipped with a motor-driven agitator, peep sights, reflux condenser, and inlet openings. To α-pipecoline, mixed with a concentrated solution of sodium hydroxide, an equal weight of trimethylene chlorohydrin is added slowly with stirring. After some hours' refluxing, the upper layer of crude 2-methyl piperidinopropyl alcohol

[71] Derick, C. G. and Bissell, D. W., J. Am. Chem. Soc. *38,* 2478 (1916).



is separated, dried, and fractionally distilled *in vacuo*.

The piperidinopropyl alcohol is added to benzene in the same still and warmed. Benzoyl chloride is added gradually with stirring, in an amount equal to the weight of piperidinopropyl alcohol used. When this addition is completed, the still contents are refluxed for some hours. On cooling, the crude 'Metycaine' (γ-[2-methylpiperidino]propyl benzoate hydrochloride)



is separated by filtration, washed with ether, and recrystallized from alcohol and acetone in a jacketed enameled pot.

ANTISEPTICS

An antiseptic is a substance which destroys bacteria either by killing them or preventing their growth. Antiseptic action is not a characteristic of any one group or any few groups of compounds. The following brief descriptions, which outline the essential features of their manufacture, cover the principal compounds that have found acceptance in the field of antisepsis.

Phenol was the first substance having antiseptic action which was used for the prevention of infection. However, the pharmaceutical use of phenol is infinitesimal compared to the total amount of phenol manufactured for other purposes. Cresol, a mixture of three isomeric cresols obtained from coal tar, is dissolved in a soap solution, and thus used as a disinfectant. When groups greater than the methyl group are introduced into the phenol radical, the germicidal efficiency is further increased. However, other factors, such as the decreased solubility of the higher alkyl phenols and the irritating action on the skin, have limited the application of the higher alkyl phenols.

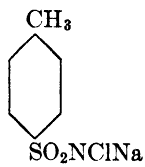
Resorcinol, $C_6H_4(OH)_2$, and many of its derivatives are used in medicine. Its monoacetate is prepared by reacting resorcinol and acetic anhydride. When alkyl groups are introduced into resorcinol, its antiseptic action becomes more pronounced, as, for example, hexyl and heptyl resorcinol.[72] Guaiacol, thymol, menthol, eucalyptol, and β-naphthol are other phenolic compounds which are employed in medicine.

Methenamine, hexamethylene tetramine, $(CH_2)_6N_4$, is used because of its ability to liberate formaldehyde in acidic media. It is prepared by treating formaldehyde with excess ammonia solution in the cold. After evaporation *in vacuo*, the methenamine crystallizes out.

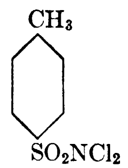
[72] Johnson, T. B. and Lane, F. W., J. Am. Chem. Soc. *43*, 348 (1921); Dohme, A. R. L., U. S. Patents 1,649,669 (Nov. 15, 1927), 1,649,670 (Nov. 15, 1927), 1,649,671 (Nov. 15, 1927), and 1,717,098 (June 11, 1929); Hirzel, H., U. S. Patent 1,717,105 (June 11, 1929).

Mandelic acid recently has found extensive use as a urinary antiseptic. Some 65,000 pounds were used in 1938, the third year of its clinical application. It is prepared from benzaldehyde, sodium cyanide, sodium bisulfite, and hydrochloric acid by adapting the laboratory procedure to large batch operations.[73]

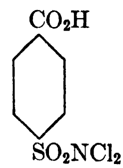
The germicidal action of free chlorine and the hypochlorites is well known. When hypochlorites act on proteins, the NH groups are chlorinated. This observation led to the preparation of substituted chloramines. Sodium *p*-toluenesulfonchloramide, chloramine T, a water-soluble derivative of this class, is prepared by the action of sodium hypochlorite on *p*-toluenesulfonamide.[74] Dichloramine-T, *p*-toluenesulfon dichloramide, an oil-soluble derivative of this group, is formed when an excess of sodium hypochlorite is added to *p*-toluene sulfonamide.[75] When sodium *p*-sulfonamidobenzoate is treated with excess sodium hypochlorite, *p*-sulfonedichloroamidobenzoic acid, halazone, is obtained.[76] 'Azochloramide,'[8] α,α'-azobis(chloroformamidine), is another chloramide derivative which has disinfectant properties.[77]



Chloramine T



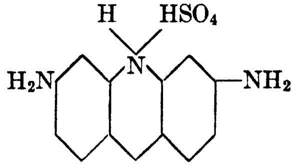
Dichloramine T



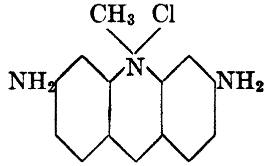
Halazone

There are a number of dyestuffs which are used as antiseptics. Proflavine, 2-8-diaminoacridinium monohydrogen sulfate, is prepared by the following general procedure.[78] Aniline and formaldehyde are reacted, forming trimethylene aniline, $(C_6H_5NCH_2)_3$, which is reacted with additional aniline hydrochloride to give methylenediphenyldiamine. This rearranges into 4,4'-diaminodiphenylmethane, which is then nitrated to form 2,2'-dinitro-4,4'-diaminodiphenylmethane. When the latter is reduced and heated with hydrochloric acid, 2,8-diaminoacridine is obtained.

Proflavine is methylated by treating the acetyl derivative with methyl chloride or methyl *p*-toluene sulfonate. This is deacetylated with hydrochloric acid, forming 2,8-diamino-*N*-methyl-acridinum chloride, acriflavine. Another member of this group is 'Rivanol,'[8] 7-ethoxy-2,5-diaminoacridine.



Proflavine



Acriflavine

[73] Gilman, H., "Organic Syntheses," Coll. Vol. I, p. 329, John Wiley & Sons, New York (1932).
[74] Inglis, J. K. H., J. Soc. Chem. Ind. *37*, 288 (1918).
[75] Chattaway, F. D., J. Chem. Soc. *87*, 145 (1905).
[76] Dakin, H. D. and Dunham, E. K., Brit. Med. J. *1*, 682 (1917).
[77] Schmelkes, F. C., U. S. Patents 1,958,370 (May 8, 1934) and 1,958,371 (May 8 1934).
[78] Ehrlich, P. and Benda, L., U. S. Patent 1,005,176 (Oct. 10, 1911).

Several of the triphenylmethane dyes are used medicinally for their bactericidal or bacteriostatic action. They are chiefly methyl derivatives of pararosaniline, rosaniline, and fuchsin. Methylene blue and malachite green also have clinical application.

SULFANILAMIDE AND DERIVATIVES

The discovery of the effectiveness of *p*-aminobenzenesulfonamide, better known as sulfanilamide, in combating streptococcic infections is illustrative of the difficulties encountered in attempting to predict clinical usefulness from the basis of chemical structure. This compound had been known since 1908 and had been used in dyestuffs, yet there was nothing in its structure to indicate its tremendous clinical value. A study of the antistreptococcic effect of a group of azo dyes derived from *p*-aminobenzenesulfonamide led to the discovery that the effectiveness resided in the sulfonamide part of the molecule.[79] Had these azo dyes been prepared from any other compound, this great contribution to chemotherapy might not have come to pass. Once again, progress in the field of synthetic medicinals has been dependent upon the fortuitous observations of keen investigators.

During the past six years thousands of derivatives have been made and studied.[80] More of these derivatives are in clinical use abroad than in the United States, where the three most widely used products are sulfanilamide, sulfapyridine, 2-(*p*-aminobenzenesulfonamido)-pyridine, and sulfathiazole, 2-(*p*-aminobenzenesulfonamido)-thiazole. (See Addendum, page 1331.)

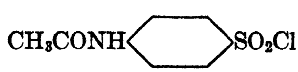
The usefulness of sulfanilamide can be judged from the fact that within three years after its introduction, the annual use in this country alone was more than 700,000 pounds.

Sulfapyridine has a specific action against pneumococcus. During the first year of its clinical application it all but eliminated the use of antipneumococcic serum, since it afforded a less expensive means of treatment.

Sulfathiazole, which is as effective in treating pneumonia as sulfapyridine, has less side effects and can be produced at a lower cost, consequently it is displacing sulfapyridine in a substantial degree.

In contrast to bactericidal compounds which cannot be used internally because of their toxic effect on the patient, sulfanilamide and its derivatives, when taken internally, cause the destruction of the bacteria without being unduly toxic to the patient. However, they are not devoid of toxic action if taken in excess. The exact nature of their specific action against bacteria is not clearly understood.

Manufacture of Sulfanilamide—Sulfanilamide, sulfapyridine, and sulfathiazole require a common intermediate, *p*-acetylaminobenzenesulfonyl chloride:



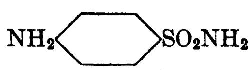
[79] Domagk, G., Deut. med. Wochschr. *61*, 250-53 (1935); Klin. Wochschr. *15*, 1585 (1936); Tréfouël, J., Tréfouël, Mme. J., Nitti, F. and Bovet, D., Compt. rend. soc. biol. *120*, 756 (1935), and Ann. inst. Pasteur *58*, 30 (1937).

[80] Mellon, R. R., Gross, P. and Cooper, F. B., "Sulfanilamide Therapy of Bacterial Infections," Thomas, Springfield, Ill. (1938); Long, P. H. and Bliss, E. A., "Clinical and Experimental Use of Sulfanilamide, Sulfapyridine and Related Compounds," Macmillan, New York (1939); Northey, E. H., Chem. Rev. *27*, 85 (1940).

This intermediate is readily prepared by adding acetanilide to an excess of chlorosulfonic acid.[81] One molecular portion of acetanilide is added gradually to five molecular portions of chlorosulfonic acid in a jacketed enameled still equipped with a stirrer. The temperature of the still contents is maintained at about 25° C., until all of the acetanilide has been added, after which the temperature is gradually raised to 60° C. and held there for several hours. The reaction mixture is then cooled to about 25° C. and cautiously run into crushed ice in a vat equipped with a powerful stirrer. The crude *p*-acetylaminobenzenesulfonyl chloride, which separates, is centrifuged, washed, and again centrifuged. It is either used in a moist condition or else rapidly dried *in vacuo* at a low temperature and then crystallized, as, for example, from ethylene dichloride.

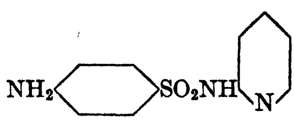
For the preparation of sulfanilamide, the moist sulfonyl chloride from one molecular proportion of acetanilide is added gradually to a dilute aqueous solution of about four molecular proportions of ammonia with constant agitation. A temperature of about 45° C. is maintained. When all of the sulfonyl chloride has been added, the contents are stirred for about half an hour. The reaction mixture is cooled below 25° C., and the crude acetylsulfanilamide is centrifuged, washed, and centrifuged again.

To hydrolyze the acetyl group, one molecular proportion of crude acetylsulfanilamide is added to a hot dilute aqueous solution of two molecular proportions of hydrochloric acid in a jacketed enameled still equipped with a reflux condenser. The mixture is gently refluxed until complete solution is effected, after which the heating is continued for 30 to 60 minutes. The hot acid solution is neutralized with sodium carbonate and cooled. Then the crude sulfanilamide is separated from the mother liquor by centrifuging. It is purified by dissolving in hot dilute alcohol and treating with activated carbon. After filtering and cooling, the sulfanilamde, which separates in crystalline form, is filtered and dried *in vacuo*.



Sulfanilamide

Sulfapyridine—In the preparation of sulfapyridine,[82] it is preferable to react molecular proportions of dry, crystalline *p*-acetylaminobenzenesulfonyl chloride and 2-aminopyridine[83] in a pyridine solution. The crude acetylsulfapyridine so obtained is hydrolyzed by heating with 1.5 molecular proportions of 6 or 8 per cent sodium hydroxide. Acid cannot be employed, since it splits off the aminopyridine group. On completion of the hydrolysis, the solution is neutralized and the crude sulfapyridine which separates is filtered off and recrystallized.



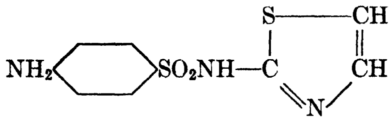
Sulfapyridine

[81] Gilman, H., "Organic Syntheses," Coll. Vol. I, p. 8, John Wiley & Sons, New York (1932).

[82] Goldyrev. L. N. and Postovskii, I. Y., J. Applied Chem. (U.S.S.R.) *11*, 316 (1938); Ewins, A. J. and Phillips, M. A., Brit. Patent 516,288 and U. S. Patent 2,259,222 (Oct. 14, 1941); Webster, G. L. and Powers, L. D., J. Am. Chem. Soc. *60*. 1553 (1938).

[83] Utgoff, V. V., U. S. Patent 1,832,799 (Nov. 17, 1931); Shreve, R. N., Riechers E. H., Rubenkoenig, H. and Goodman, A. H., Ind. Eng. Chem. *32*, 173 (1940).

Sulfathiazole—Sulfathiazole is prepared by the interaction of molecular proportions of crystalline *p*-acetylaminobenzene sulfonyl chloride and 2-aminothiazole in pyridine. The acetyl group may be hydrolyzed by the use of hot acid or alkali.



Sulfathiazole

METALLIC AND ORGANOMETALLIC COMPOUNDS

There are a great many inorganic acids, salts, and bases used directly or indirectly in the pharmaceutical industry. Among the acids we find boric, hydrochloric, hypophosphorous, nitric, phosphoric, and sulfuric. In addition to ammonia water, ammonium bromide, carbonate, and chloride are used. Calcium hydroxide, bromide, carbonate, and chloride; potassium bicarbonate, bromide, carbonate, chloride, hydroxide, iodide, nitrate, and permanganate; sodium bicarbonate, biphosphate, borate, bromide, carbonate, chloride, hydroxide, iodide, nitrate, perborate, phosphate, sulfate, and thiosulfate; alum, barium sulfate, chromium trioxide, ferric chloride and phosphate, ferrous sulfate, iodide and carbonate, reduced iron, nitrous oxide, zinc chloride, oxide and sulfate, magnesium oxide, hydroxide, carbonate, phosphate, and sulfate are employed.

A number of relatively toxic inorganic compounds have come into use, such as: silver nitrate, arsenic trioxide and tri-iodide, copper sulfate, mercury bichloride, mercuric oxide, and mercurous chloride and iodide.

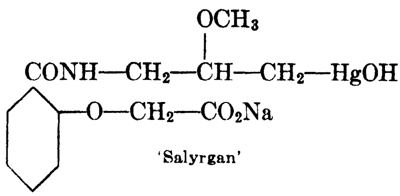
There are a great many metallic salts of organic acids and pseudo acids employed, in some instances merely to obtain the drug in a more soluble form, in other instances because of some specific effect of the metal.

Mercury and Its Compounds—Metallic mercury and its inorganic salts, both water-soluble and water-insoluble, have a variety of clinical uses. The more widely used of the soluble salts are mercury bichloride, red mercuric iodide, mercuric cyanide, mercuric oxycyanide, mercuric succinimide, and potassium mercuric iodide. The insoluble compounds, for which it is claimed that administration is not so frequently required, include mercuric sulfide and yellow mercuric oxide. Insoluble mercury salts of organic acids include mercuric benzoate, mercuric salicylate, and mercuric oleate. These compounds have been employed medicinally for a long time; however, their use is being replaced to a rather marked degree by soluble organic-mercury compounds, in which the beneficial action of the metal is retained but in which toxicity is less than that observed when the metal is present in an ionizable form.

Of the many soluble organic mercury [84] compounds known, only a few have a disinfectant action sufficiently powerful to be of clinical value, or a diuretic effect sufficiently great to be useful clinically, and still not be too toxic for the patient. On the other hand, there are soluble organic mercury derivatives which have neither diuretic nor bactericidal action, which are also relatively non-toxic.

[84] Whitmore, F. C., "Organic Compounds of Mercury," Chemical Catalog Co., New York (1921).

Organic mercury derivatives having a diuretic action may be prepared by the action of mercuric acetate and methyl alcohol on an organic compound containing the allyl group and a solubilizing group, as, for example, 'Salyrgan,'[8] sodium [o-(hydroxymercuric methoxypropylcarbamyl)phenoxyl] acetate.[85]

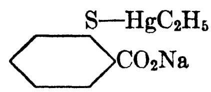


'Salyrgan'

Other diuretics can be prepared by reacting organic mercuric anhydrides of the type of ortho-hydroxy-mercuric salicylic anhydride, in the presence of an alkali, with an imino-containing compound which has a solubilizing group in addition to the imino group.[86]

When mercury is connected directly to the carbon atom of an organic radical, as, for example, the phenyl radical, which contains a carboxyl or a sulfonic acid group, the resulting acid and its salts have no, or at the most a relatively low, bactericidal action, compared to mercurated phenolic or nitro-phenolic compounds, or to mercury derivatives of aromatic acids which form lactones at a hydrogen ion concentration of about that of the body, or to mercury compounds wherein a sulfur atom intervenes between the mercury and the carbon atom.

A representative of the latter group, in which mercury is separated by a sulfur atom from the aromatic nucleus containing the carboxylic acid group, is sodium ethylmercuri thiosalicylate, 'Merthiolate,'[8]



'Merthiolate'

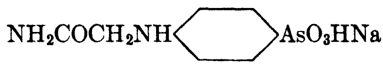
This is prepared[87] by reacting ethylmercuric chloride with thiosalicylic acid in an alcoholic solution in the presence of sodium hydroxide. Thiosalicylic acid is prepared by coupling diazotized anthranilic acid with potassium ethylxanthate, hydrolyzing, and reducing the dithio acid with zinc in the presence of sodium carbonate. In these reactions, due to the presence of the —SH group, it is necessary to eliminate traces of iron and copper, consequently all equipment is enameled. The units, which vary from 100 to 300 gallons, are jacketed enameled stills, most of which are equipped with agitators. 'Merthiolate' has a high bactericidal and bacteriostatic action, with a toxicity reported to be about one-seventh that of mercurated cresol derivatives having approximately the same bactericidal action.

Arsenic Compounds—Organic arsenicals[88] are of use in combating protozoal infections. Due to their ability to liberate arsenic slowly in the body, it is pos-

[85] Bockmühl, M. and Schwarz, A., U. S. Patent 1,693,432 (Nov. 27, 1928).
[86] Engelmann, M., U. S. Patents 1,034,092 (July 30, 1912) and 1,074,781 (Oct. 7, 1913).
[87] Kharasch, M. S., U. S. Patent 1,672,615 (June 5, 1928).
[88] Raiziss, G. W. and Gavron, J. L., "Organic Arsenical Compounds," Chemical Catalog Co., New York (1923).

sible to have arsenic present in the circulating blood for a longer period of time than occurs when inorganic arsenicals are administered. The trivalent organic arsenicals, which are more active and more toxic than the pentavalent, provide us with our most effective treatment for syphilis.

The pentavalent organic arsenicals, which include both aliphatic and aromatic arsonic acids, are used in the treatment of amebiasis, certain trypanosome diseases, and syphilis of the central nervous system. Sodium *N*-phenylglycineamide-*p*-arsonate, 'Tryparsamide,'[8]

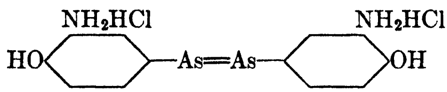


'Tryparsamide'

is one of the most widely used organic pentavalent arsenicals. It is prepared by refluxing an aqueous solution of sodium *p*-aminophenylarsonate with an equivalent amount of chloroacetamide. On cooling, crude phenylglycinamide-*p*-arsonic acid crystallizes out. It is purified by extracting with hydrochloric acid, then dissolving in dilute alkali, filtering and acidifying with acetic acid. The addition of alcohol to a concentrated aqueous solution of the sodium salt causes it to precipitate.[89]

Organic trivalent arsenicals which are very toxic for spirochetes and trypanosomes, could not have been used clinically had Ehrlich not been able to elaborate derivatives in which the human toxicity was reduced without losing the effectiveness against parasites. Ehrlich's work is the outstanding example of how chemical structure can be modified to bring about the desired therapeutic effects. The trivalent arsenicals now used fall into two groups, the arsenobenzenes and arsenoxides.

Arsphenamine is 3,3'-diamino-4,4'-dihydroxyarsenobenzene dihydrochloride.[90]



Arsphenamine

The direct reduction of 3-nitro-4-hydroxyphenylarsonic acid by means of sodium hyposulfite appears to be the most satisfactory procedure for making arsphenamine base. This is accomplished by using an excess of an aqueous solution of sodium hyposulfite, to which have been added magnesium chloride and sufficient caustic to make it alkaline in reaction. By heating around 60° C. and stirring vigorously, complete reduction is obtained in about 2 hours. The crude yellow arsphenamine base is separated and dried *in vacuo*. After being suspended in methyl alcohol, it is then converted into the dihydrochloride, through the addition of dry hydrogen chloride. The dihydrochloride is precipitated by the addition of anhydrous ether. All these operations are carried out as far as possible in the absence of air and in glass or enameled equipment of moderate size.

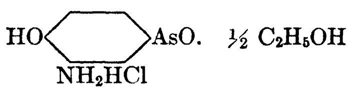
[89] Jacobs, W. A., Brown, W. H., Heidelberger, M. and Pearce, L., U. S. Patent 1,280,119 (Sept. 24, 1918).

[90] Raiziss, G. W. and Gavron, J. L., "Organic Arsenical Compounds," p. 185, Chemical Catalog Co. (1923), and Ehrlich, P. and Bertheim, A., U. S. Patents 986,148 (Mar. 7, 1911), 1,081,592 (Dec. 16, 1913), 1,081,897 (Dec. 16, 1913), and 1,116,398 (Nov. 10, 1914).

Neoarsphenamine—Neoarsphenamine, sodium 3,3′-diamino-4,4′-dihydroxy-arsenobenzene methanalsulfoxylate, is more widely used than arsphenamine, because it can be administered intramuscularly. It is prepared by reacting an aqueous solution of arsphenamine with sodium formaldehyde-sulfoxylate.[91]

Exceedingly great care is required for the manufacture of these arsenobenzene derivatives. This, together with the small sized dose administered, sets a limit to the batch size which can be prepared economically. According to the U. S. Tariff Commission Reports, the following amounts of the arsenobenzenes were sold during the year of 1939: neoarsphenamine, 9609 lbs.; arsphenamine, 233 lbs.; sulfarsphenamine, 135 lbs. With five or six companies manufacturing each of the above materials, the batch size is probably in many instances less than economy of processing would determine.

The hemialcoholate of 3-amino-4-hydroxyphenylarsine oxide hydrochloride, called 'Mapharsen,' [8] is an oxidized form of arsphenamine and the one which presumably is formed in the body from arsphenamine.[92]



'Mapharsen'

It is prepared by reducing the corresponding aminohydroxyphenylarsonic acid with sulfur dioxide in the presence of potassium iodide. Its clinical use depended on the evolving of a stable highly purified product.[93]

Antimony Compounds—Organic antimony compounds,[94] both trivalent and pentavalent, are used for the treatment of various protozoal diseases. Among the trivalent compounds we find products in which one molecule of antimony has been reacted with two or three molecules of a thio acid, as, for example, antimony trithioglycolamide. Pentavalent aromatic stibonic acids [95] are widely used in some of the tropical and oriental countries, while tartar emetic, antimonyl potassium tartrate, has long been used in medicine.

Bismuth—The insoluble compounds of bismuth which are used as protective agents for inflamed or irritated surfaces must be in a very finely divided form, so as to permit an even distribution throughout the intestinal tract or over the wound surface. Bismuth compounds of the insoluble type are bismuth β-naphtholate, bismuth tribromophenate, and various preparations of magma of bismuth, which is a suspension of bismuth hydroxide and bismuth subcarbonate in water.

In the early 1920's the use of bismuth compounds in the place of mercury for the treatment of syphilis was initiated. In contrast to the highly specific effect of organic arsenicals, it was soon established that a wide variety of organic

[91] Raiziss, G. W. and Gavron, J. L., "Organic Arsenical Compounds," p. 195, Chemical Catalog Co., New York (1923); Korndörfer, G. and Reuter, B., U. S. Patent, Reissue, 13,848 (Dec. 15, 1914).

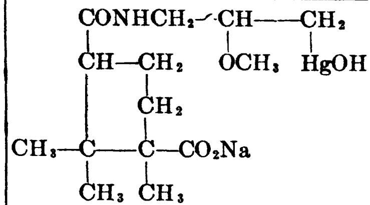
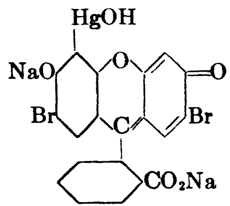
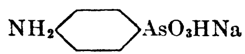
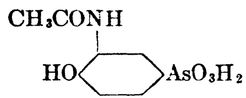
[92] Ehrlich, P. and Bertheim, A., Ber. *45*, 759 (1912).

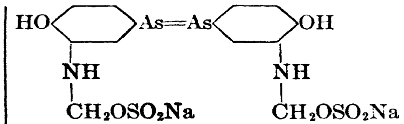
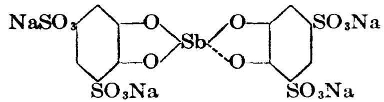
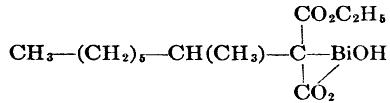
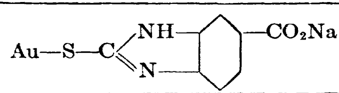
[93] Scott, A. B. and Gruhzit, O. M., U. S. Patent 2,092,028 (Sept. 7, 1937); Tatum, A. L., U. S. Patent 2,092,036 (Sept. 7, 1937); Scott, A. B., Hummel, R. D., Tullar, B. F. and Wainwright, H., U. S. Patent 2,221,817 (Nov. 19, 1940).

[94] Christiansen, W. G. O., "Organic Derivatives of Antimony," Chemical Catalog Co., New York (1925).

[95] Gray, W. H., Trevan, J. W., Bainbridge, H. W. and Attwood, A. P., Proc. Roy. Soc. (London), B, *108*, 54 (1931); Dunning, F. and Reid, E. E., J. Am. Chem. Soc. *48*, 2959 (1926).

TABLE 5—ORGANO-METALLIC COMPOUNDS USED IN MEDICINE

Name	*Structure*	*Method of Preparation*	*Use*
'Mercurin' [a] Sodium β-methoxy-γ-hydroxymercuripropylamide of trimethylcyclopentane dicarboxylate		Reacting *d*-camphoric acid allylamide with mercuric acetate.[b]	Diuretic
'Mercurochrome' [a] Disodium salt of 2,7-dibromo-4-hydroxymercurifluorescein		Dibromofluorescein is heated with mercuric acetate in aqueous acetic acid.[c]	Disinfectant
'Metaphen' [a] Anhydride of 4-nitro-5-hydroxymercuri-*ortho*-cresol	$C_6H_2 \cdot CH_3 \cdot O \cdot NO_2 \cdot Hg$	A sodium hydroxide solution of 4-nitro-*o*-cresol is reacted with mercuric acetate.[d]	Disinfectant
Atoxyl Sodium *p*-aminophenylarsonate		Prepared from aniline and arsenic acid.[e]	Chiefly as an intermediate in the manufacture of Carbarsone and 'Tryparsamide.'
Carbarsone *p*-Carbamidophenylarsonic acid		Prepared from sodium *p*-aminophenylarsonic acid and sodium or potassium cyanate.[f]	Treatment of amebiasis.
Acetarsone 3-Acetylamino-4-hydroxyphenylarsonic acid		Prepared by acetylating 3-amino-4-hydroxyphenylarsonic acid.[g]	Treatment of amebiasis.

Sulfarsphenamine Di-sodium 3,3′-diamino-4,4′-dihydroxyarsenobenzene *N*-di-methylene sulfonate		An alcoholic solution of arsphenamine is treated successively with formaldehyde solution and aqueous bisulfite solution.[h]	Treatment of syphilis.
'Fuadin'[a] Sodium Antimony III bis-catechol-2,4-disulfonate		Freshly prepared antimony oxide is reacted with an aqueous solution of sodium pyrocatechol disulfonate.[i]	Treatment of granuloma venereum and of schistosomiasis.
Sodium bismuth thioglycollate	$Bi(SCH_2CO_2Na)_3$	Prepared from sodium thioglycollate and bismuth suboxide.[j]	Treatment of syphilis.
'Biliposol'[a] Bismuth derivative of α-carboxyethyl-β-methyl nonoic acid.		An aqueous-glycerin solution of bismuth nitrate is reacted with sodium methylcarbethoxy nonate.[k]	Treatment of syphilis.
Sobisminol		Sodium bismuthate is warmed with triisopropanolamine in propylene glycol.[l]	Treatment of syphilis.
'Triphal'[a] Sodium aurothiobenzimidazole carboxylate		Prepared from sodium thiobenzimidazole carboxylic acid and potassium auri-bromide in moist ethyl acetate.[m]	Lupus erythematosis.

[a] Trade-mark. See trade-mark explanation at the end of the chapter.
[b] Wolf, E., U. S. Patent 2,116,872 (May 10, 1938).
[c] White, E. C., U. S. Patent 1,535,003 (Apr. 21, 1925).
[d] Raiziss, G. W., U. S. Patent, Reissue, 17,563 (Jan. 14, 1930).
[e] Gilman, H., "Organic Syntheses," Coll. Vol. I, p. 63, John Wiley and Sons, New York (1932).
[f] Ehrlich, P. and Bertheim, A., U. S. Patent 937,929 (Oct. 26, 1909) and Reed, A. C., Anderson, H. H., David, N. A. and Leake, C. D., J. Am. Med. Assn. *98*, 189 (1932).
[g] Ehrlich, P. and Bertheim, A., U. S. Patent 1,077,462 (Nov. 4, 1913); Raiziss, G. W. and Gavron, J. L., J. Am. Chem. Soc. *43*, 583 (1921).
[h] Raiziss, G. W. and Gavron, J. L., "Organic Arsenical Compounds," p. 198, Chemical Catalog Co., New York (1923).
[i] Schmidt, H., U. S. Patents 1,549,154 (Aug. 11, 1925) and 1,873,668 (Aug. 23, 1932).
[j] Myers, C. N., J. Lab. Clin. Med. *6*, 364 (1921).
[k] Levaditi, C., Ann. inst. Pasteur *42*, 1489 (1928).
[l] Hanzlik, P. J., U. S. Patent 2,125,561 (Aug. 2, 1938).
[m] Bockmühl, M., Ehrhart, G. and Fritzsche, P., U. S. Patent 1,558,584 (Oct. 27, 1925).

bismuth preparations were of clinical value and that the variations shown between the different compounds was due in large measure to differences in solubility. Water-soluble compounds are very rapidly absorbed and excreted, while oil-soluble compounds are more slowly absorbed. Insoluble compounds administered as suspensions give varied effects, due to uncontrollable rates of absorption by the body tissue.

Other Metals—Silver compounds have caustic, astringent, and antiseptic effects which are caused by the presence of free silver ions. Since the antiseptic action of silver nitrate is complicated by irritation and astringent action, colloidal compounds of silver are preferred, such as the silver protein preparations, and colloidal silver, or colloidal silver halides.

The silver protein preparations are for the most part prepared by dissolving reduced silver or silver oxide, or some protein silver precipitate in an excess of denatured protein and then drying *in vacuo*. Chemically, they are indefinite mixtures of metallic silver and silver oxide and various silver protein compounds, which disperse in water.

Metallic silver may be reduced to the colloidal form by chemical or electrolytic means and stabilized by the addition of a small amount of protein. Colloidal silver halides, either the chloride or the iodide, are held in suspension by suitable stabilizing agents, such as gelatin. For example, an aqueous solution of colloidal silver [96] suspended in an oxidized protein base, such as 'Argyrol,' [8] is treated with iodine to form colloidal silver iodide. Sufficient protein must be present to prevent the silver iodide from precipitating. The resulting "solution" is then evaporated to dryness under vacuum.

Solutions of ferric iron are used as styptics and astringents, as, for example, ferric chloride. The principal use of iron, however, is in the treatment of various anemias and in fortifying our diets, since iron is necessary for hemoglobin formation and modern diets tend to be low in iron. The ferrous salts are preferred to the ferric salts for this purpose. Reduced iron, ferrous carbonate, iodide, lactate, sulfate, and complex compounds of iron such as iron and ammonium citrate are employed. The most effective form of iron appears to be that contained in the liver preparations.

Calcium may be used either to produce salts of therapeutically effective acids having desired solubility characteristics or it may be used for the calcium effect itself. Calcium ethyl isopropyl barbiturate is an example of the former use, while calcium gluconate represents the latter use. Calcium gluconate came into use only when an inexpensive method of preparing gluconic acid became available.[97] Tribasic calcium phosphate is used for its anti-acid properties.

Since it is not possible to describe in detail all of the organo-metallic compounds used in medicine, representative compounds were selected which would illustrate the various methods of manufacture. Some of the other more important products are described in Table 5.

[96] Smith, T., U. S. Patent 1,610,391 (Dec. 14, 1926).
[97] Herrick, H. T. and May, O. E., U. S. Patent 1,726,067 (Aug. 27, 1929); Bleyer, B. and Braun, W., Biochem. Z. *199*, 186 (1928).

IODINE DERIVATIVES

Iodine compounds are used partly for their systemic action, partly for X-ray diagnosis, and partly for their local antiseptic action. Iodides are necessary for the production of thyroxin by the body, and their lack results in goiter. They also cause a rapid absorption of certain inflammatory lesions of tertiary syphilis. In addition to the iodides, a varied number of organic iodine compounds are used for systemic effect; for example, hexamethylenetetramine tetraiodide, 'Siomine,'[8] iodo-albumin, iodo-casein, and many iodized fats and fatty acids. Some of the iodized oils in which the iodine content is high are used as a contrast media in roentgenography.

Satisfactory roentgen pictures of certain organs of the body may be secured by the intravenous injection of soluble organic iodine compounds of low toxicity. Among the compounds used for this purpose are: sodium *o*-iodohippurate, 'Hippuran';[8] sodium monoiodomethane sulfonate,[98] 'Skiodan,'[8] sodium phenoltetraiodophthalein, and sodium tetraiodophenolphthalein.[99]

Iodoform, the first organic iodine compound to be used for its bactericidal action, has been replaced largely by more effective disinfectants. Tetraiodopyrrole, iodochlorhydroxyquinoline, thymol iodide, and 7-iodo-8-hydroxyquinoline-5-sulfonic acid have been introduced as substitutes for iodoform.

Thymol iodide is prepared by adding a solution of thymol in caustic soda to an aqueous solution of iodine and potassium iodide. The product so obtained is a mixture of iodine derivatives of thymol, chiefly the diiodide.

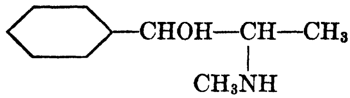
Iodochlorhydroxyquinoline, 'Vioform,'[8] is obtained by introducing an atom of iodine in 5-chlor-8-hydroxyquinoline.[100] 7-Iodo-8-hydroxyquinoline-5-sulfonic acid, Chiniofon, is prepared from 8-hydroxyquinoline-5-sulfonic acid by refluxing a solution of its sodium salt with sodium iodide and bleaching powder. The 8-hydroxyquinoline-5-sulfonic acid is obtained by the action of fuming sulfuric acid on 8-hydroxyquinoline. The latter is obtained from *o*-nitrophenol, *o*-aminophenol, glycerin and sulfuric acid. The sulfate of 8-hydroxyquinoline, called Chinosol, is also of clinical value.

PHENYLETHYLAMINE DERIVATIVES

There is a large series of compounds having the β-phenylethylamine structure which have a wide clinical usefulness since they cause a constriction of the blood vessels and have a direct stimulant action on the heart. Epinephrine, one of the most important of these, belongs to the class of drugs termed hormones, and is obtained from the suprarenal glands. Ephedrine, another important member of this group, is of plant origin. There are, in addition, a large group of synthetic products which are chemical variants of the above two compounds, that are of medical value.

Ephedrine, *l*-α-hydroxy-β-methylaminopropyl benzene,

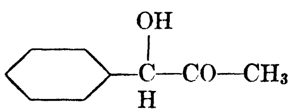
[98] Allardt, H. G., U. S. Patent 1,867,793 (July 19, 1932).
[99] Orndorff, W. R. and Mahood, S. A., J. Am. Chem. Soc. *40*, 937 (1918).
[100] Bischler, A., U. S. Patent 641,491 (Jan. 16, 1900).



was first obtained from the Chinese herb ma huang. While used for countless centuries by the Chinese for its action on the heart, its specific clinical value was discovered comparatively recently.[101] The crude extract of the drug contains as its chief contaminant, an optical isomer of ephedrine, which must be separated. Many synthetic methods have been proposed for the preparation of ephedrine. While it is comparatively easy to prepare the racemic product, little use has been made of this synthesis since the racemic mixture is less active than the *l*-isomer and furthermore it is not economical to resolve it into its optical isomers.

A method of synthesizing *l*-ephedrine, through the use of a yeast fermentation, has been adapted to large scale production which is more economical than isolation from natural sources.[102] The yeast converts benzaldehyde into *l*-phenylacetylcarbinol. The latter is reacted with methylamine and reduced to form *l*-ephedrine.

Equal parts of glucose and brewer's yeast are mixed in 20 parts of water. Fermentation starts at once. After seven hours, one-twelfth part of benzaldehyde is added and the mixture is allowed to ferment for 3 days. The mixture is then centrifuged and filtered. The filtrate is exhaustively extracted with ether and the ether extract dried and freed from ether by evaporation. The oily residue, which is *l*-phenylacetylcarbinol



is purified by fractional distillation. The yield is about 80 per cent of the weight of the benzaldehyde used. The carbinol is added to an excess of an alcoholic solution of methylamine and hydrogenated. If the catalyst used is palladium or platinum, hydrogenation can be accomplished at low pressures. The catalyst is filtered off, the solvent evaporated, and the residue is dissolved in a mixture of absolute alcohol and ether. When dry hydrochloric acid is passed into this solution, crude *l*-ephedrine hydrochloride separates. Instead of using a catalyst, reduction may be carried out with activated aluminum.

The various synthetic derivatives differ from epinephrine and ephedrine in certain qualitative effects which render them clinically useful. Of the hundreds of compounds synthesized and tested only a few are used. 4-(Methylaminoaceto)catechol hydrochloride, 'Kephrine'[8] hydrochloride, is an intermediate in the synthesis of epinephrine which recently has been used. Other synthetic compounds in use are the hydrochlorides of *l*-α-hydroxy-β-methylamino-3-hydroxyethylbenzene,[103] 'Neo-Synephrin'[8] hydrochloride; *dl*-phenyl-1-amino-2-propanol-1,[104] 'Propadrine';[8] *dl*-3-4-dihydroxyphenylethanolamine, 'Arterenal';[8]

[101] Chen, K. K. and Schmidt, C. F., Proc. Soc. Exp. Biol. Med. *21*, 351 (1924); J. Pharmacol. *24*, 339 (1924).
[102] Freudenberg, K., Schoeffel, E. and Braun, E., J. Am. Chem. Soc. *54*, 234 (1932); Hildebrandt, G. and Klavehn, W., U. S. Patent 1,956,950 (May 1, 1934).
[103] Legerlotz, H., U. S. Patent 1,680,055 (Aug. 7, 1928).
[104] Hartung, W. H., U. S. Patent 1,989,093 (Jan. 29, 1935).

3-4-dihydroxyphenylethylmethylamine, 'Epinine';[8] and *l-p*-hydroxyphenyl-2-methylaminopropane, 'Veritol.'[8]

Phenylethylamine and benzylmethylcarbinamine[105] are representative volatile members of this series. The racemic form of the latter is in clinical use under the name 'Benzedrine.'[8]

PURGATIVES

Certain drugs which have a specific irritant action on the bowel are used as purgatives. Most of the naturally occurring drugs of this group, such as aloe, cascara, rhubarb, and senna, contain hydroxymethylanthraquinones. In spite of much work in this field, as yet no synthetic anthraquinones have been prepared which are suitable for medical use.

Phenolphthalein is the only synthetic purgative which is widely used. It is prepared[106] by heating 5 parts of phthalic anhydride, 4 parts of concentrated sulfuric acid, and 10 parts of phenol. The first two are preferably heated to about 115° C. before the phenol is added and heating is maintained at about 120° for some time. The reaction contents are dumped into boiling water, and the phenol is separated by steam distillation. Caustic soda is used to dissolve the phenolphthalein from the granular solid. Acidification of this extract precipitates crude phenolphthalein, which is then recrystallized. The yield is about 75 per cent, based on the weight of phthalic anhydride.

Diacetyldihydroxyphenylisatin, 'Isacen,'[8] which also is used for its laxative properties, somewhat resembles phenolphthalein in structure.[107]

SEDATIVES

A large and varied series of organic compounds have sedative action. In general they contain non-polar lipo-soluble alkyl groups attached to polar water-soluble groups which may contain besides carbon, oxygen, and hydrogen, either nitrogen or sulfur, or both. None of the organic sedatives have pronounced acidic or basic properties. Included in this group are sulfones, urethanes, acetamides, acetylureas, alkylureas, acetals, ketones, homophthalimides, hydantoins, barbituric acids and thiobarbituric acids.

Since the use of barbituric acid derivatives is more widespread in this country than the use of the various other sedatives, the methods of the manufacture of the barbituric acids will be given in some detail. The other sedatives are summarized in Table 6.

BARBITURIC ACIDS

Many alkyl and some alkaryl derivatives of barbituric acids are effective as sedatives or hypnotics. 5,5-Diethylbarbituric acid[108] was first of this series to be used clinically. One or both of the ethyl groups may be replaced by other groups to form a very large series of compounds. This series of 5,5-disubstituted bar-

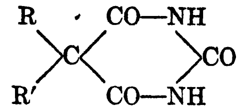
[105] Alles, G. A., U. S. Patent 1,879,003 (Sept. 27, 1932); Nabenhauer, F. P., U. S Patents 1,921,424 (Aug. 8, 1933) and 2,015,408 (Sept. 24, 1935).
[106] Baeyer, A., Ann. *202*, 36-140 (1880).
[107] Preiswerk, E., U. S. Patent 1,624,675 (Apr. 12, 1927).
[108] Fischer, E. and Dilthey, A., Ann. *335*, 334 (1904).

TABLE 6—SEDATIVES AND HYPNOTICS

Name	*Structure*	*Method of Preparation*
Sulfonal, Diethylsulfone-dimethyl methane	$C_2H_5—SO_2 \diagdown \quad \diagup CH_3$ C $C_2H_5—SO_2 \diagup \quad \diagdown CH_3$	Acetone is condensed with ethyl mercaptan, and the resulting sulfide is oxidized by potassium permanganate.[b, c]
Urethane, Ethylcarbamate	$NH_2COOC_2H_5$	Heating urea nitrate with an excess of ethyl alcohol at 125° C.
Carbromal Bromodiethylacetyl urea	$C_2H_5 \diagdown$ $CBrCONHCONH_2$ $C_2H_5 \diagup$	Diethylacetic acid is converted to bromodiethylacetyl bromide and condensed with urea.[d]
'Neuronal,'[a] Bromodiethylacetamide	$C_2H_5 \diagdown$ $CBrCONH_2$ $C_2H_5 \diagup$	Bromodiethylacetyl bromide is condensed with ammonia.
'Sedormid,'[a] Allylisopropyl acetamide	iso-$C_3H_7 \diagdown$ $CHCONH_2$ $C_3H_5 \diagup$	Isopropylallylacetyl chloride is condensed with urea.[e]
Hypnone, Acetophenone	—$COCH_3$	Acetyl chloride is condensed with benzene.
Chloral hydrate	$CCl_3—CH(OH)_2$	Chlorination of alcohol followed by distillation in the presence of sulfuric acid.[f]
Chloralose, Glucochloral	$C_8H_{11}O_6Cl_3$	Heating chloral and glucose at 100° C.[f]
Chlorobutanol, Trichlorotertiary butyl alcohol	$CH_3 \diagdown \quad \diagup OH$ C $CH_3 \diagup \quad \diagdown CCl_3$	Potassium hydroxide is gradually added to a mixture of acetone and chloroform.[g]
Paraldehyde	$(C_2H_4O)_3$	Acetaldehyde is polymerized by hydrochloric acid.[h]

[a] Trade-mark. See trade-mark explanation at the end of the chapter.
[b] Barrowcliff, M., and Carr, F. H., "Organic Medicinal Chemicals," pp. 31–36, D. Van Nostrand Co., New York (1920).
[c] Schwyzer, J., "Die Fabrikation pharmazeutischer und chemisch-technisher Produkte," pp. 143–147, Julius Springer, Berlin (1931).
[d] German Patent 225,710.
[e] Boedecker, F., U. S. Patent 1,633,392 (June 21, 1927).
[f] See pp. 26–28, reference b, and p. 90, ref. c.
[g] See p. 30, reference b and p. 150 ref. c.
[h] See p. 15, reference b.

bituric acids are prepared in general by the introduction of the alkyl groups into ethyl malonate and condensing the purified ester with urea. The 5,5-disubstituted barbituric acids have the formula:



Manufacture—The first intermediate required for the synthesis of barbituric acids is ethyl malonate, $CH_2(CO_2C_2H_5)_2$, which is prepared by saponifying and esterifying cyanoacetic acid obtained from chloroacetic acid and sodium cyanide.

$$ClCH_2CO_2Na + NaCN \rightarrow CNCH_2CO_2Na +$$
$$H_2SO_4 + C_2H_5OH \rightarrow CH_2(CO_2C_2H_5)_2.$$

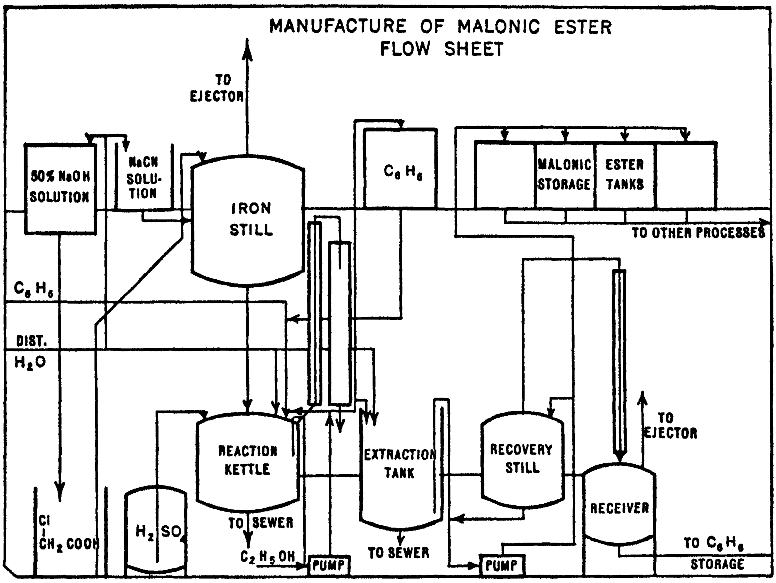


FIG. 9. Flow Sheet for Plant Production of Malonic Ester.

In plant production[109] these reactions are carried out in the following steps: (1) neutralization of the chloroacetic acid, (2) reaction of sodium chloroacetate with sodium cyanide, (3) removal of water from the sodium cyanoacetate, (4) hydrolysis and esterification of the sodium cyanoacetate, (5) extraction of the ethyl malonate with benzene, and (6) the removal of the benzene. See Figure 9.

The chloroacetic acid is placed with an equal weight of ice in a 300-gallon stoneware jar and neutralized with 50 per cent sodium hydroxide to a pH of 9.0. The solution of sodium chloroacetate is then drawn by vacuum to a 900-gallon jacketed iron still and warmed to 60° C. with steam. At this point a hot concentrated solution of sodium cyanide, equimolar with respect to the chloroacetic acid, is added. A vigorous reaction ensues, the rate of which is controlled by the initial temperature of the reactants and the rate of addition of the sodium cyanide solution. Suitable exhaust facilities must be employed to remove the steam and cyanogen vapors. When this reaction has subsided, the solution of

[109] Ross, A. A. and Bibbins, F. E., Ind. Eng. Chem. 29, 1341 (1937).

sodium cyanoacetate is concentrated by means of a three-stage Elliott steam ejector-condenser to about one-fourth of the original volume. The residue, a thick, semi-solid mass, which flows readily while hot but solidifies on cooling, is dumped through the bottom outlet by means of an iron chute into a 500-gallon enameled, jacketed reaction kettle containing alcohol.

This kettle is equipped with an anchor type direct driver agitator, peep sights and vertical 9 foot condenser connected with a scrubbing tower. See Figure 10.

FIG. 10. Stills Used for Saponification and Esterification of Malonic Ester.

The agitator thoroughly mixes the thick sodium cyanoacetate with the alcohol. When the charge is in the reaction kettle, sulfuric acid is automatically forced under air pressure into the kettle at such a rate that the reaction does not become too vigorous. After all the acid has been added, the contents are refluxed overnight. Water and benzene are then added to the still and after thorough agitation, the benzene layer, containing the ethyl malonate, is pumped by means of a 'Duriron' pump into an enameled tank equipped with an agitator. Several extractions are necessary. The benzene extracts are washed with caustic soda solution and water and dried with sodium sulfate. The benzene is distilled off and the malonic ester is then stored in iron tanks. The average over-all yield based on the chloroacetic acid, is 70 per cent. By good control of the operations it is possible to obtain the crude ethyl malonate as a pale straw colored liquid, of sufficient purity to use it in the subsequent synthetic steps without fractionally distilling.

The introduction of alkyl groups into the ethyl malonate follows a general procedure. Sodium is dissolved in 10 times its weight of absolute alcohol, and a molecular equivalent of ethyl malonate is added. The desired alkyl group in the form of the bromide or chloride is added and the still contents refluxed until they are neutral.

In practice this reaction runs as smoothly in plant equipment as it does in the laboratory. An enameled or stainless steel jacketed still with bottom outlet is employed, which is connected to a large capacity, tubular condenser adapted for refluxing and collecting the distillate. The still is equipped with agitator, peep sights and openings for adding the sodium and the alkyl halide. When ethyl chloride is used, the still should be capable of withstanding several hundred pounds internal pressure, although the usual operating pressure is about 75 pounds. The size of the batch and of the still is dependent solely on economic considerations.

An amount of absolute alcohol equal to 10 times the weight of sodium to be used is charged into the dried still. Sodium in small pieces is added as rapidly as necessary to give a vigorous rate of refluxing. Toward the end heat is needed to complete the formation of sodium ethylate. The ester is then added and the alkyl halide is introduced at a rate sufficient to cause moderate refluxing. If ethyl chloride is used, it is necessary to shut off the condenser and peep glasses with valves before adding the ethyl chloride, controlling the rate of addition by the rise in pressure, and keeping the latter well under the limit of safety of the still. About 12 to 18 hours' refluxing is usually required to assure complete reaction.

At the end of the refluxing the alcohol is removed by distillation. Water is added and the malonic ester layer is separated and dried. It is then fractionally distilled under a pressure of 10-15 mm. to separate the unreacted ethyl malonate and the ethyl dialkylmalonate from the desired ethyl alkylmalonate. If both groups are to be the same, as, for example, ethyl diethylmalonate, two molecular equivalents of sodium and of ethyl chloride are used. Unsymmetrically disubstituted malonic ester is prepared by repeating the above procedure on the desired ethyl monoalkylmalonate.

Final Preparation—The disubstituted barbituric acid is prepared from the disubstituted malonic ester by condensing the latter with 1.6 molecular equivalents of urea in the presence of about three molecular equivalents of sodium ethylate in absolute alcohol. This can be carried out in equipment similar to that used in the production of the substituted malonic esters. After about twelve hours' vigorous refluxing the alcohol is removed and the still contents, dissolved in water, are drawn off and acidified in enameled pots. This precipitates the barbituric acid, which is collected on a rubber-lined basket centrifuge and purified by recrystallization from water or dilute alcohol.

Among the various barbituric acids now used medicinally in this country are: allylisopropylbarbituric acid,[110] 'Alurate'; [8] isoamylethylbarbituric acid,[111] 'Amytal'; [8] calcium ethylisopropylbarbiturate,[112] 'Ipral' [8] calcium; *n*-butylethylbarbituric acid,[113] 'Neonal';[8] bromallylisopropylbarbituric acid,[114] 'Nostal';[8] sodium

[110] Preiswerk, E., U. S. Patent 1,444,802 (Feb. 13, 1923).
[111] Shonle, H. A., U. S. Patent 1,514,573 (Nov. 4, 1924).
[112] Thorp, L., U. S. Patent 1,255,951 (Feb. 12, 1918).
[113] Layraud, E., U. S. Patent 1,609,520 (Dec. 7, 1926).
[114] Boedecker, F., U. S. Patent 1,622,129 (Mar. 22, 1927).

ethyl-*n*-hexylbarbiturate,[115] 'Ortal'[8] sodium; sodium ethyl-(1-methylbutyl) barbiturate,[116] pentobarbital sodium; sodium ethyl-(1-methylbutyl)thiobarbiturate,[117] 'Pentothal'[8] sodium; β-bromallylbutylbarbituric acid,[118] 'Pernoston';[8] cyclohexenylethylbarbituric acid,[119] 'Phanadorn';[8] ethylphenylbarbituric acid,[120] phenobarbital; allylisobutylbarbituric acid, 'Sandoptal,'[8] and sodium allyl-(1-methylbutyl)barbiturate,[121] 'Seconal'[8] sodium. (See Addendum, page 1331.)

Certain barbituric acids and hydantoin derivatives which have a relatively weak hypnotic action are used for their quieting action in epilepsy. Among these are ethylphenylhydantoin, diphenylhydantoin, and *N*-methylphenylethylbarbituric acid.

In the preparation of thiobarbituric acids, thiourea is used instead of urea. In the preparation of *N*-alkyl-substituted dialkylbarbituric acids, alkyl ureas may be used or the dialkylbarbituric acid alkylated. Ethyl cyanoacetate can be used instead of the ethylmalonate, and the imino-barbituric acid which is formed is converted into the barbituric acid by acid hydrolysis. Ethylphenylbarbituric acid must be prepared by a more indirect means.

TRADE-MARK EXPLANATION

Many trade-marks are used in this chapter. Since trade-marks are *not names* of products, but instead are *indicators of origin* and of *particular brands* of products, they are enclosed in single quotation marks in the text to show their trade-mark character. The attempt has been to do this consistently, and it is hoped that there has been no oversight. The trade-marks used, and the brands they indicate of particular products,[a] include the following:

'Adrenalin'	Parke, Davis and Co.'s brand of epinephrine.
'Alurate'	Hoffmann-La Roche's brand of allyl isopropyl barbituric acid.
'Alypin'	Winthrop Chemical Co.'s brand of 2-benzoxy-2-dimethylamino-ethyl-1-dimethyl-aminobutane hydrochloride.
'Amytal'	Eli Lilly and Co.'s brand of isoamyl ethyl barbituric acid.
'Apothesine'	Parke, Davis and Co.'s brand of γ-diethylaminopropyl cinnamate hydrochloride.
'Argyrol'	A. C. Barnes Co.'s brand of mild silver protein.
'Atabrine'	Winthrop Chemical Co.'s brand of 7-methoxy-3-chloro-9-(4-dimethylamino-1-methylbutyl)-aminoacridine.
'Azochloramid'	Wallace and Tiernan Products, Inc.'s brand of *N*,*N*-dichloroazodicarbonamidine.
'Benzedrine'	Smith, Kline and French's brand of alphamethyl-phenethylamine.
'Biliposol'	Ulmer Laboratory's brand of bismuth carboxyethyl-β-methylnonoate.
'Butyn'	Abbott Laboratories' brand of *p*-aminobenzoyl-γ-di-normalbutyl-aminopropanol sulfate.
'Dilaudid'	E. Bilhuber, Inc.'s brand of dihydromorphinone.
'Diothane'	Wm. S. Merrell Co.'s brand of piperidinopropanediol-di-phenyl-urethane.

[a] As recorded in the U. S. Patent Office.

[115] Dox, A. W., U. S. Patent 1,624,546 (Apr. 12, 1927).
[116] Shonle, H. A., Keltch, A. and Swanson, E. E., J. Am. Chem. Soc. *52*, 2440 (1930)
[117] Volwiler, E., U. S. Patent 2,153,729 (Apr. 11, 1939).
[118] Boedecker, F., U. S. Patent 1,739,662 (Dec. 17, 1929).
[119] Schulemann, W. and Meisenburg, K., U. S. Patent 1,690,796 (Nov. 6, 1928).
[120] Hoerlein, H., U. S. Patent 1,025,872 (May 7, 1912).
[121] Shonle, H. A., U. S. Patent 1,954,429 (Apr. 10, 1934).

'Epinine'	Burroughs Wellcome and Co.'s brand of 3,4-dihydroxyphenylethylmethylamine.
'Ergotrate'	Eli Lilly and Co.'s brand of ergonovine maleate.
'Fuadin'	Winthrop Chemical Co.'s brand of sodium antimony-III-bis-catechol-2,4-disulfonate.
'Hippuran'	Mallinckrodt Chemical Works' brand of sodium ortho-iodohippurate.
'Ipral'	E. R. Squibb and Sons' brand of ethylisopropylbarbituric acid.
'Isacen'	Hoffmann-La Roche's brand of diacetyldihydroxyphenylisatin.
'Kephrine'	Alba Pharmaceutical Co.'s brand of methylaminoacetocatechol.
'Larocaine'	Hoffmann-La Roche's brand of *p*-aminobenzoyl-2,2-dimethyl-3-diethylaminopropanol hydrochloride.
'Mapharsen'	Parke, Davis and Co.'s brand of the hemialcoholate of 3-amino-4-hydroxyphenylarsine oxide hydrochloride.
'Mercurin'	Campbell Products, Inc.'s brand of a mixture of β-methoxy-γ-hydroxymercuripropylamide of trimethyl cyclopentane dicarboxylic acid and its sodium salt.
'Mercurochrome'	Hynson, Westcott and Dunning's brand of the disodium salt of 2:7-dibromo-4-hydroxymercurifluorescein.
'Merthiolate'	Eli Lilly and Co.'s brand of sodium ethyl mercuri thiosalicylate.
'Metaphen'	Abbott Laboratories' brand of the anhydride of 4-nitro-5-hydroxymercuriortho cresol.
'Metycaine'	Eli Lilly and Co.'s brand of γ-[2-methyl-piperidino]-propyl benzoate hydrochloride.
'Monocaine'	Novocol Chemical Manufacturing Co.'s brand of mono-isobutylaminoethyl *p*-aminobenzoate hydrochloride.
'Neonal'	Abbott Laboratories' brand of *n*-butylethyl barbituric acid.
'Neo-Synephrin'	Frederick Stearns and Co.'s brand of laevo-α-hydroxy-β-methylamino-3-hydroxy ethylbenzene hydrochloride.
'Nostal'	J. D. Riedel-E. de Haen, A.G.'s brand of isopropyl bromallyl barbituric acid.
'Novasurol'	Winthrop Chemical Co.'s brand of merbaphen—the double salt of sodium mercurichlorphenyl oxyacetate.
'Nupercaine'	Ciba Pharmaceutical Products, Inc.'s brand of 2-butyloxyquinolinecarboxylic acid-4-diethylene-diamide.
'Optochin'	Rare Chemicals, Inc.'s brand of ethyl hydrocupreine.
'Ortal'	Parke, Davis and Co.'s brand of ethyl-hexyl barbituric acid.
'Pentothal'	Abbott Laboratories' brand of sodium ethyl (1-methylbutyl) thiobarbiturate.
'Pernoston'	J. D. Riedel-E. de Haen, A.G.'s brand of butyl-β-bromallyl barbituric acid.
'Phanadorn'	Winthrop Chemical Co.'s brand of cyclohexenyl ethyl barbituric acid.
'Plasmochin'	Winthrop Chemical Co.'s brand of 4-diethylamino-1-methylbutylamino-6-methoxy-quinoline dihydrochloride.
'Pontocain'	I. G. Farbenindustrie's brand of *p*-butylamino-benzoyl-dimethylaminoethanol.
'Propadrine'	Sharp and Dohme, Inc.'s brand of *dl*-phenyl-1-amino-2-propanol-1.
'Rivanol'	Winthrop Chemical Co.'s brand of 2-ethoxy-6,9-diaminoacridine.
'Salyrgan'	H. A. Metz Laboratories, Inc.'s brand of sodium [*o*(hydroxymercuricmethoxypropylcarbamyl) phenoxyl] acetate.
'Sandoptal'	Sandoz Chemical Works' brand of isobutylallylbarbituric acid.
'Seconal'	Eli Lilly and Co.'s brand of sodium propyl-methyl-carbinyl allyl barbiturate.
'Sedormid'	Hoffmann-La Roche's brand of allyl isopropyl acetamide.
'Siomine'	Pitman-Moore Co.'s brand of hexamethylenetetramine tetraiodide.
'Skiodan'	Winthrop Chemical Co.'s brand of the sodium salt of mono-iodomethane sulfonic acid.

'Syntropan'	Hoffmann-La Roche's brand of the phosphate of *dl*-tropic acid ester of 3-diethyl-amino-2,2-dimethyl-1-propanol.
'Trasentin'	Society of Chemistry Industry in Basle's brand of 2-diethylaminoethyl diphenyl acetate.
'Triphal'	Winthrop Chemical Co.'s brand of sodium aurothiobenzimidazole carboxylate.
'Tryparsamide'	Merck and Co.'s brand of sodium *N*-phenylglycineamide-*p*-arsonate.
'Tutocain'	Winthrop Chemical Co.'s brand of *p*-amino-benzoyldimethylaminoethyl-butanol hydrochloride.
'Veritol'	Knoll and Co.'s brand of *l*-*p*-hydroxyphenyl-2-methylaminopropane.
'Vioform'	Society of Chemical Industry in Basle's brand of iodochlorhydroxyquinoline.

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READING LIST

Monographs dealing solely with specific sections of this chapter in most instances have been referred to at the beginning of the various sections. Reference should be made, however, to a number of books which cover the entire field of medicinal chemistry, or large sections of it. Among these are:

American Medical Association, Council on Pharmacy and Chemistry and Council on Foods, "The Vitamins," American Medical Association, Chicago (1939).

Barger, George, "Some Applications of Organic Chemistry to Biology and Medicine," McGraw-Hill Book Co., Inc., New York (1930).

Barrowcliff, M. and Carr, Francis H., "Organic Medicinal Chemicals," D. Van Nostrand Co., New York (1920).

Dyson, G. Malcolm, "The Chemistry of Chemotherapy," Ernest Benn, Ltd., London (1928).

Evers, Norman, "The Chemistry of Drugs," D. Van Nostrand Co., New York (1926).

Fieser, L. F., "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York (1936).

Findlay, G. M., "Recent Advances in Chemotherapy," second edition, J. and A. Churchill, Ltd., London (1939).

Fischl, Victor and Schlossberger, Hans, "Handbook of Chemotherapy," Part I, H. G. Roebuck and Son, Baltimore (1933).

Fourneau, Ernest, "Organic Medicaments and Their Preparation," P. Blakiston's Son and Co., Philadelphia (1925).

Fränkel, Sigmund, "Die Arzneimittel-Synthese," sixth edition, Julius Springer, Berlin (1927).

Henry, T. A., "The Plant Alkaloids," third edition, J. and A. Churchill, Ltd., London (1939).

May, Percy and Dyson, G. M., "May's Chemistry of Synthetic Drugs," fourth edition, Longmans, Green and Co., London (1939).

Oesterlin, Manfred, "Chemotherapie," Friedr. Vieweg und Sohn, Braunschweig (1939).

Schwyzer, Julius, "Die Fabrikation pharmazeutischer und chemisch-technischer Produkte," Julius Springer, Berlin (1931).

Slotta, K. H., "Grundriss der modernen Arzneistoff-Synthese," Ferdinand Enke, Stuttgart (1931).

Von Oettingen, W. F., "The Therapeutic Agents of the Pyrrole and Pyridine Group," Edwards Brothers, Inc., Ann Arbor, Mich. (1936).

Von Oettingen, W. F., "The Therapeutic Agents of the Quinoline Group," Chemical Catalog Co., New York (1933).

ADDENDUM

Since the submission of this manuscript, many advances have taken place in the field of medicinal chemistry, of which the following are the more important.

Sex Hormones—While a great many synthetic substances, unrelated to sterols, have slight estrogenic activity, a recently synthesized product, 4,4′-dihydroxy-α,β-diethylstilbene (called diethylstilbestrol) possesses a high degree of activity, and is now being marketed [Dodds, E. C., Goldberg, L., Lawson, W. and Robinson, R., Proc. Roy. Soc. London *B 127,* 140 (1939); Council on Pharmacy and Chemistry, J. Am. Med. Assoc. *119,* 635 (1942)]. Because it is very much cheaper and also is active orally, it has reached a far wider market than estrone. Although the total synthesis of estrone has not been reported, a complete synthesis of a stereoisomer of estrone has been published [Bachmann, W. E., Kushner, S. and Stevenson, A. C., J. Am. Chem. Soc. *64,* 974 (1942)].

Vitamins—The production of vitamins C, B_1, B_2 and nicotinic acid has expanded greatly with further improvements in manufacture [Major, R. J., Chem. Eng. News *20,* 517 (1942)]. A formula has been proposed for biotin [du Vigneaud, V., Hofmann, K. and Melville, D., J. Am. Chem. Soc. *64,* 188 (1942)]. Folic acid, a new member of the B complex, has been isolated [Mitchell, H. K., Snell, E. E. and Williams, R. J., J. Am. Chem. Soc. *63,* 2284 (1941)]. Once more, another known chemical p-aminobenzoic acid, has been found to be a growth factor [Filfes, P., Lancet *1,* 955 (1940)]. A new reference book on vitamins has been published [Rosenberg, H. R., "Chemistry and Physiology of the Vitamins," Interscience Publishers, Inc., New York (1942)].

Sulfanilamide Derivatives—Within the last year, sulfathiazole has displaced sulfapyridine and is competing with sulfadiazine, 2-(p-aminobenzenesulfonamido)-pyrimidine in the treatment of infections [Roblin, R. O., Jr., Williams, J. H., Winnek, P. S. and English, J. P., J. Am. Chem. Soc. *62,* 2002 (1940)]. The production of the "sulfa" drugs now exceeds 1,000,000 pounds annually. Other "sulfa" drugs of interest are: sulfaguanidine [Winnek, P. S., U. S. Patent 2,218,490 (Oct. 15, 1940)], sulfapyrazine [Ellingson, R. C., J. Am. Chem. Soc. *63,* 2524 (1941); Raiziss, G. W., Clemence, L. W. and Freifelder, M., J. Am. Chem. Soc. *63,* 2739 (1941); Sausville, J. W. and Spoerri, P. E., J. Am. Chem. Soc. *63,* 3153 (1941)], and succinylsulfathiazole [Poth, E. J. and Knotts, F. L., Proc. Soc. Exptl. Biol. Med. *48,* 129 (1941)].

Sedatives—A new barbituric acid, 'Delvinal,'[8] ethyl-methylbutenylbarbituric acid, has been placed on the market [Cope, A. C., U. S. Patent 2,187,701 (Jan. 16, 1940)].

SECTION VIII

NATURAL ORGANIC MATERIALS

The modification of the properties of natural organic materials by chemical methods dates far back in history. The tanning of leather, extraction of glue, the making of paper, have come down through the annals of art and tradition. New materials, new uses, new methods often involving organic synthesis, keep adding to the industrial importance of the natural organic materials. The chapters are roughly arranged in the order of the subject matter sequence: carbohydrates, fats, and proteins, though any exact classification is not possible.

CHAPTER 35

SUGAR

J. W. HASSLER
Director of Research, Industrial Chemical Division,
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Expressions such as "sweet tooth" that have grown up in our language provide a better illustration than any discourse as to the value mankind places on sugar products. Another phrase, "the land of milk and honey," gives historical significance to the claim that "sweetness is to taste what beauty is to the eye." Even the phrase "busy as a bee" can have a dual meaning since it is probable that the bee enjoys the task of collecting sugar from the flowers.

Although carbohydrates are an essential item of diet this need can be supplied by starches which, in fact, constituted almost the entire source of carbohydrates in diet until comparatively recent times. Today sugar is so plentiful and so cheap that we take it for granted and overlook how much science and industry have accomplished in making refined sugar so generally available. Primitive man had to depend mainly on roots, fruits, and saps from certain trees for any sweetness in his diet.

As late as the Middle Ages sugar was a rare article to be used chiefly in medicine, and which appeared only on the tables of the wealthy on rare occasions. Benjamin Franklin's account book, November 28, 1746, gives the price of sugar as equivalent to 30¢ per pound which presumably was the refined sugar of that day, and in this connection it is to be noted that refined sugar then did not compare with today's product. However, by that time other sources of sweetness were available in America, including maple sugar and molasses. Molasses continued in general use for many years, and one does not have to be old to remember when it was regularly placed on the table of the average American family.

In commerce the term "sugar" refers to "sucrose" ($C_{12}H_{22}O_{11}$) and is so used in this chapter.

Sucrose has many practical advantages over other sugars in that it is available in a dry crystal form which is convenient for ultimate handling, and it does not deteriorate in storage. Also, in the refined form, it does not add any flavor other than sweetness. The two main sources of sucrose are the sugar cane and the sugar beet.

SOURCES OF SUGAR

Sugar Cane—The history of the cultivation of the sugar cane is buried in antiquity. It seems possible that it was first cultivated in India from whence it spread eastward to China, westward to Arabia, Egypt, Spain, and finally, to the New World.

The sugar cane (Saccharum officinarum) is a tall perennial grass having numerous bamboo-like stems which grow to a height of twelve feet or more. The seed is rarely formed and is used only for the propagation of new varieties. Commercially the plant is propagated by cuttings of the stalks. The sugar cane succeeds best in a warm, damp climate, and is essentially a tropical plant, although it is grown to a limited extent in sub-tropical climates such as Natal, Louisiana, and Florida. The period of growth will vary according to the region where grown, and in some cases lasts from 15 to 18 months. It should be harvested when just ripe, as it then contains the maximum amount of sucrose. Since it is not possible for the mills to handle the entire crop at one time, and since the juice in the cane rapidly deteriorates after cutting, it follows that much of the cane must be harvested before and some after it has reached the fully ripened state. In sub-tropical climates such as Louisiana the climate "calls the tune" and much cane must be harvested before the mill would like to take it. In Louisiana a practice known as "windrowing" is employed whereby the cane is stacked in the field until it can be taken care of by the mill. This practice is not entirely satisfactory as some cane is damaged by frost, and moreover, the types of cane suitable for windrowing are not the most efficient sugar producers. In the tropics, 30 tons of cane per acre are usually obtained from the first planting. Generally after the crop is harvested the roots are permitted to throw up another growth of cane known as the "ratoon" crop. In many regions a number of ratoon crops are harvested from each planting, even though ratoon crops give less yield per acre. Representative types of cane will contain 70 to 75% of water, 11 to 15% of crystallizable sugar, 0.5 to 1.5% uncrystallizable sugar, 10% of fiber, 1% of ash, and about 1% of organic acids, gums and nitrogenous bodies.

Sugar Beet—While we can only guess regarding the original cultivation of the sugar cane, the situation is different with respect to the sugar beet. In 1747, Marggraf found that the juice of the beet contained a sugar identical with that found in cane, and this discovery was put into practical use about the beginning of the 19th century. The cultivation of the sugar beet was given considerable impetus by Napoleon, who offered a bounty to producers of beet sugar when the British blockade of continental Europe shut off imports of cane sugar. In the early years of its cultivation the sugar beet contained from 5 to 6% of sucrose, but as a result of improved varieties, a yield of 13 to 17% is now common, and in this respect compares favorably with sugar cane. From a commercial angle the sugar beet is essentially a plant of the temperate climate, and many regions, both humid and semi-arid, appear to be adapted to its cultivation. The average yield in the United States in 1936-1937 was 11.6 tons per acre.[1]

The beet seeds are planted in the spring, and the matured beets are harvested during the fall. The sugar in the beets does not deteriorate as rapidly as in the case of the cane, and therefore the beets can be stored for a certain period of time after harvesting, although repeated freezing and thawing will do considerable damage.

[1] Lynsky, M., Sugar Economics, Statistics & Documents, United States Cane Sugar Refiners Assoc., New York (1938).

MECHANIZATION OF BEET AND CANE AGRICULTURE

Beets—The cultivation of sugar beet is a very tedious, laborious task. It is commonly referred to as "stoop labor." Much of it is done by floating gangs of contract labor that are not considered desirable either from an economic or social point of view. Apart from any question of economics, the beet industry is interested in relieving itself of the stigma of "stoop labor." As a result there

FIG. 1. Handling Sugar Beets with Belt Conveyor. (Courtesy "Facts About Sugar," Hoboken, N. J.)

has been a serious study of the possibilities of mechanization in sugar beet agriculture. Properly, the study begins with the planting of the beet, and machines are now available that plant single seeds at intervals of 2, 3, or 4 inches in the row. After the plants have developed another machine known as the blocking machine reduces them to the proper spacing and the only work left to be done by hand is to remove the superfluous plants which arise from the same seed. Studies are being made on the selection and development of a beet seed that will throw out only a single plant, and thereby still further reduce the labor of thinning. The proper spacing of the plants simplifies the utilization of machines for cultivation and for harvesting. Harvesters are now available that will dig, cut off the tops, and pile the beets in one operation. However, these machines have not been completely satisfactory under all field conditions, and it is still too early to properly assess their economic value. After beets are harvested they are handled almost entirely by mechanical means. (See Figure 1.)

Cane—In the cane sugar regions one finds agriculture in all stages of mechanization ranging from the use of two-wheeled carts pulled by oxen up to the most modern methods of cultivation, harvesting and hauling. Diesel engines are becoming more common even in backward regions. Simple as it may seem, one of the most notable advances has been the adoption of pneumatic rubber tires which greatly reduce the time and effort to move heavy loads in muddy fields. There is an abundance of cheap labor in most of the countries where cane is grown, but even in backward regions the present trend of social legislation has been toward shorter hours and increased pay, and this has caused many planters to consider the adoption of agricultural machinery. Unfortunately, this will not help the social conditions for there is little else that labor can find to do in the regions where the sugar cane is grown.

In Hawaii, the labor situation is quite different from most sugar-producing countries, since in that country there is a definite shortage of labor. This has resulted in somewhat greater attention being given there to the use of agricultural machinery. Mechanical harvesters have been tried, one of which is the grab type which breaks the cane off at the roots, and a still more recent development is the rake type, by which the entire cane, leaves and trash, are gathered up. Both methods gather up a considerable amount of soil and trash with the cane, and this introduces complications in the grinding mill, and also in the clarification.

This concludes the agricultural aspect of sugar manufacture apart from the mention of the fact that the relation of the growers of the crop and the factory is generally viewed as somewhat of a partnership. The payment to the grower is based on the price paid for the sugar during the season. In continental America, the amount paid to the beet farmer roughly approximates one-half the market value of the sugar produced. The cane grower receives about 60%.[2]

STEPS IN SUGAR MANUFACTURE

The sugar is synthesized by the growing plant, and the processing in the factory is only a succession of separations whereby the sugar is separated from the other constituents of the plant.

These may be somewhat arbitrarily considered as follows:

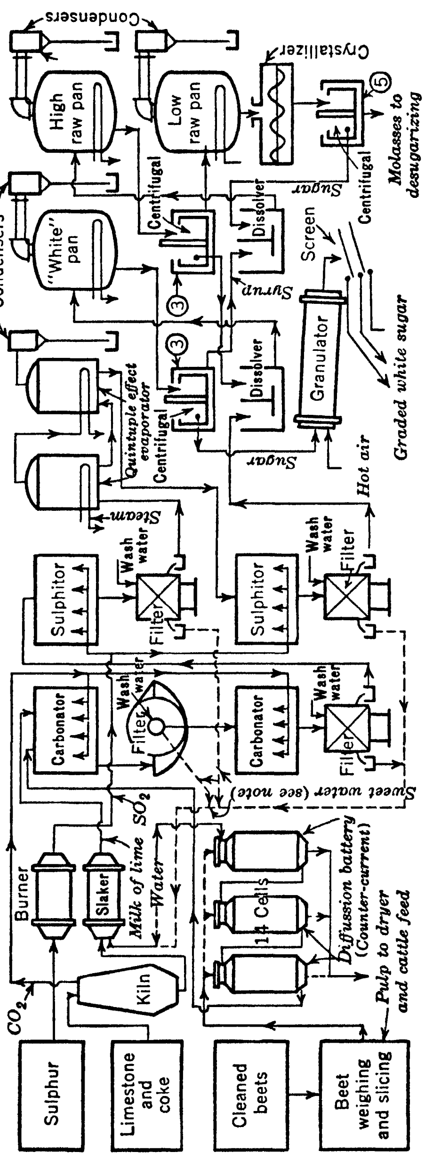
1. Separation of the juice from the fiber by pressure or by diffusion.
2. Clarification and removal of impurities that interfere with the subsequent evaporation and crystallization.
3. Removal of much of the water by evaporation.
4. Conversion of sugar from a dissolved condition into the solid crystal form.
5. Separation of the crystal sugar from the mother liquor or molasses by centrifuges.
6. Drying and packaging of sugar.

Flow sheets for the production of beet sugar and of raw cane sugar are shown in Figures 2 and 3. The details of the various operations will be better understood

[2] Lynsky, M., Sugar Economics, Statistics & Documents, U. S. Cane Sugar Refiners Assoc. (1938).

if frequent reference is made to these flow sheets while reading the word descriptions.

In some cases, as described later, the sugar is then ready for direct consumption. However, about 75% of the sugar consumed in the United States is subjected to a refining operation that involves a further purification by adsorption of impurities followed by re-crystallization.[3]



Note: The use of fresh water and sweet water from filter washing for slaking lime is about evenly divided by all plants.

Land (farm)	0.6 acre	Coal (for power and heating)	1 ton	Requirements for Production of One ton Sugar (Refined) 50% Sucrose Molasses (800 lbs.) Pulp (dried) 800 lbs.
Sugar beets	8.0 tons	Sulphur	1 lb.	
Limestone	½ ton	Water	9 tons	
Coke	0.05 ton	Direct man-hour labor	16–20 hour	

FIG. 2. Flow Sheet of Beet Sugar Manufacture. ("Chemical and Met. Flow Sheets of Process Industries," 2nd ed., McGraw-Hill Book Co.)

[3] The discussion of the refining process starts on page 1358.

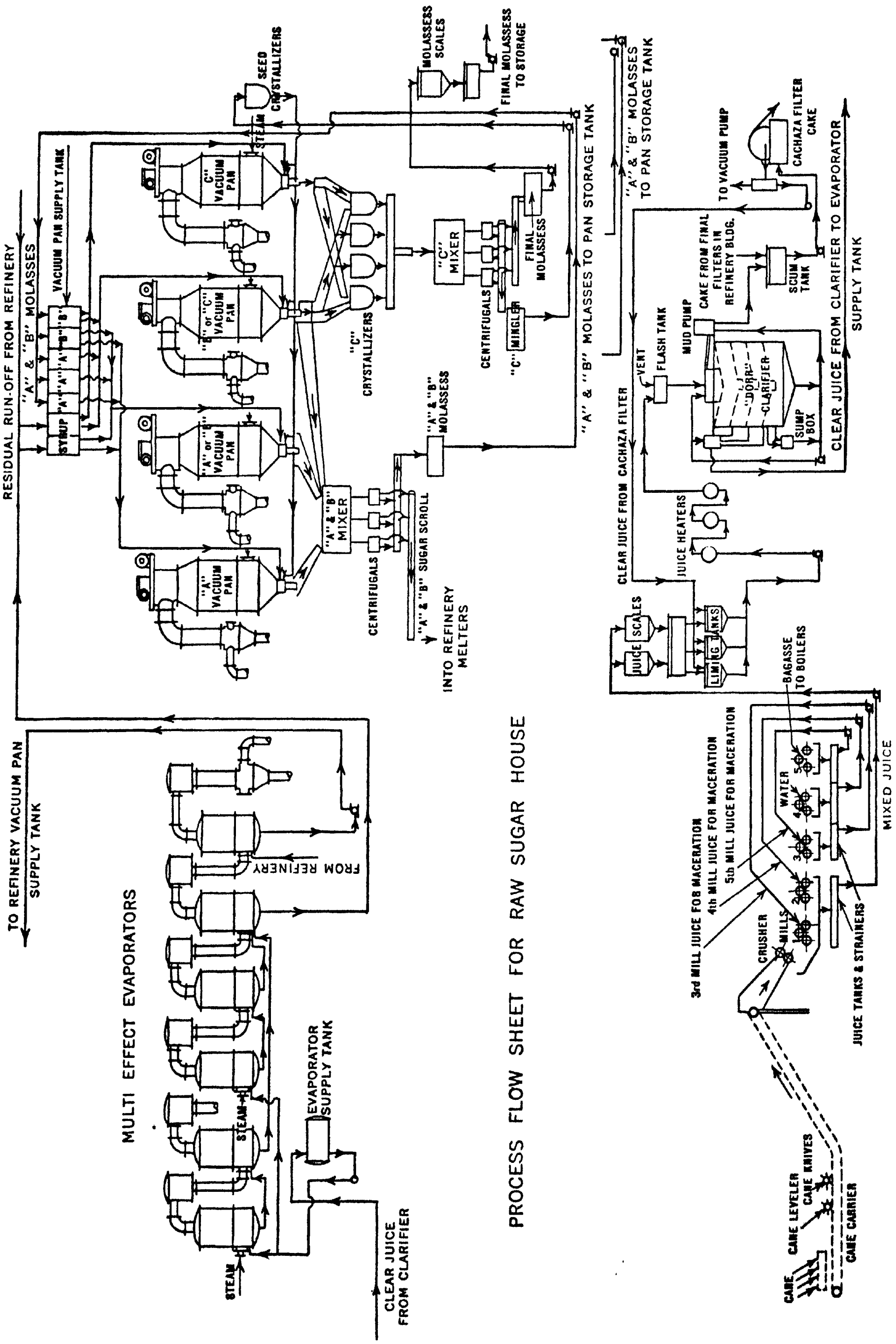


FIG. 3. Flow Sheet of Cane Sugar Manufacture. (Sugar Reference Book and Directory (1939). Russell Palmer, Hoboken, N. J.)

Milling of Sugar Cane—From remote times, cane juice has been extracted by a squeezing or crushing operation. In early times this was done by various primitive methods, one of which was a moving beam.

Today the roller mill is in universal use. It operates on the principle of a clothes wringer except that the cane mills are equipped with one top and two bottom rolls, the rollers arranged at the corners of a triangle. The rolls are generally made of open-grained gray iron, and are of various sizes. The diameter of the roll will range from ten inches to forty-two inches, and the length of the rolls from twenty-four inches to eighty-four inches. Hydraulic pressure is applied on the top roll.

Since a single three-roller mill can squeeze only part of the juice from the cane, it is general practice to arrange a number of these mills in series called a "tandem" or "train." (See Figure 4.) A frequent installation is the nine-roller

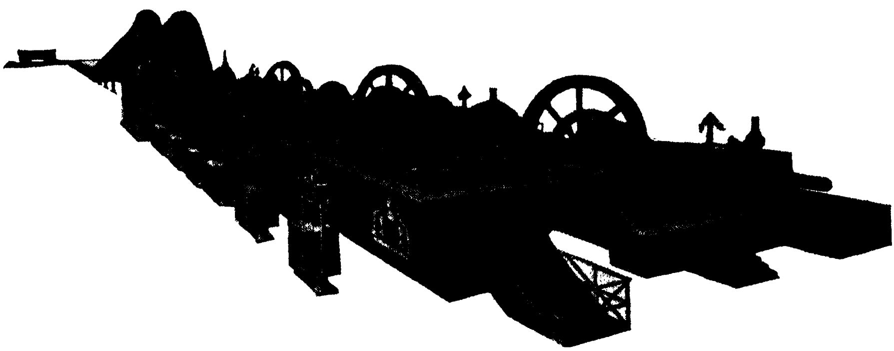


FIG. 4. Train of 3-Roller Mills for Crushing Sugar Cane. (Courtesy Fulton Iron Works Co.)

mill which is a series of 3 three-roller mills. Other installations may have as many as 6 three-roller mills. A tandem usually also includes a preliminary crusher which is similar to a three-roller mill except that it has only two rolls, a top and bottom roll. Some tandems are equipped with two crushers in series, known as a "double crusher."

The cane may be fed into the mill tandem in the form of the whole cane, or it may be cut into short lengths by revolving knives. The cane passes first through the crusher which is equipped with prominent teeth of various kinds, the Fulton type being widely used. (See Figure 5.) The teeth on the crusher partially disintegrate the cane, and the pressure squeezes out about 50% of the juice. Some tandems have a shredder between the crusher and the first of the three-roller mills. The shredder, as the name implies, tears the cane into fine shreds. However, in many tandems, the cane passes directly from the crusher to the first of the three-roller mills. The surface of the shells of the three-roller mills contains various types of grooves. Some of these grooves are designed to increase the gripping power of the surface, and other type grooves are designed to drain the extracted juice. This latter provision is necessary since the cane fiber, when it leaves each mill, quickly expands and will eagerly suck up any liquid.

Advantage is taken of this sponge-like property by adding water to the fiber when it leaves the mill roll. The cell walls have been torn, and this added water dilutes the sugar juice remaining in the fiber. This diluted juice is then squeezed out in the next mill. This process, called "maceration" or "imbibition," makes it possible to extract much more of the sugar from the cane. However, it is necessary to strike a balance between the recovery of sugar and the cost of fuel to evaporate the additional water. In order to make the maceration water serve several times, it is first applied to the fiber before it enters the last mill in the tandem, and then the diluted juice from this mill is used to macerate the fiber of the preceding mills.

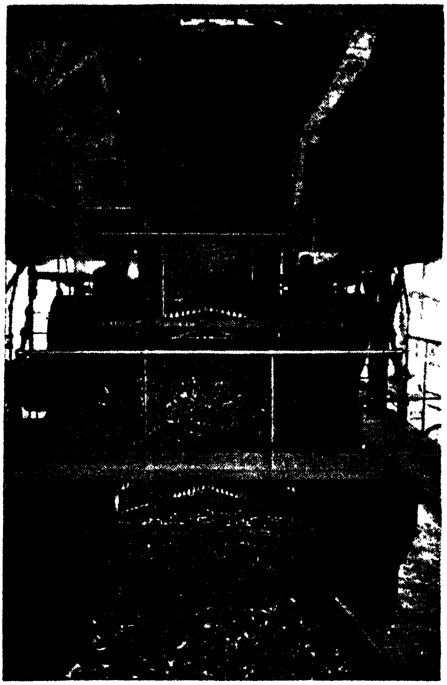


FIG. 5. Sugar Cane Passing Through Double Crusher. (Courtesy Fulton Iron Works Co.)

The extracted juice flows into a trough below the mills where it passes through screens to remove any particles of cane fiber and the juice is then ready for clarification.

The juice from the crusher and the first mills has less impurities than that from the latter mills in the tandem. Some factories find it advantageous to keep these juices separate, and clarify them separately.

The cane, after leaving the last mill, is termed "bagasse," and in most factories is employed as a fuel, though an increasing proportion is being used as a raw material for wall board.[4]

The important factors to be considered in the selection of a roller mill are:

1. Dependability.
2. Flexibility.
3. The degree of extraction.
4. The capacity.

The mills must be dependable inasmuch as they are subjected to a very great mechanical strain, and a break-down would seriously interfere and delay the operation of the factory. This is a matter of great importance since the cane, once it is harvested, must be processed practically at once. Moreover, many cane factories are located at points where it is not possible to secure quick replacement of parts.

Flexibility is important because of variations in the amount of cane that is

[4] See Chapter 37.

brought to the mills from time to time due to irregularities of harvesting, hauling, etc., and a mill must be designed to be able to take care of a small load, or of a much greater load according to the prevailing conditions.

The extraction must be good since, unless the greater proportion of the sucrose is extracted from the cane, it will involve a serious loss of production.

The capacity of the mill depends on a variety of factors including the design; the type of grooves; the type of cane—some canes being much harder and containing more fiber; the size of the mill rolls; the speed at which they operate; and the care that is taken to provide uniform distribution of cane over the entire length of the rolls. Therefore, it will suffice to indicate the results in a very efficient operation that employs a tandem system consisting of a thirty-seven inch by eighty-four inch Fulton eighteen-roller mill equipped with a double crusher, and one set of knives. This Fulton mill tandem, during the Cuban crop of 1940, ground an average of 5,267 tons of cane per day with a sucrose extraction of 97.41%. This tandem was driven by three engines. The double crusher was driven by a 525 H.P. engine, the first nine-roll mill took 1,100 H.P., and the second nine-roll mill took 1,250 H.P.[5]

The Diffusion Process for Extraction of Juice from Sugar Beets—In the early days of the beet sugar industry the beet roots were torn into a pulp, and the juice extracted by hydraulic pressure. The diffusion process which today is universally employed dates from about 1860, and is based on the following principle.

The sugar is contained in the cell juice of the plant. When sliced beets are placed in water, the sugar and other crystalloids pass through the cell wall until the concentration of sugar in the surrounding water is equal to that remaining in the cell juice. The diffused juice is purer since most of the colloids such as gums and albumin cannot pass through the cell wall. This is an example of the utilization of osmotic pressure exerted on a semi-permeable membrane—the cell wall.

The Diffusion Battery. The process is carried out in a battery of large cylindrical vessels which are manufactured in various sizes. These vessels are arranged either in a row or in a circle, and are connected so that the liquid can be passed from one vessel to another. The number of vessels in a battery will vary from eight to sixteen.

The beets, after being washed, are cut into v-shaped slices called "cossettes" which are then placed in the diffusion vessels. Fresh hot water is added to the vessel in the battery that was the first to have been filled with beet slices. The sugar contained in the cells of the cossettes diffuses through the cell walls into the water. The water thus becomes a weak sugar solution. This is then piped through a heater into the second vessel in the battery where it comes in contact with beet cossettes that have not been in process so long and, therefore, contain more residual sugar and the diffusion continues. From here the somewhat stronger sugar solution is pumped through the remaining vessels in the battery. By the time this solution has reached the last vessel, it is in contact with freshly sliced beets, and will acquire a sugar concentration almost equal to that

[5] Communication (Nov. 6, 1940) H. Hurter, Chief Engineer, Fulton Iron Works, St. Louis, Mo.

originally present in the beet. The solution is then ready for the next step, namely, clarification. Meanwhile, other charges of water have been flowing through the preceding vessels, and by this time, the sugar has been practically exhausted from the beets in the first unit. The contents of the vessel are then discharged, and re-filled with freshly sliced cossettes. This vessel will now become the last instead of the first vessel of the battery.

The general principle is that the freshly sliced beets which are best able to give up their sugar come in contact with the strongest solution, whereas the almost exhausted slices come in contact with fresh water.

A battery of diffusers is a good example of the application of countercurrent flow of materials for the transfer of a substance from one phase to another. It is quite similar in principle to liquid-liquid extraction.[6]

The quantity of water that is to be used must be carefully controlled, as too little water will give poor extraction, and too much water increases the evaporation cost out of proportion to the value of the extra sugar that is recovered. A general practice is to use sufficient water to extract from 95 to 98% of the sugar in the beet. While it is desirable to use water at the highest possible temperature to reduce the bacterial activity, temperatures above 80° C. are not practical since they cause the cossettes to become soft and pack down, and in this way slow down the circulation. In the case of beets that have been damaged by repeated freezing and thawing, temperatures even lower than 80° C. are required.

It is desirable that the knives that cut the beets should be very sharp since this does less damage to the cell wall, and, in general, a thin slice will diffuse more readily than a thick one, although there is a limit in this direction, since thin slices are more liable to become soft and mushy.

Use of Pulp. After extracting the sugar the beet pulp is pressed free of moisture and dried for use as cattle feed. Today many beet factories avoid the cost of pressing and drying by providing feeding corrals adjacent to the factory where cattle are fattened during the manufacturing season. The beet tops are also used for this purpose.

Diffusion Not Practical for Cane. Since the diffusion not only separates the sugar from the fiber, but, also, from many colloidal impurities in the plant juice, it may be asked why diffusion has not been applied in the cane industry. As a matter of fact, diffusion has been tried in the cane industry, but various objections have been found to its use. A diffusion process must be operated continuously, and should the diffusion battery be stopped for lack of raw material, all of the juice in the battery would have to be worked up "as is." Much of it would be very thin, and this would add considerably to the fuel cost. Any interruption of the diffusion process can be guarded against in the case of beets since they are not as perishable as cane, and an adequate supply can be stored in the plant at all times. This is not practical with cane because it deteriorates so rapidly. Moreover, large amounts of cane frequently come into the mill at one time. Roller mills have sufficient flexibility to permit the processing of this extra cane, whereas the diffusion process cannot be speeded up without loss in the extraction of sugar. Also, in order to be used in the diffusion process, the cane would have to be shredded very finely, and would lose much of its value as a fuel. The many

[6] For further discussion of this type of extraction, see Chapter 2.

improvements made in cane mills in recent years have made the question of the application of diffusion to cane juice a matter of only academic interest.

Clarification—The juices extracted from the cane or beet are strained to remove most of the particles of dirt, fiber, or pulp, after which the juice is ready for the next step, clarification. The purpose of clarification is to free the juice as far as possible from all constituents except sugar, without altering the sugar itself.

Many materials have been proposed for this purification. Von Lippmann,[7] in 1937, gave a list of over 700 substances that have been proposed at one time or another. However, lime, which was one of the first chemicals to be used,

CANE JUICE FROM MILL

↓

SUFFICIENT MILK OF LIME ADDED TO ADJUST pH TO APPROXIMATELY 7.6 TO 8.4

↓

HEATED TO 212° TO 215° F.

↓

SETTLED

FIG. 6. Flow Sheet—Simple Clarification.

still remains the universal basis of most schemes of clarification, since it is both an effective and inexpensive material.

The action of lime upon the constituents of the juice is complex and is not completely understood. The lime neutralizes the natural acidity of the juice, and converts many of the organic acids into insoluble calcium salts. The change in the hydrogen ion concentration produced by the alkalinity of the lime prevents any inversion of sucrose, and is also responsible for the precipitation of many colloidal impurities. Further, the various precipitates that are formed will adsorb still other impurities, and will also trap much of the finely divided suspended matter.

Expressed numerically, the clarification does not accomplish any great removal of impurities. However, the clarification does produce a remarkable change in the physical character of the juice. The appearance which was dark and murky before clarification becomes clear and lighter in color. The improved physical character is definitely reflected in an improved performance in many of the subsequent operations, including filtration, evaporation, and in the recovery of sugar in the crystallization. Because of all this, clarification remains an essential and integral part of the manufacture of sugar.

Methods of Clarification—There are many methods of applying lime for clarification. A simple method (Figure 6) of clarifying or defecating cane juice is to add sufficient milk of lime to produce a neutral reaction. The limed juice

[7] Von Lippmann, Deutsche Zuckerind, *62*, 67-69, 87-89, 105-106, 125-126, 151-152 (1937).

is then rapidly heated. This heating is necessary to promote the clarifying action of the lime, and is also essential to check all biological processes which would otherwise rapidly occur in freshly clarified juices and cause deterioration. Defecation with lime may be carried out as a batch or a continuous operation.

Batch System. In a typical batch system, the juice is placed in tanks to which the required amount of lime is added. The limed juice is then heated until a heavy blanket of scum forms, after which the precipitated matter is allowed to subside or rise, according to its specific gravity. The clear juice is decanted from between the scum and settled mud, and placed in a storage tank. The mud and

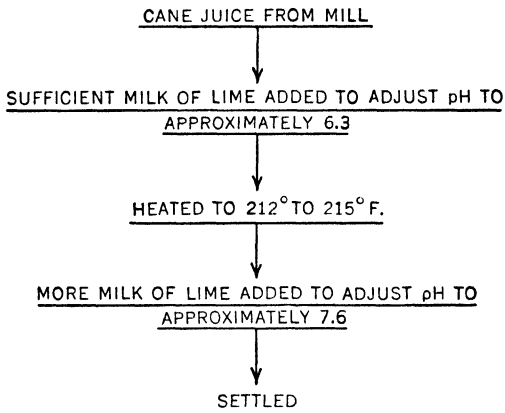


FIG. 7. Flow Sheet of Fractional Liming.

scums are sent to a press and the clear filtrates are added to the decanted liquor from the feeding tanks. The juice is then ready for the evaporation station.

Continuous Process. In a continuous process the juices flow continuously through a treatment tank to which the regular addition of the proper quantity of lime is controlled by a pH meter. From the treatment tank the limed juices flow through a clarifier of the Dorr type, which separates the muds from the clear juices, and the latter go to the evaporator station.

Some cane juices are rather refractory to the simple defecation treatment just described. The sludges do not settle or filter well, and the decanted and filtered juices do not have good clarity. Many of the newer varieties of cane which have been developed for disease resistant properties and for higher sugar content, provide juices that are inherently difficult to clarify, and this condition is intensified by the efforts to obtain a greater extraction of the juice which at the same time extracts more of the undesirable non-sugars. The problem of refractory juices has been met by various modifications of the simpler defecation.

Fractional Liming. One process, known as "fractional liming" (Figure 7), is based on the knowledge that there are various types of colloidal impurities present in sugar juice. Some of these colloids are precipitated at one hydrogen ion concentration, whereas other colloids are precipitated at a different hydrogen ion concentration. Therefore, instead of adding all the lime at one time, it is added in successive portions, thereby changing the hydrogen ion concentration in a series of steps. This accomplishes the precipitation of the different types of colloids.

Compound Clarification. Another procedure, known as "compound clarification" (Figure 8), takes advantage of the fact that the juice from the crushers and the first one or two mills in the roll mill tandem is easier to clarify than the juice from the latter mills in the tandem. Therefore, in this procedure the juice from

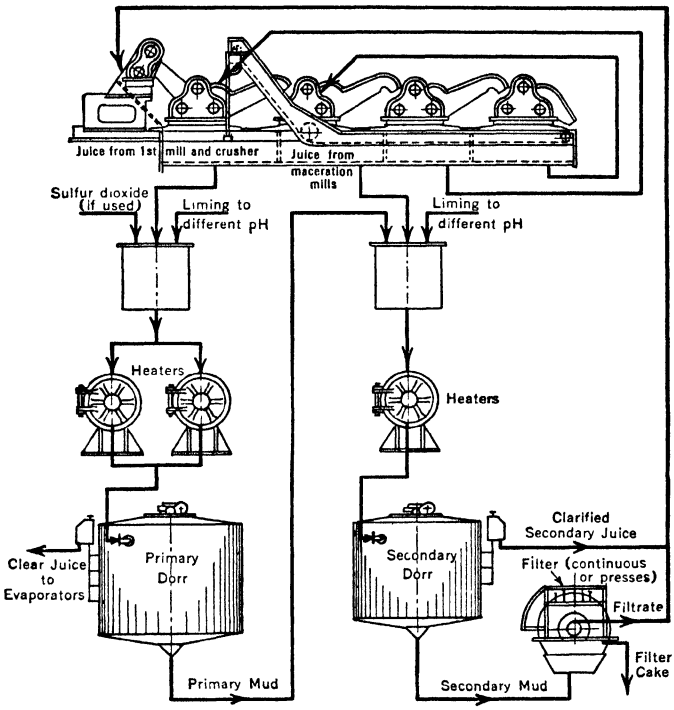


FIG. 8. Typical Flow of Compound Clarification. (Courtesy Dorr Co., Inc.)

the latter stage is kept separate, and is given an initial defecation before being mixed with the juice from the crusher and the first mill for the regular defecation. The juice extracted by the last part of the roll mill tandem thereby receives a double defecation.

Other Defecation Agents. Various other agents which elaborate the simple defecation are frequently employed. Sometimes these are adopted because of the refractory nature of the juice, and sometimes because they are considered valuable to the finished quality of the sugar. Two of the more important of these agents are sulfur dioxide and phosphoric acid, or mono calcium phosphate. In addition to their specific clarifying properties, both sulfur dioxide and phosphoric acid are satisfactorily precipitated by lime, and such precipitates possess an adsorptive power for many of the colloidal impurities.

The Carbonation Process. In a procedure known as "carbonation"[8] an excess amount of lime is added to the juice. The excess lime is then precipitated as

[8] See Beet Sugar flow sheet, Figure 2.

calcium carbonate by the addition of CO_2. The application of this process is not general in the case of cane juice, but it is almost universal for beet juice. This is because the simple defecation with lime that is effective for producing raw sugar from cane juice does not give the clarification required for the direct crystallization of white sugar from beet juices.

The quantity of lime required in the carbonation process usually amounts to from 1.5 to 2.5% of the weight of the beets. In plants where a Steffens process is employed,[9] the saccharate of lime from that process is added to supply all or part of the necessary lime. The carbonation is generally carried out in two stages, and either a batch or continuous system can be used. The continuous process has the advantages generally inherent in a continuous method, and in addition, forms a more granular precipitate that is easier to settle and to filter. There are many variations in the carbonation procedure. The following represents the practice as carried out in one of the newer plants.

Typical Carbonation Process. The juice coming from the diffusion cells is pumped through heaters which raise the temperature to about 90° C., from which the juice goes to a tank where the lime is added. The limed juice then goes through a carbonating tank where CO_2 is bubbled through the juice till a pH of about 11.0 is reached. From here the juice flows through a Dorr thickener which separates the juice from the sludge, and the sludge is delivered to drum filters. The clear juice from the clarifier is pumped through a second carbonation tank for further treatment with CO_2 where the pH is reduced to about 9.0. The clear juice from this is treated with SO_2, to adjust the pH to approximately 7.5, again filtered, and is ready for the evaporator station.

Certain precautions should be observed in the carbonation. The first carbonation must not be carried too far as otherwise some of the precipitated impurities will be redissolved, and in the second carbonation it is necessary to avoid carbonation to the point where bicarbonates will form, since these will be decomposed later in the evaporator, and cause incrustation. Formerly the end point of carbonation was determined by the appearance of precipitate, and titration. Today conductivity and pH instruments are generally employed for this purpose. Some installations are arranged to provide automatic control of the CO_2 valves. It is necessary to provide good contact between CO_2 and the liquid phase and this is assisted by introducing CO_2 in the form of very fine bubbles.

Use of Active Carbon in Clarification. Many beet sugar factories add active carbon at the clarification station. Dosages as low as one quarter pound active carbon per ton of beets have been found to result in improved behavior of the liquor during the subsequent evaporation and crystallization.

EVAPORATION

The thin juices from the clarification station must now be evaporated in order to produce crystal sugar. This operation must not be delayed since the thin juice rapidly decomposes with loss of sugar. In early times the evaporation

[9] See page 1358.

was conducted in a "copper wall." This consisted of a number of copper kettles placed in a flue between a chimney and an open fire. The thin juice was added to the kettle nearest the chimney, and as the evaporation proceeded the juice was ladled successively into the other kettles until it finally reached the kettle over the open fire where the final concentration was made. This method of evaporation was wasteful of fuel and labor, and much sugar was decomposed at the high temperatures used. Today evaporation is conducted by means of steam in evaporators. In the first stage of the evaporation the juice is concentrated to about 50% to 60% sugar. This stage is conducted in multiple effect evaporators which make very effective and efficient use of the steam.

Multiple Effect Evaporators [10]—A multiple effect evaporator in the sugar industry consists of a series of large cylindrical vessels (in sugar work three or four vessels are commonly used, known as triple or quadruple effect respectively). All of the effects in a multiple effect evaporator are of similar construction and design, consisting of a large vertical cast-iron or metal plate cylindrical vessel. In the sugar industry the steam-heating unit (usually a calandria) is placed in the lower portion of the effect. The calandria is a drum-shaped steam chest provided with a large vertical central tube (the downtake) which extends from the top to the bottom plate of the drum. In the rest of the drum are numerous small-diameter vertical tubes also extending from the top to the bottom plate.

Exhaust or low pressure steam is introduced into the calandria of the first effect which also receives the thin juice. The effective heat in the steam is transferred through the walls of the calandria tubes to the juice, causing it to boil. The boiling juice rises in the tubes, releases the vapors which leave the effect through the dome and are piped to the calandria of the succeeding effect. The liquor then descends at the center of the effect through the "downtake" in which no heating takes place. The effectiveness of the natural circulation thus established depends on proper design of the effect and on the viscosity of the liquor. The viscosity increases as the evaporation proceeds, and hence the circulation is somewhat poorer in the last effect.

The vacuum maintained in each of the effects is the force that causes the liquor to flow from one effect to the following one, the rate of flow being controlled by a valve. In the case of the last effect, the concentrated liquor is removed by means of a pump, and is ready for final evaporation in the vacuum pans.

Even the clearest clarified juices contain constituents that become insoluble when the juice is concentrated by water removal. Some of the precipitate thus formed remains in the thick juices, making it turbid, and must be removed by a subsequent filtration. Other impurities are deposited as an incrustation on the heating surface of the calandria, particularly in the last effect. Such incrustation must be removed from time to time since it slows the transfer of heat and impairs the evaporator efficiency.

The vapors leaving the surface of the liquor have a certain velocity and may carry small droplets of liquor—a condition known as "entrainment." En-

[10] For further discussion of the principles and illustrations of Evaporators, see Chapter 2.

trainment is avoided by proper design of the effect and by keeping the level of the liquor at a correct height. A baffle known as a "catch-all" is built into the dome of each effect for the purpose of separating any entrained droplets from the vapor.

The vacuum is maintained in the last effect by condensing the vapors arising from it by means of cooling water. In the other effects the vacuum is obtained by the condensation of the vapor in the calandria of the succeeding effect. The proper degree of vacuum is controlled by the pump, trap, or barometric drain employed to remove the condensate from the calandria and also by a vacuum pump which removes the non-condensable gases.

TABLE 1—SOLUBILITY OF SUCROSE IN WATER *

Temp. °C.	*% Weight*
30	68.70
40	70.42
50	72.25
60	74.18
70	76.22
80	78.36

* Inter. Critical Tables, Vol. 2, page 344.

Crystallization. At this stage the evaporation is continued to the point where sugar crystals form and separate from the remaining water and impurities.

The Role of Supersaturation. The data on the solubility of sucrose in water at various temperatures are given in Table 1. If a saturated solution of sucrose is cooled, or if some of the water is evaporated, the solution becomes supersaturated with no immediate separation of crystals. The degree of supersaturation is conveniently expressed by the coefficient of supersaturation, a value obtained by dividing the amount of sugar in solution by the theoretical solubility at that temperature. There is a natural tendency for sugar to crystallize from a supersaturated solution, but time is required for this, and the length of time depends on a variety of conditions. When the coefficient of supersaturation is small, that is, when there is only slight supersaturation, then the sugar will crystallize only on crystals already present in solution. When such crystals are not present, a solution may remain supersaturated for an indefinite period of time. However, a solution that is strongly supersaturated, e.g., 1.5 coefficient of supersaturation, will form crystals spontaneously. There is an intermediate zone of supersaturation, wherein new crystals (false grain) will form in the presence of crystals already present, but will not form in their absence.

Supersaturation acts as a positive force to cause crystallization but there are negative influences which retard it, one of which is viscosity. A higher coefficient of supersaturation must exist in viscous solution in order to obtain spontaneous crystallization. Sugar factory syrups are not solutions of pure sucrose, but contain non-sugars which not only increase the viscosity, but, also, alter the solubility of the sugar. Certain non-sugars have the apparent ability to increase the solubility of sugar, whereas other non-sugars have the opposite property of decreasing the solubility of sugar. The non-sugars in sugar juices have a very definite technical importance in the boiling operation.

THE BOILING OPERATION

The boiling operation is conducted in vacuum pans (see Figure 9), which may be heated either by coils or by a calandria unit. In appearance and in certain other respects vacuum pans are quite similar to single effect evaporators.

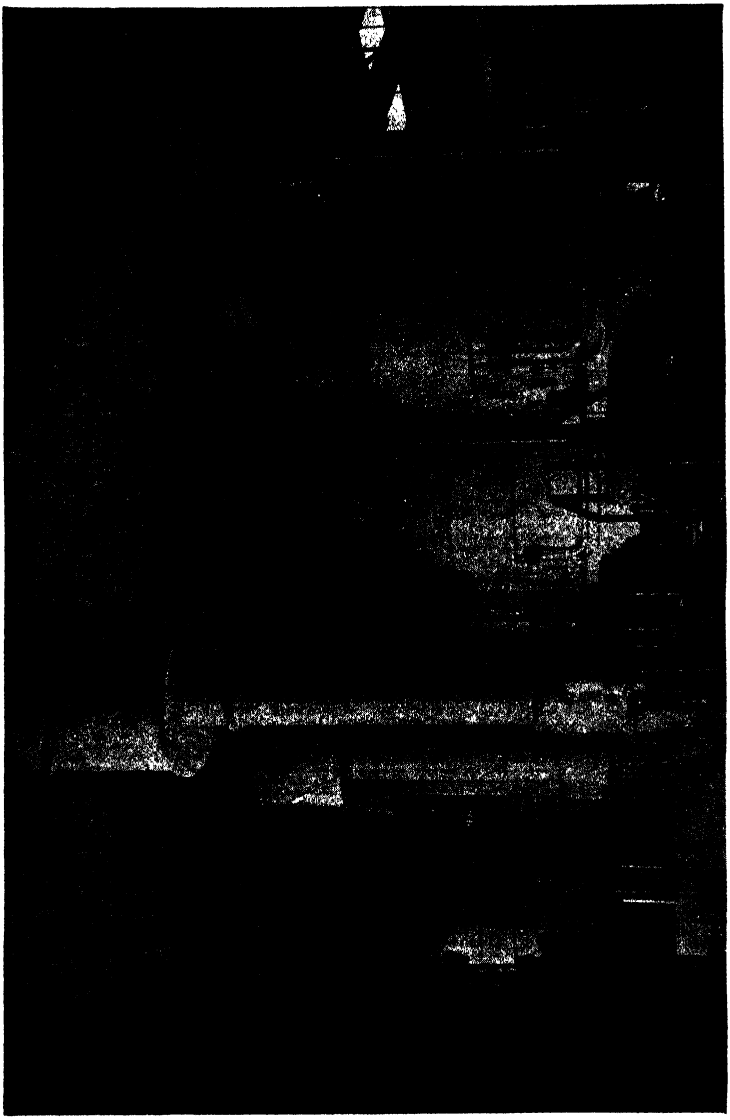


FIG. 9. One Type of Vacuum Pan. (Courtesy U. S. Pipe and Foundry Co., Burlington, N. J.)

The procedure for conducting the crystallization by boiling in pans is very much of an art, and, in general, no substitute has thus far been found for experience and personal judgment. It has been stated that it is quite impossible for a sugar boiler to prepare written instructions for the inexperienced operator, and moreover, a sugar boiler accustomed to the operation in one factory may have difficulty in becoming accustomed to the operation at another plant. However, conductivity and other instruments are now available which accurately indicate the condition of the liquor in the pan, and in some factories the use of such instruments has been developed to a point where it enables the boiling to be conducted on the basis of a "written prescription."

There are many methods, and, also, modifications of each method for conducting the boiling operation. This fact must be kept in mind in reading the following discussion.

Different Methods of Operation—In one method the operator (boiler) first adds a portion of evaporator syrup to the pan. The amount to be added is based on what the operator considers will be sufficient to produce the correct number of crystal nuclei or as it is termed, "to form the proper grain." The graining charge varies in extent, but is frequently equal to from one-fourth to one-third the full capacity of the pan. After this charge is admitted to the pan, a vacuum is established, and steam is admitted to the heating unit, that is, to the coils or calandria. The liquor is thereby concentrated until it has reached a degree of supersaturation where crystals will form. There are several ways of conducting this stage of the operation. Some operators use the so-called "waiting method" in which the liquor in the pans is kept at a high degree of supersaturation until the proper number of crystals are formed. Other operators employ what is known as a "shock" which can be produced in various ways. One method is to boil the liquor at not so high a vacuum, and consequently, at a higher temperature. When the liquor has reached the desired degree of supersaturation the vacuum is rapidly increased, and the flow of steam through the heating units is reduced. The temperature in the pan is thereby lowered, and results in greater supersaturation due to the reduced solubility of sugar at lower temperature. In other cases the shock is administered by drawing in a small amount of cold juice. Often if air is admitted to the pan, the dust present will induce the formation of nuclei. A shock method that many prefer is to draw some powdered sugar into the pan immediately after the metastable stage has been reached, and wait for the development which comes gradually and smoothly. The shocking must not be done too late as this results in forming, not only nuclei, but conglomerates as well.

The graining must be carefully controlled since, when too few crystals are formed, there is not sufficient crystal surface for the sugar to deposit upon, and this results in a slow and incomplete crystallization. On the other hand, when too many crystals are formed, particularly if this occurs during several periods of operation, it will result in an infinite variety of crystal sizes. The small grains plug up the drainage between the large ones, and thus make for difficult centrifugal work.

Seeding—A procedure known as seeding provides a very effective method of conducting the graining operation. In this the full and proper number of minute sugar crystals is introduced into the pan as soon as saturation has been exceeded, and the concentration is not allowed to reach the point where new crystals will form.

Building the Crystals—After the grain is established in the pan by any of the various methods, the supersaturation is henceforth kept below the point where additional crystals known as "false grain" will form. This is accomplished by admitting more liquor to the pan, either intermittently or continuously, although a continuous feed is preferable. From here on a balance must be struck between the rate of evaporation and the amount of liquor that is admitted to the pan. Evaporation must proceed at a rate that will maintain a supersaturation sufficient to cause rapid growth of the crystals. On the other hand, the evaporation must not exceed the rate at which sugar can deposit on existing crystals since this would lead to a much higher supersaturation at which "false grain" will form.

The whole mass must be kept in motion since each crystal rapidly depletes the sucrose from the surrounding film of liquor, and must be continually brought into contact with a fresh film. Circulation is also necessary to prevent local over-heating of the portion of the liquor in contact with the heating coils. Apart from any decomposition effect of sugar, local overheating would also produce a case of local undersaturation of the sugar.

At first the natural circulation is reasonably good, but after a time the fluidity of the mass decreases. This is due to the fact that the growing crystals soon occupy considerable volume, and the fluid space becomes relatively small. Various methods exist for promoting circulation. The incoming liquor flows upward and promotes circulation. Steam may be admitted to the bottom of the pan, and as the steam bubbles rise under vacuum conditions they expand, and in that way assist the circulation. Much study has been given to the influence of the shape of the pan, and as a result of these studies very definite improvement has been made in pan design.

Webre, who has done much to clarify [11] our understanding of sugar boiling, has designed a slowly revolving screw placed in the central tube which boosts the circulation, but in exactly the same direction as the original natural circulation, namely, up the outer periphery and down the center. This device has been incorporated into some types of vacuum pans. While many believe the benefits of mechanical circulation are more apparent when obtaining the second and third crop of crystals, actually, very advantageous results have been accomplished from the use of mechanical circulators on refinery white liquors of high purity. In this latter case, although the gain of speed is not very great, the formation and the color of the crystals is very much better.

Discharging the Pan—When the crystallization has proceeded to the point where, for practical purposes, it is considered complete, the contents of the pan are discharged, or, as it is termed, "a strike is made." The mixture of crystals and mother liquor is termed a "massecuite" or a "fill mass." This massecuite or fill mass then goes to the centrifugal machines where the mother liquor is spun off from the crystals.

Multiple Boiling—The mother liquor that is spun off is called a "first molasses" in cane sugar factories, or a "high green syrup" in beet sugar factories. This liquor still contains much crystallizable sugar which can be recovered by further boiling. Some factories employ a two-boiling system, but the three-

[11] Webre, A. L., Amer. Soc. Mech. Engineers, Dec. 3, 1934, Mech. Eng. *58*, 99-102 (1936).

boiling system is more common. In a three-boiling system, the liquor from the first or "A" crystallization is reboiled in the second vacuum pan, known as the intermediate pan in which a second or "B" crop of crystals is produced. The mother liquor from the B crop of crystals is again boiled to produce a third or "C" crop of crystals. The mother liquor from the C crystals constitutes the final molasses.

Obtaining the "C" Crystals. During the course of this process the non-sugars become more concentrated in the liquor, and increase the difficulties in crystallization. This difficulty becomes particularly pronounced in the third boiling, and since, in many factories, this is the last chance to recover the sugar, much study has been given to this stage.

The procedure generally employed for obtaining the third or "C" crop of crystals involves two steps. The manner of conducting the first step varies in different plants, but one satisfactory way is to boil a relatively small quantity of high purity syrup to form the grain. After the grain has formed the mother liquor from the second, or "B" crystals is then admitted to the pan, and the boiling is continued until it is strongly supersaturated. The supersaturated massecuite is then discharged to a crystallizer in which the crystallization proceeds to completion.

Crystallizers—There are various types of crystallizers for these operations. They are frequently horizontal, cylindrical, or U-shaped tanks equipped with stirring paddles. The mixture is permitted to cool to take advantage of the lower solubility of sugar at lower temperatures. In order to hasten the cooling, water cooling coils are frequently installed in the crystallizer. The increase in supersaturation due to cooling must not exceed the rate at which the sugar will deposit on existing crystals. Therefore, the cooling must not be too rapid since this would lead to excessive supersaturation with consequent formation of false grain. The cooling increases the viscosity of the mother liquor, and retards the rate at which the supersaturated sugar in the solution can reach the surface of the crystal. When the temperature has fallen to about 30° C. further crystallization is so slow as to be impractical.

This mass is generally too viscous to be readily centrifuged, and various methods are employed to reduce the viscosity. One of these methods is to mingle the semi-liquid massecuite with a small amount of water. Another method reduces the viscosity by elevating the temperature to about 45° C. The sugar dissolves rather slowly under either of these conditions, and, therefore, only a small amount of sugar is lost by being redissolved. The heating method seems to be more generally preferred since the addition of water is difficult to control, and unless properly added can cause a condition of local undersaturation and dissolve considerable amounts of sugar. Proper and exact temperature is most important when massecuites are heated. Heating in the crystallizers by means of water jackets, stationary or rotating heating surfaces, while generally employed, has certain objectionable features. Relatively recent process development provides rotating heating surfaces in the mixers supplying the centrifugals by which temperature adjustments are made under complete control and immediately prior to the centrifugal separation between crystals and mother-syrup.

In addition to the crystallizers already mentioned there are various other types, some of which combine the principle of a vacuum pan and a crystallizer.

One recent type consists of a horizontal pan which rotates on trunnions. After the massecuite is discharged from the pan into this type of crystallizer, the evaporation is continued until a still higher degree of supersaturation is reached. Then the steam is shut off, and cooling water is admitted to the coils. The cooling water at first is only slightly cooler than the massecuite, and this temperature is lowered gradually as the cooling progresses. In this crystallizer the final warming of the massecuite for centrifuging can be accomplished by allowing warm water to flow through the cooling coils. An instrument known as a "Saturoscope" has proved of value for the control of the temperature of the water for cooling and for warming.

PURGING AND CURING

In the early days of sugar manufacture, after completing the crystallization, the mother liquor or molasses was separated from the crystals of the sugar by placing the massecuite in wooden barrels fitted with perforated bottoms. The molasses slowly drained away from the crystals, an operation which frequently required weeks.

Centrifuges—The adoption of centrifugal machines marked a definite advance in the manufacture of sugar because it became possible to obtain a far better separation of molasses and crystals, and, moreover, the operation requires only a few minutes of time. (See Figure 10.)

The baskets of the centrifuge are generally 40 inches in diameter, although 48-inch diameter baskets are in use. Considerable improvements have been made in recent years in basket design, materials specifications, filtration area, syrup separation and methods of acceleration to top speed. Until recent years a maximum speed of 1200 r.p.m. was employed, but higher speeds to a present maximum of 2200 r.p.m. have been proved advantageous. While these higher speeds can be used to hasten the process, the chief advantage lies in other directions, one of which is greater crystal recovery. Another advantage is that more of the molasses film is spun off the crystal, and a purer sugar is obtained. Moreover, the high speed machines make it possible to handle massecuites of higher viscosity. In consequence, it is possible to boil the liquor to a higher concentration to obtain more complete crystallization, and still be able to separate the molasses from the sugar crystals.

Finishing Beet Sugar—It will have been noted that the method of separating the juice from the fiber, and of clarifying the juice differs in the case of canes from that of beets, but that the evaporation, boiling and centrifuging operations are similar for both types of juice. However, after the centrifuging, the processing of cane and beet sugar tend to follow different paths.

In the American beet sugar factory, the first crop, or "A" crystals, is very pure, and is equivalent to refined cane sugar in quality. These crystals, after thorough washing, drying and screening, are sold directly as granulated sugar without further processing. The type of dryer used is shown in Figure 11. The second, "B," and third, "C," crops of beet sugar crystals are not sufficiently pure to be sold as white sugar, so these crystals are returned to the process, and are subsequently recrystallized.

Finishing Plantation and Raw Cane Sugars—The impurities in the cane juice adhere more strongly to the sugar crystal, and most cane sugar is recrystallized or refined before being marketed to the ultimate consumer. However, in those cane sugar factories in which the clarification is elaborated to include carbonation, sulfitation, or both, the "A" crystals are sufficiently pure to be sold in certain localities for direct consumption, and are marketed under the name of "plantation white," "Java white," etc. Such sugar, however, generally

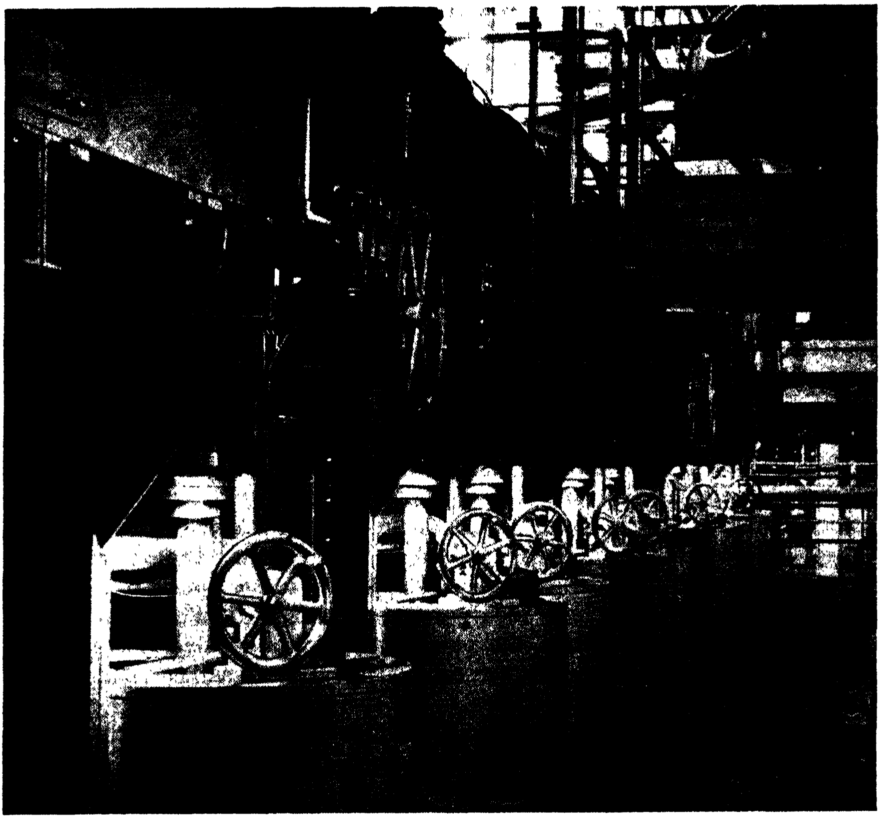


FIG. 10. A Battery of Centrifuges. (Courtesy Western States Machine Co., New York City)

is not as pure as the similar "A" crystals from beet sugar manufacture, and cannot be sold as a fully refined product. Since the process requires a higher order of technical skill, and an additional cost over what is required for raw sugar manufacture, most cane sugar is first produced in the form of a raw sugar of about 96% purity. This is later processed by a refining operation before going into ultimate distribution to the consumer. In raw cane sugar factories, the second, or "B" crop of crystals, is generally sufficiently pure to be mixed with the "A" crystals for sale as raw sugar. The third, or "C," crop of crystals, has lower purity[12] and is returned to the process. Frequently these

[12] With modern centrifugal equipment it is possible to produce "C" crystals of a purity suitable to be mixed with "A" and "B" crystals for sale as raw sugar.

"C" crystals are returned to the vacuum pans where they provide the crystal grain or footing for the boiling of subsequent batches of syrup.

Since the successful crystallization of sugar depends upon keeping the impurities in the mother liquor, it is obvious that the production of molasses is inevitable in the manufacture of sugar. Molasses is the mother liquor containing nearly all the impurities plus considerable sugar, after the relatively pure sugar crystals have been removed. The water that is required to keep the impurities in solution will dissolve considerable quantities of sugar due to its high solubility. Certain impurities have the ability to increase the solubility

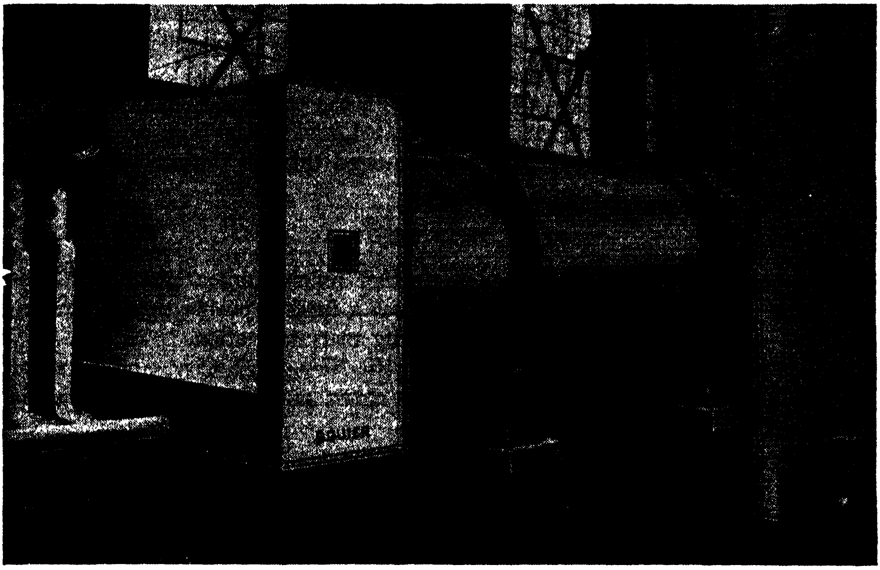


FIG. 11. Dryer Used for Sugar Crystals. (Courtesy G. L. Squier Co., Buffalo, N. Y.)

of sugar, and this is particularly so in the case of beet molasses (see Table 2—Analysis of Typical Cane and Beet Molasses). The amount of sugar left in the molasses is affected by other factors, including the viscosity, for after this reaches a certain point, there are practical difficulties in the further

TABLE 2—ANALYSIS OF TYPICAL CANE AND BEET MOLASSES *

	Cane Molasses	*Beet Molasses*
Water	20%	20%
Sucrose	30%	50%
Raffinose	0	present
Invert Sugar	32%	trace
Ash	6%	10%
Organic Non-sugars	12%	20%

* Chem. & Met. Eng., *16*, 437 (1917).

crystallization of sugar. Although beet molasses contains a greater amount of sugar than cane molasses, it has the advantage that it is possible to recover much of the sugar by various processes which cannot be satisfactorily applied to cane molasses. Of these the Steffens process is most commonly employed in America.

The Steffens Process—To recover the sugar from the beet molasses, the molasses is diluted with water to about 7% sucrose, and then finely pulverized lime is added. The lime reacts with the sucrose to form tribasic saccharate of calcium (apparently $C_{12}H_{22}O_{11} \cdot 3CaO$) together with smaller quantities of the mono- and dibasic saccharate. The reaction must be conducted at low temperatures—preferably at 10° C. or less. The insoluble tribasic saccharate (cold cake) is removed by filtration and the mother liquor which contains soluble mono- and dibasic saccharate is heated to convert these into tribasic saccharate (hot cake). The "hot" and "cold" cakes are reduced to a creamy suspension with water and used to replace lime at the carbonation station.

At the carbonation station, CO_2 reacts with the tri-basic calcium saccharate to form calcium carbonate which is precipitated, and at the same time releases the sucrose which goes into solution and is passed through the process with the fresh beet juices.

REFINING

The raw cane sugar is subjected to further refining operations before it is ready for consumption. This usually involves a further purification by defecation and adsorption of impurities followed by recrystallization.

In 1730 a sugar refinery was operating in New York City, and so sugar refining can justly claim to be one of the oldest manufacturing industries in this country.

Early methods of refining were crude, and the product would hardly pass for a refined product today. As late as 1790, 200 pounds of raw sugar were required to make 100 pounds of refined at a refining cost of 10¢ a pound. Both the raw sugar process and the refining process have been improved. Today, 107 pounds of raw sugar will provide 100 pounds of refined of far better quality, at a refining cost of less than 1¢ a pound. Many technical developments have contributed toward reaching this end; including centrifugals, vacuum pans, and granulators. These had to undergo a testing and waiting period before being generally adopted, and it was not until the Civil War Period that modern sugar refining can be considered to have really begun.

The subsequent growth occurred during a period in which every governmental encouragement was given to the development of the domestic industry. Refined sugar carried a higher import duty than raw sugar, a policy that had prevailed since 1790, and which was continued until comparatively recent years. During the period of active growth, most sugar refineries located in continental cities, but the tariff was not the sole factor that caused refineries to be built on the continent rather than in the tropics where most raw sugar was produced. Refineries employing bonechar require a high type of skilled labor, plenty of water, cheap fuel, and also a large capital investment. These are not always available in the regions where sugar cane is grown. Transportation was also a factor in the choice of a location and most refineries were built in seaboard cities where they had the advantage of access to ocean, rail and canal transportation.

Sugar Refining Practice—Modern sugar refining involves a number of stages:

1. Affination.
2. Melting.
3. Defecation.
4. Purification, with bonechar or active carbon.
5. Filtration.
6. Crystallization.
7. Centrifuging.
8. Finishing.

Affination—Raw sugar imported into the United States is usually 96°, that is, 96% sugar. Most of the impurities are contained in the thin film of molasses surrounding each crystal, and the first step, the affination, removes most of this film. To do this, the raw sugar is mingled with a syrup which softens and dissolves the molasses film without, at the same time, eroding the sugar crystals. This selective solvent power is due to the fact that the syrup is saturated with respect to the sugar, but has considerable solvent power for the impurities, or non-sugars. The mingled mass is then centrifuged, and the liquor is spun off, after which a small amount of water is sprayed on the crystals in the centrifuge to wash off most of the remaining film.

Melting—After washing the crystals have a purity of about 99°, and are dissolved (melted) in water to form about a 60% sugar solution. This liquor is treated to remove more impurities. The first step in removal of impurities is called defecation.

Defecation—In one method, sufficient lime is added to make the solution alkaline, and the alkalinity is then neutralized with mono calcium phosphate or phosphoric acid. The precipitated calcium phosphate adsorbs much of the impurity. A more general method today is to add sufficient lime to neutralize any acidity, and then add diatomaceous earth to adsorb much of the colloidal material. After this, the mixture is pumped through a leaf filter press, and the filtered syrup is ready for treatment with bonechar or active carbon.

Treatment with Bonechar—Bonechar, in granular form, is utilized in most continental American refineries. The composition of bonechar is approximately as follows:

Carbon	10%
Tricalcium Phosphate	83%
Calcium Carbonate	4%
Iron, Calcium Sulfide, Nitrogen and Silicates	Traces

The bonechar is placed in char filters which are large cylindrical iron cisterns about 10 ft. in diameter and 20 ft. in height. The filtered liquor, heated to about 70° C., is allowed to circulate through these cisterns. While the purpose of the bonechar treatment is, primarily, to remove color, other organic and considerable inorganic constituents are also removed from the raw sugar solution. The efficiency of the char falls off rather gradually, and the exhaustion is indicated by an increasing color in the filtrate. When, in the judgment of the operator, the char filter, for all practical purposes, is exhausted, the flow of liquor is stopped, and hot water is allowed to flow slowly through the filter to displace the sugar. The early portions of the wash water contain considerable sugar, and are concentrated for return to the process. In order to prepare the char properly for revivification it is necessary to continue the washing of the char after the concentration of sugar in the exit water falls below a point where evaporation is profitable, so the final washings must be run to waste.

The thoroughly washed char is dried, and heated at a dull red heat in retorts. This process, known as revivification, burns off any remaining adsorbed organic impurities, and restores the char to practically as good condition as before use. By revivifying after each use, the char can be reused many times. A certain amount of char is lost by dusting, and is replaced by the addition of virgin char.

In addition to the filtered washed sugar liquor, other intermediate liquors from the process are also purified by percolation through bonechar filters, and the liquors flowing from the char are separated into grades according to their color and test. Bonechar refineries produce many grades of sugar to meet the needs of different consumers, and the treatment of the various liquors in the char house must be modified according to the type of sugar that is to be produced. It is apparent that the operation of the char station is one that requires skill and thorough control. Judgment born of experience is needed to avoid excessive cost on the one hand, and an inferior product on the other.

Use of Active Carbon—During the past two decades there has been considerable growth in the use of active carbon for sugar refining. Active carbon is a more powerful decolorizer than bonechar, and much smaller quantities are required to decolorize the sugar solution properly. This reduces the quantity of water required for washing the char, and of fuel for revivification. Active carbon is more generally employed for producing a refined granulated sugar only, and in the regions where raw sugar is manufactured. Where active carbon is used, from 0.25 to 2.0 per cent is thoroughly mixed with the melted washed sugar, and after a short contact time the syrup is filtered, and is ready for crystallization by the conventional process. The spent carbon is washed with water, and since only small amounts are required, this can be utilized for dissolving fresh batches of raw sugar. When the refining plant has a large capacity, the washed spent carbon is reactivated by burning. In the case of smaller plants, the active carbon is employed in a two-stage countercurrent system after which the carbon is discarded.

Boiling and Finishing—The decolorized sugar liquors are crystallized in vacuum pans. The conditions under which the boiling is conducted will vary according to the type of sugar to be produced. Hard or granulated sugars are boiled at a higher temperature than are the soft or brown sugars. After the first crop of crystals is produced, the mother liquor is reboiled with fresh liquor to produce another strike of refined sugar, and this operation can be repeated as many times as the color will permit. The subsequent course of the liquor through the plant can best be followed from the flow sheet (shown in Figure 12). The final molasses is sold as filtered refiners' syrup for baking and table use when of good quality, but inferior qualities are disposed of as ordinary blackstrap molasses.

Grades of Sugar—Even though the refining industry is restricted in growth by the constantly overhanging problem of over-production, nevertheless it has followed a very progressive policy on quality standards. In recent years important developments have been made in the form in which sugar has been made available to the consumer. In addition to the standard granulated, cube, and the

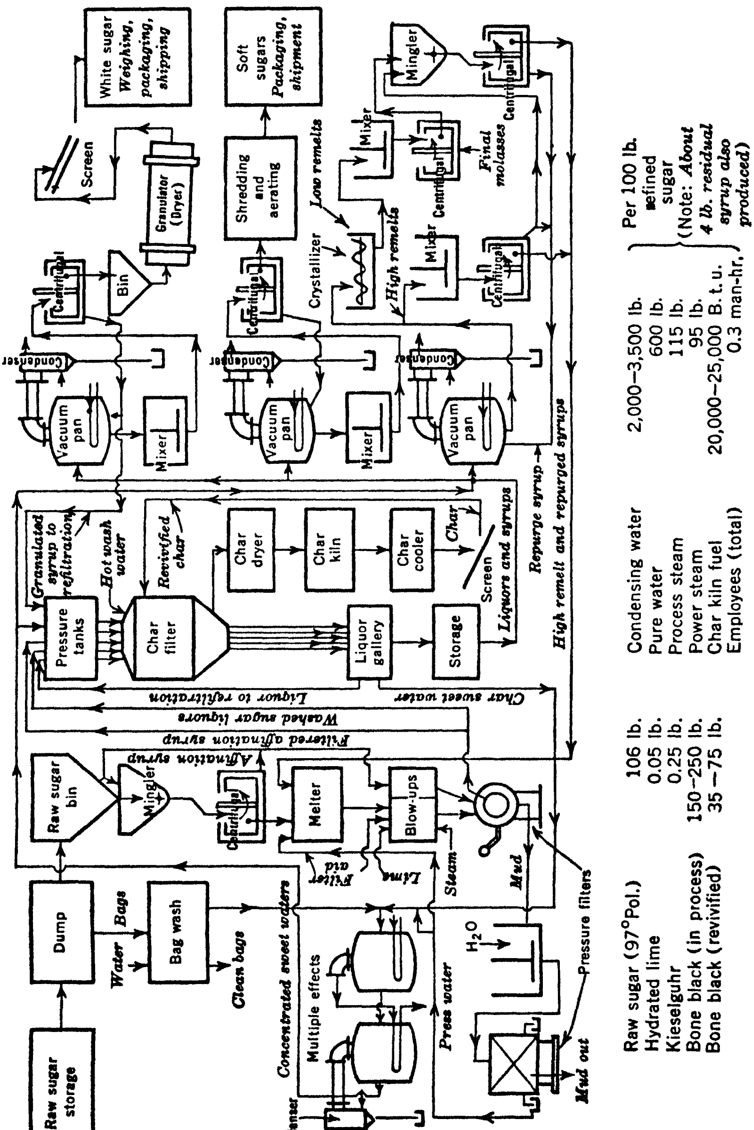


FIG. 12. Flow Sheet of Cane Sugar Refining. ("Chemical and Met. Flow Sheets of Process Industries," 2nd ed., McGraw-Hill Book Co.)

12 or more grades of soft or brown sugar, many new forms have been developed. For example, one recent form is designed for rapid dissolving, and another type, made for fruit and vegetable canners, is carefully freed from thermophilic bacteria. All special sugars, and indeed, all of the regular grades of sugar are

marketed by the refiner under the brand name, and this has served to maintain high standards of quality.

Liquid sugar is another recent development. To produce this the raw sugar is melted and decolorized in the usual manner, and the syrup is then concen-

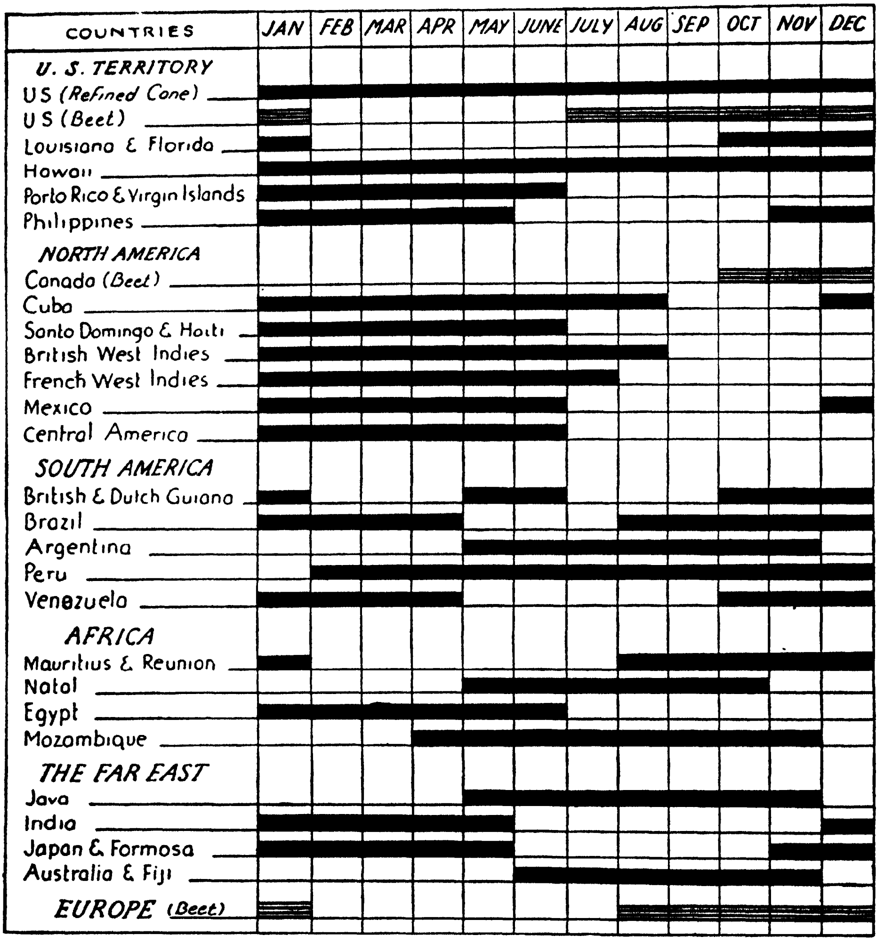


FIG. 13. Distribution of Sugar "Campaigns." (Sugar Reference Book and Directory (1939). Russell Palmer, Hoboken, N. J.)

trated to the desired consistency. This provides an economic product for certain industries such as ice cream and confectionery manufacturing since the cost of crystallizing, drying and bagging has been eliminated.

MISCELLANEOUS FACTORS IN OPERATION

Refineries converting raw sugar into the refined grades, utilize a raw material which, when dry, can be safely stored for a considerable period of time. This permits the refinery to operate over the entire year. On the other hand, factories producing raw sugar from the cane or sugar from beets, utilize a perishable raw material which must be processed when harvested. As a result, these factories operate only for a short portion of each year known as a "campaign," and during the rest of the year must remain idle. (See Figure 13.) The year's return on the capital investment must be obtained during this short period, and necessitates very efficient operation. This is not always an easy task, since only a skeleton labor force can be maintained during the "off" season, and much of the labor must be hurriedly trained after the campaign has started. It is imperative to have continuous operation once the campaign has started because the process deals with a perishable material that rapidly deteriorates during any interruption.

Sugar Losses—There are many points in the factory process where sugar can be lost, and it is important to watch each stage of the process carefully. However, there are economic limits to the technical efficiency of each stage and a broad point of view is required. Thus, it would be possible to recover more sugar from beets by the use of more diffusion water, but the cost of evaporating this extra water finally reaches a point where it is greater than the value of the extra pounds of sugar recovered. Similarly, in clarification, there are chemicals which have been reported to give better clarification than lime, but most of these have never received more than laboratory consideration since their cost would outweigh the additional benefits to be realized from their use. It is apparent that considerable thought should be given to determining yardsticks of the most profitable efficiency at each stage of the process. Such yardsticks will, of necessity, vary accordingly to the local setup, and should be flexible to meet changing conditions.

Steam and Power Production—Since the manufacture of sugar requires considerable power as well as large quantities of process steam, it is general practice to develop the steam at a sufficiently high temperature and pressure to take off the necessary power, and then utilize the exhaust steam for process work. For many years it has been recognized that the exhaust steam should be available at as few places as possible from which it can be piped to the various points of processing, and this has resulted in a concentration of power units, with a trend toward electrification. By careful planning of the flow of heat through the process it is possible to recover much of the available heat obtained from the fuel. The intermittent use of considerable quantities of steam by the vacuum pans is the largest single factor in preventing more effective use of steam.

FUEL

In most cane factories bagasse is the chief source of fuel. Bagasse, when dry, is equivalent to wood in fuel value, but since it ordinarily contains about 50% moisture, the actual fuel value is considerably less. The burning of bagasse requires a special type of furnace. The economy at which steam is produced from bagasse depends on the moisture content, type of cane, and the design, and operation of the boiler.[13] It is possible to obtain all the fuel requirements from the bagasse, and efficient operation in some cases permits the

[13] Tromp, L. A., Intern. Sugar J. 42, 59-63, 90-93, 135-137 (1940). A. F. Shillington, Intern. Sugar J. 41, 258-261 (1939).

accumulation of a surplus. In some cases where bagasse is used for making wall board,[14] it is more profitable to utilize it for this manufacture and use other fuels.

In the beet sugar industry coal, oil or gas is employed, depending on which is available at the lowest cost. The quantity of fuel required depends on the efficiency of the boiler and upon the effective re-use of the steam. It was formerly considered that fuel equivalent to eight to ten thousand B.T.U.'s was required to produce one pound of refined beet sugar, but recently beet sugar has been produced with less than six thousand B.T.U.'s per pound.[15] The condensed water from the evaporators is used in the boilers and for process work. In addition some fresh water is also required—the amount of which depends on the local setup.

Where the carbonation process is employed for clarification, the factory requires a lime kiln to furnish lime and CO_2. Sulfur dioxide is usually obtained by burning sulfur, although a few factories find that better control is obtained by using liquid sulfur dioxide.

ECONOMIC ASPECTS

Sugar's rise within the past century to the position of one of the world's great staple food crops is graphically illustrated by Figure 14. "A significant feature is the tremendous expansion of the past fifty years, halted only temporarily by the world war. In the earlier years some sugar produced in small local mills for neighborhood use probably did not figure in statistics of production and consumption. Until 1898-99 the product of India, rising to 2,000,000 tons yearly, did not appear in statistical compilations. Even with these qualifications, it is clear that sugar has experienced a tremendous growth, responsive to the accelerating movement toward world industrialization. As standards of living rise and population collects in urban groups, the demand for sugar and for sugar-containing foodstuffs constantly expands."

Competition Between Cane and Beet Sugar—The economic and technical history of the sugar industry is interwoven with the competitive struggle of the beet and cane sugar producers to maintain a position in the world markets. The cane industry had the advantage of cheap labor, a favorable climate, and an agricultural product particularly adapted for sugar production. On the other hand, the beet industry was fortified by a high level of scientific research and technical achievement in nations where the national will demanded self-sufficiency in this important food.

Therefore, the relative merits of these two sources of sugar cannot be evaluated on a simple cost of production basis, and any discussion of such relative merit is outside the scope of a technical text. However, a brief review of the history of this competition can be of value since the competition between the two groups led to many technical developments, and has been largely responsible for the reduction in the cost of producing sugar which today is less than one-third the cost in 1840.

[14] See Chapter 37.
[15] Shafor, R. W., Chem. & Met. Eng. 47, 464-7 (1940).

Beet Sugar Development—The impetus provided by Napoleon's beet sugar bounty ended with his final defeat, and beet sugar production had a feeble growth for many years thereafter. Shortly after the middle of the 19th century, the German Government, which had levied a tariff on imported sugar to protect the domestic beet industry, decided to take a more direct step. A tax was levied on beets based on the weight of the roots, and since high and low quality beets paid the same rate, this amounted to a higher tax on sugar produced from low grade

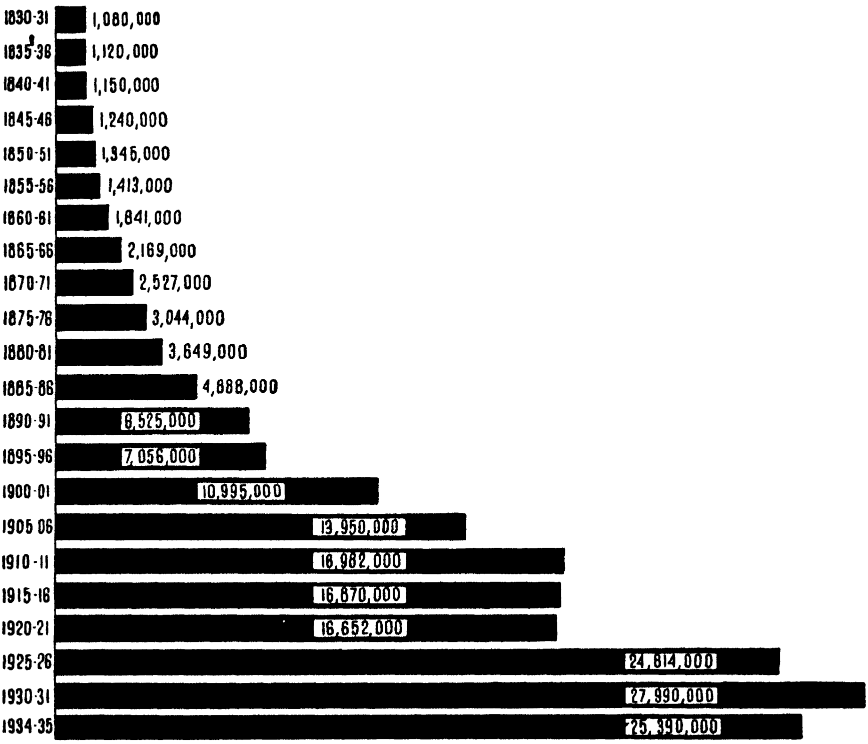


Fig. 14. World Sugar Production over a Century, in Tons. (Sugar Reference Book and Directory (1939). Russell Palmer, Hoboken, N. J.)

beets. This stimulated research and soon resulted in increasing the average sugar content in beets from 6% to 11%. The venture was so successful that it was copied in other countries, and soon continental European production exceeded the domestic consumption. In order to market this surplus, bounties were paid on exported beet sugar, and by the close of the century beet sugar represented 67% of the world consumption. By then beet sugar dumped on the world market was being sold so far below the cost of production that the very existence of the cane sugar industry was threatened.

Results of Competition—Had all the cane-producing countries been independent nations, it is entirely possible that the cane industry would have disappeared, save in exceptionally favored regions. But many sections of the British Empire were among the cane-raising regions that were threatened with this disaster, and since the British Empire was a cardinal factor in sugar consumption, it was in a position to do something about it. Steps were taken which culminated in an international conference held at Brussels in 1902, and resulted in an agreement to restrict the payment of bounties on exports and thereby restored the competitive position of the cane industry.

Since the Brussels Convention, beet sugar production has continued to increase although at a slower pace, the only exception being during the World War period of 1914-1918 when European beet fields became battlefields, and beet sugar production fell to low levels from which it has since recovered.

The fall in beet production during the World War provided a great stimulus to the cane industry which soon reached the position of producing two-thirds of the world's sugar. This great expansion of the cane industry, together with the subsequent recovery of the beet industry, has led to a condition of constant over-production ever since. The trend in beet sugar production in the United States is shown in Table 3. Numerous efforts have been made to solve the

TABLE 3—U. S. BEET SUGAR PRODUCTION, 1895–1938 *

(Tons of 2,000 Pounds)

1895	32,726
1900	86,082
1905	312,921
1910	510,172
1915	874,220
1920	1,089,021
1925	899,944
1930	1,207,318
1935	1,178,934
1938	1,685,833

* Sugar Reference Book & Directory, 8th edition, page 44. Published by Russell Palmer (1939).

problem by international agreement, the latest being that in 1937. In general these agreements restrict the total quantity of sugar that can be produced for export, and each of the sugar-exporting nations is allotted a definite quota of the free export market.

Quota Control—Until comparatively recent times, the United States sugar problem was relatively simple, as it involved only the problem of adequate tariff protection for the refiner and for the Louisiana planter. Since the turn of the century, many tropical cane-raising lands have entered the domain of the United States or within its protection, and the same period has witnessed the development of the continental beet sugar industry. The net result has been an oversupply of sugar, and has led the United States into the world-wide problem of a perpetual sugar surplus. Governmental quotas are now established for different producers within the United States and its territories, the Philippine Islands, and also for Cuba. Since the producers represent different geographical and economic divisions, it is not an easy task to provide equitable allotments. The quota allotments of the principal producing groups are shown in Table 4.

The domestic quota system, although a means of raising prices, has not solved a depressed price situation, and this is a condition that the sugar producers must probably continue to face. This is because the central authority has a responsibility to the consumer to provide an adequate supply. Since sugar production is subject to all the uncertainties that surround any agricultural product, the central authority will make the consumers' position safe by establishing a basis for the quotas that is larger than the visible demand. Even normal crops will thus result in a surplus and, although that surplus is less than under an unregulated system, experience has shown that a definitely established surplus, however small, is sufficient to depress the price.

TABLE 4—OUTLINE OF MAIN CHANNELS OF DISTRIBUTION THROUGH WHICH SUGAR FLOWS FROM THE PRIMARY PRODUCERS TO THE CONSUMER

(Estimates at Beginning of 1939) *

Sugar group	*The sugar in finished form ready for consumption to be furnished by* tons, refined value	*The quantities in terms of quota regulations* tons, raw value	*The sugar in raw form for refining to be furnished by*	tons, raw value
Mainland cane sugar refiners	4,220,000	4,470,000	Louisiana and Florida	320,000
			Hawaii	920,000
			Puerto Rico	680,000
			Philippines	920,000
			Cuba	1,560,000
			Others	70,000
U. S. beet sugar manufacturers	1,470,000	1,570,000		
Louisiana and Florida manufacturers	90,000	100,000		
Offshore and foreign refiners and manufacturers (Hawaii, Puerto Rico, Philippines, and Cuba and other foreign)	580,000	620,000		
Total	6,360,000	6,760,000		

* Lynsky, M., Sugar Economics, Statistics & Documents, supplementary volume, page 308. Published by the United States Cane Sugar Refiners Association (1939).

Incentive to Efficient Operation—The individual producer can take some measures to meet the sugar situation of today, and other measures can be taken by the industry as a whole. Since the quota places a limit on individual output, it is no longer possible to reduce cost by an expansion of the plant production. However, there are no restrictions on inventions and efficiency. Thus, there is additional incentive to improve the equipment and the operation so as to produce the quota in the shortest possible time, and at the minimum operating cost per day.

Careful control of all details of operation becomes of great importance, for this affects not only the quality of sugar, but also the yield. In this, the use of many of the control instruments now available is of great value. Instruments for recording and controlling pH, temperature, flow of liquids or steam, are desirable even where it may not be practical to modernize in other ways.[16] The

[16] For a discussion of the principles of instrumentation, see Chapter 5.

savings resulting from more accurate control following installation of carbon dioxide recorders on the steam boilers in a cane factory has sometimes been found to convert a shortage of bagasse into a surplus. Attention to minor details of operation in the beet industry between 1917-1935 resulted in cutting in half the man-hours of labor required per ton of sugar.[17]

The indirect placing of limits on new construction by the quota system may in turn provide a stimulus for modernization of many of the older plants. The equipment in some of the older plants will represent all stages of technical development, ranging from units that are very obsolete, up to recently installed equipment of the most modern types.

The savings to be effected by the installation of new equipment must be balanced against the remaining useful life of the older equipment and from an economic angle, it is possible to have too much modernization as well as too little. Moreover, for one reason or another, many factories have difficulty in raising funds to defray any extensive modernization program. Therefore, the modernization of each plant must be treated as an individual problem, and new equipment must be selected, not only on a basis of individual efficiency, but also on how well it will fit into the general arrangement of the older units that are retained.

BY-PRODUCTS

A more profitable utilization of by-products warrants consideration.

Molasses—Molasses is extensively used for cattle feed although it has the limitation of providing only the carbohydrate ration. Now that a high protein yeast can be made from molasses and inorganic nitrogen salts, molasses can also serve as a basis of the protein portion of cattle feed.

Much industrial alcohol[18] is produced from molasses, but except where governmental policy in various countries requires the utilization of ethyl alcohol in motor fuel, such an outlet will adsorb only a small part of the world's production of molasses.

In many regions molasses actually constitutes a disposal problem which is indicated by the fact that efforts have been made to use it as a road binder, and as a fuel.

Much study is given to the recovery of the sucrose that is left in the molasses, and another line of approach is to regard molasses as a potential source of other products. It has been suggested that the present status of molasses is somewhat similar to that of coal tar in former years. Already methods and processes have been developed whereby molasses is converted into valuable products; most of these processes being based on some form of biological action. Among the products so far produced on a commercial or semi-commercial scale are: amino-acids, acetone, butyl alcohol, acetic acid, butyric acid, lactic acid, citric acid, glycerine. Incidentally, the process of producing citric acid from molasses has placed the United States in a position where it can become independent of foreign imports of this commodity.

[17] Adamson, R. K., and West, M. E., Productivity and Employment in Selected Industries, Works Progress Administration, Phila. (1938).
[18] See Chapter 30.

Utilization of Bagasse—About 28,000,000 tons of bagasse are produced each year.[19] Although most of this is utilized as fuel in the sugar factories, it constitutes a potential source of other products including wall board, plastics, and paper pulp. Of these only wall board is at present produced to any extent, 100,000 tons annually.[19] There are economic obstacles to any great expansion of such uses of bagasse, since it must be sold at a higher price than the cost of imported fuel, and fuel cost is high in many sugar cane regions. Although more effective combustion of bagasse and more efficient use of steam often result in creating a surplus of bagasse over fuel requirements, even then certain other difficulties still remain. The capital, fuel and water necessary for converting bagasse into other products are often lacking in the regions where the cane is grown, and since bagasse is bulky, and subject to certain fire hazards, this presents certain difficulties in the transportation of bagasse to industrial centers at any distance. It has been suggested that a widespread adoption of pre-fabricated houses would result in greater demand for wall board, and lead to steps that would overcome some of the apparent difficulties that have been mentioned. This would be another case of the economic impact of one industry upon another.

TABLE 5—INDUSTRIAL CONSUMPTION OF BEET AND CANE SUGAR (1937) *

Industry	*Beet and Cane Combined*		
	Quantity *1,000 Tons Refined*	*Share of Usage* *%*	*Value* *1,000 Dollars*
Beverages	164	8.6	16,130
Bread and bakery products	536	28.0	52,892
Canning and preserving	314	16.4	29,439
Chewing gum	30	1.6	2,824
Chocolate and cocoa products	126	6.6	11,636
Confectionery	386	20.2	36,646
Dairy products	71	3.7	6,922
Flavoring extracts and sirups	167	8.7	16,563
Food products not elsewhere classified	97	5.1	9,117
Tobacco industries	20	1.0	1,650
Other industries	2	.1	155
	1,913	100.0	183,974

* Does not include sugar in molasses used in fermentations to produce industrial solvents.

Lynsky, M., Sugar Economics, Statistics & Documents, supplementary volume, page 311. Published by the United States Cane Sugar Refiners Association (1939).

Conversion of Sugar to Other Products—Sugar represents practically a chemically pure product available at low cost, and it is natural to find that serious study has been given to the development of processes to convert sugar into other products by chemical methods.[20] Various of these efforts have been fruitful although many of the processes that have been developed have not yet reached the commercial stage.

The various conversions that have been considered for molasses can also generally be used for sugar, but it is naturally doubtful whether any extensive

[19] Gastrock, E. A., and Lynch, D. F. J., Facts about Sugar, *34*, No. 6, pages 37-39 (1939).

[20] Cox, G. J., and Metschl, J., Ind. & Eng. Chem., News Edition 10: No. 11, 149 (1932). Cox, G. J., and Dodds, M. L., Ind. & Eng. Chem. *25*, 967 (1933).

development along this line can take place until far greater use has been made of the potential supply of molasses for such purposes. Even so, some semi-commercial undertakings combine the manufacture of sugar with the production of ethyl alcohol, butyl alcohol, acetone, etc., by fermentation.[21] This is done in a rather novel combination. Mention already has been made that the juice from the crusher and the first grinding mill is more readily manufactured into sugar, as compared to the juice from the latter mills which has less purity. Therefore, the juice from the first one or two mills and the crusher are used for sugar production, and the juice from the latter mills is employed in the fermentation process.

Many of the developments that have been suggested for converting sugar or sugar juices into other products could benefit the individual concern developing the process, but it is seen from Table 5 that, at present, the utilization of sugar for miscellaneous non-food uses amounts to less than 0.1% of the total production. Therefore, any development that would make an impression of the potential over-production of sugar would have to be projected on a far larger scale than anything that has so far been considered.

POSSIBILITY OF INCREASED CONSUMPTION

There remains the possibility of developing the consumption of sugar as food. It is interesting to compare the per capita consumption of the various countries—Table 6. It is apparent that the world per capita consumption, 30 lbs. per year,

TABLE 6—RETAIL PRICE OF SUGAR AND CONSUMPTION IN 10 COUNTRIES (1937-8) *

Country	*Price 1938*	*Consumption per Capita 1937-8*
	cents per pound	*pounds refined value*
United Kingdom	4.7	111.6
United States	5.3	96.5
Canada	5.9	103.0
Australia	6.6	116.8
Norway	7.2	73.9
Irish Free State	6.8	90.6
France	7.2	54.7
Netherlands	12.2	64.4
Germany	13.7	59.1
Italy	15.7	20.1

* Lynsky, M., Sugar Economics, Statistics & Documents, supplementary volume, page 306. Published by United States Cane Sugar Refiners Association (1939).

is greatly below that of nations such as Great Britain and the United States. Moreover, even in nations such as the United States, the per capita consumption is the statistical average composed of high and low groups. Any increase by the low consumption groups within the United States would make a big difference in the domestic sugar situation, and would take care of a considerable portion of the surplus problem. Other countries have tried methods of doing this. In South Africa an effort to increase consumption has been carried out by placing

[21] See Chapter 30.

a low grade of sugar at a price within the range of a large native population, but the price is not so low that it will tempt the well-to-do away from the use of refined sugar. In some countries a special low price is placed on sugar to be used for the canning of fruits, and this has stimulated both the fruit-canning industry and the consumption of sugar.

Fortunately, any propaganda to increase sugar consumption need not be based on the necessity for aiding a struggling sugar industry, but on data that enters into the economic life of the individual and of the nation. Based on food energy content or caloric value, sugar represents one of the cheapest forms of food. Of course, it is to be kept in mind that carbohydrates represent only one item of diet, and it cannot be expected that sugar could or should constitute the entire carbohydrate portion.

INCREASING YIELDS

From a national point of view, it is coming to be realized that sugar, whether beet or cane, will give a greater yield of carbohydrates per acre than practically any other agricultural product, a fact which is illustrated in Table 7. This is coming to be so well recognized, that in some countries where cultivated land is at a premium, governmental efforts are made to increase the consumption of sugar. In a few nations this has gone as far as to cause the state to authorize the re-writing of cook books [22] to include a greater percentage of sugar in the recipes.

TABLE 7—FOOD-PRODUCING CAPACITY OF VARIOUS AGRICULTURAL PRODUCTS

	Million Calories per Hectare *
Sugar Beets	16.5
Potatoes	9.0
Garden Beets	4.9
Wheat	4.5
Rye	4.5
Beans	4.0

* 1 hectare equals 2.471 acres.
Taken from Barten's "Deutsche Zuckerindustrie," *61* (No. 51), 1179 (1936).

While the present average yields of sugar cane and sugar beet are sufficient to place them as a most productive agricultural product, even so—these yields are considerably below what can be reached. It is now known that the net crop yield of an agricultural plant is related to the quantity of combined nitrogen in the dry substance of that plant. The potential yield is greater in plant life that has little combined nitrogen. O. W. Willcox,[23] proponent of this "Quantity of Life" theory, has developed a formula whereby probable maximum crop yields can be calculated. Some varieties of cane are theoretically capable of producing more than 200 tons of cane per acre, and in the case of the beets, about 53 tons.[24] At times these figures have been closely approached in actual

[22] Barten, "Deutsche Zuckerindustrie," *61*, 1179 (1936).
[23] Willcox, O. W., "ABC of Agrobiology," W. W. Norton Co., New York (1937).
[24] On a unit of time basis, the sugar beet is not necessarily inferior to the sugar cane since the time required for the record yields of sugar cane covers a growing-period of 20 to 24 months, whereas, a beet crop generally requires 10 months or less, to reach maturity.

cultivation. Certain plantations occasionally have yielded close to 200 tons of cane. The "record" yield of California beets now stands at 45 tons of roots containing 16,000 lbs. (8 tons) of sugar to the acre.[25]

Since the possibility of achieving these yields depends on proper fertilization and on an abundant supply of water, this new knowledge may have an important effect in determining the future of where sugar cane or beets should be raised. As O. W. Willcox has pointed out, whether a land is "arid" or "humid" for the purpose of growing a crop, depends on economic conditions as well as it does upon the annual inches of rainfall. The average crop in the United States has been around 11 tons per acre, and any land that has sufficient moisture to produce a crop of this size would be economically profitable for such use. However, if there is any extensive development of the strains of beet that are capable of producing up to 50 tons per acre, then much of the land that is now capable of producing an 11-ton crop will not have sufficient moisture to produce a 50-ton crop, and because of competition it might not be profitable to use such land for raising beets. Thus, the land which might contain sufficient moisture to be economically profitable under the present average conditions of the 11-ton crop may not be sufficiently humid to produce a 50-ton crop, and because of the resulting economic pressure would cease to be considered sufficiently humid for the production of sugar beets.

The sugar industry during the last century has made tremendous strides in bringing a pure commodity within the price range of all the people. The existing productive capacity appears adequate to take care of any visible increase in the consumption of sugar as a food. Because of this we can hardly expect any sizable expansion of the industry. Since expansion is improbable, this gives added impetus to the improvement of the existing processes. Although no basically different method of processing appears on the horizon, improvements in the art and science of sugar-making are constantly being made, and the cumulative effect of many small changes can in a relatively brief period of time accomplish a striking improvement.

There is a definite trend toward continuous operation, and much study is being given to the possibility of converting steps which are now handled as a batch or intermittent manner into continuous operation.

Although the sugar market appears stabilized, this picture could be completely changed if some large-scale non-food use could be developed for sugar. In 1906, a syndicate of French refiners offered 100,000 francs to anyone who could develop uses of sugar for non-food purposes that would consume 100,000 tons of sugar annually. So far this prize appears to be unclaimed. However, this reward is small in comparison with the total reward that would accrue to the individual or organization who could develop extensive non-food uses for sugar.

[25] Willcox, O. W., Communication, Jan. 1941.

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READING LIST

AGRICULTURE

Willcox, O. W., "ABC of Agrobiology," W. W. Norton & Co., New York (1937).
"Year Books of Agriculture." U. S. Dept. of Agriculture.

BEET SUGAR

Murke, F., "Manufacture of Beet Sugar," John Wiley & Sons, New York (1921).

CANE SUGAR

Davies, J. G., "Principles of Cane Sugar Manufacture," Norman Rodgers, London (1938).
Deer, Noel, "Cane Sugar," Norman Rodgers, London (1921).
Geerligs, H. C. Prinsen, "Cane Sugar—Its Manufacture," Norman Rodgers, London (1924).
Spencer-Meade, "Cane Sugar Handbook," 7th Ed., John Wiley & Sons, New York (1929).
Tromp, L. A., "Machinery & Equipment of Cane Sugar Factory," Norman Rodgers, London (1938).
Webre, A. L., "Massecuite, Molasses & Sugar," published by United States Pipe & Foundry Co., Burlington, N. J. (1930).

ECONOMICS AND STATISTICS

Geerligs, H. C. Prinsen & Geerligs, R. J. Prinsen, "Cane Sugar Production, 1912-1937," Norman Rodgers, London (1938).
Lynsky, M., "Sugar Economics, Statistics & Documents," U. S. Cane Sugar Refiners Assoc. (1938), suppl. 1939.
"Manual of Sugar Companies," Farr & Co., New York (1940).
"Sugar Reference Book and Directory," published annually by Russell Palmer Co., Hoboken, N. J.

ANALYSIS

Browne, C. A., "Handbook of Sugar Analysis."

PERIODICALS

"Sugar and Facts About Sugar." Hoboken, N. J.
"International Sugar Journal." London, England.
Statistical data are available from Willett & Gray, N. Y.

AGRICULTURE OF CANE AND BEET

Brandes, E. W. & Coons, G. H., "Beet Crop Problems." Facts About Sugar, *29*, No. 3, 83-85; No. 4, 117-21 (1934).

Balch, R. T. & Lauritzen, J. I., "Windrowing Qualities of CO-281 and Other Canes in La." U. S. Dept. of Agr. Circular No. 304 (1933).

Denley, C. L., "Windrowing Cane for the Mill." Before International Soc. of Sugar Cane Technologists, Baton Rouge, 1938: Paper No. 51.

Owen, F. V. and others, "Curly-Top Resistant Beet Varieties in 1938." U. S. Dept. of Agr. Circular No. 513, Jan., 1939: 9 pages.

Robbins, W. W. & Price, C., "Sugar Beet Production in California." Calif. Agricultural Extension Circ. No. 95 (1936).

Wright, K. T., et al. "Cost of Producing Sugar Beets in Michigan." Proceedings American Soc. Sugar Beet Technologists, Eastern Division, Detroit, 1939: 69-79.

MECHANIZATION OF CANE AND BEET AGRICULTURE

Anon., "Mechanical Harvesters in La." Facts About Sugar, *35*, No. 4, 24-27 (1940).

Buschlen, M. J., "Beet Crop Mechanization: Its Problems and Possibilities." Facts About Sugar, *33*, No. 4, 27-31 (1938).

Cook, H. A., "From Evolution to Revolution in Sugar Growing and Manufacturing." Reports Assoc. Hawaiian Sugar Technologists, *16*, 59-62 (1937).

Hawaiian Sugar Planters Assoc., "Report on Labor Saving Devices," Int. Sugar J., *42*, 236-239 (1940); *41*, 179-181 (1939).

Higgins, F. Hal., "Mechanization Makes Strides Toward Solving Beet Farming Problems." Facts About Sugar, *34*, No. 12, 23-27 (1939).

Mervine, E. M. & McBirney, S. W., "Developments in Mechanical Equipment and Methods in Sugar Beet Production." U. S. Dept. of Agriculture Circular No. 488: Oct. 1938: 38 pages.

MILLING

Hurter, H., "Design of Cane Mill Equipment." Annual Convention of the Association de Tecnicos Azucareros de Cuba (Dec. 1938).

Kopke, E. W., "Constantly Effective Pressure: A Problem in Milling." Facts About Sugar, *32* (No. 7), 259-262; (No. 8), 321-324; (No. 10), 409, 410, 418 (1937).

CONTINUOUS DIFFUSION

Anon., "Continuous Diffusion: Berge System." Facts About Sugar, *31*, No. 10, 373-377 (1936).

CLARIFICATION

Behne, E. R., "Clarification Tests, 1938 Season." Bureau of Sugar Experiment Stations (Queensland) Technical Communications, 1939, Nos. 1 and 2, 1 to 17.

Copp, E. M., "A Factory Test on Compound Clarification in Hawaii," Int. Sug. J., *40*, 467-469 (1938).

Davies, J. G., et al., "Fractional Liming and Double Heating in the Clarification of Cane Juice," Int. Sug. J., *38*, 298-300 (1936); *39*, 67 (1937).

Dedek, Prof. Dr. J., "Lime Salts in Beet Sugar Juices." Facts About Sugar, *34* (No. 11), 42-44; (No. 12), 38-39, 41 (1939).

Fort, C. A. & Walton, C. F. Jr., "The Effect of Clarification on Quality of Raw and Plantation White Sugars," Ind. Eng. Chem., *25*, 675-681 (1933).

Fort, C. A., "Changes in the Composition of Cane Juice Produced by Clarification." Facts About Sugar, *34*, No. 9, 34-39, 41 (1939).

Springer, H. B., "Clarification of Refractory Juices," Int. Sug. J., *40*, 189-191 (1938).

Woodcock, G. A. N., "Multifeed Dorr Clarifier," Int. Sug. J., *43*, 84-86 (1941).

CRYSTALLIZATION

Bass, H. H., "Investigations on Sugar Boiling." Proc. Queensland Soc. Sugar Technol., *5*, 59-83 (1934).

Behne, E. R., "Circulation in Calandria Vacuum Pans," Int. Sug. J., *40*, 382-84 (1938).

Copp, E. M., "The Lafeuille Rotary Vacuum Pan in Puerto Rico." Facts About Sugar, *29*, No. 11, 395-396, 399 (1934).

Committee Report, "Vacuum Pan Operations." Proc. Queensland Soc. Sugar Cane Technologists, *5*, 9-14, 23-25 (1934).

Deer, N., "Theory of Molasses Formation," Int. Sug. J., *39*, 178-181, 228-230 (1937).

Keane, J. C. and Ventre, E. K., "Pan Boiling Operations and Quality of Raw Sugar." Trans. Fourth Cong. Intern. Soc. Sugar Cane Technol. (1932).

Smith, N., "Circulation in Coil Vacuum Pans," Int. Sug. J., *40*, 101-104, 145-147 (1938).

Smith, W. E., "Vacuum Pan Control and Automatic Sugar Boiling." Facts About Sugar, *28*, No. 2, 84-89; No. 3, 127-132 (1933).

Webre, A. L., "The Rehabilitation of the Calandria Vacuum Pan." Sixth Conf. Assoc. Sugar Technologists Cuba (1932).

"Design and Use of Pan Control Instruments," Ind. Eng. Chem., *27*, 1157-1161 (1935).

"Growth of Crystals in Vacuum Pans," Int. Sug. J., *38*, 379-381 (1936).

"Temperatures in Vacuum Pans." Facts About Sugar, *31*, No. 1, 13-14 (1936).

"New Possibilities of the Two-Boiling System." Memoria XII Conferencia Anual Asociacion Tecnicos Azucareros Cuba, English Edition: 1938, pp. 171-178.

Willcox, O. W., "The Exhaustability of Molasses." Facts About Sugar, *30*, No. 10, 371-372 (1935).

PURGING

Greven, J. P., "Centrifugal Processing of White Sugar." Facts About Sugar, *32* (No. 4), 47-48 (1939).

Johnson, R. B., "High Speed Centrifugals." Facts About Sugar, *31* (No. 2), 55-59 (1936).

Stevens, G. E., "Processing Low Grade Massecuites." Facts About Sugar, *31*, No. 4, 135-137 (1936).

"Handling Third Sugars a New Way." Facts About Sugar, *34* (No. 1), 54 (1939).

REFINING

Anon., "Two Centuries of U. S. Refining." Facts About Sugar, *28* (No. 7), 269-272 (1933).

Anon., "The United States Refining Industry." Facts About Sugar, *27* (No. 8), 311-12 (1932).

Anon., "The Sugar Refining Industry in 1938." Facts About Sugar, *33* (No. 7), 38-40 (1938).

Anon., "The Work of the Domestic Cane Sugar Refining Industry." Facts About Sugar, *33* (No. 7), 32-35 (1938).

Fowler, A. P., "Sucro Blanc Process," Int. Sug. J., *39*, 384-386 (1937).

Meade, G. P., "Use of Phosphoric Acid in Cane Sugar Manufacture and Refining," Int. Sug. J., *42*, 103-105 (1940).

Ray, David T., "The American Cane Sugar Refining Industry." Facts About Sugar, *33* (No. 7), 25-31 (1938).

Wills, L. A., "Technical Progress in Cane Refining." Facts About Sugar, *33* (No. 7), 41-43 (1938).

REFINING WITH ACTIVE CARBON

Anon., "Mexico's Most Modern Sugar Plant." Facts About Sugar, *28* (No. 1), 25-41 (1933).

Anon., "Refinery Plant of the Ingenio Central Emiliano Zapata." Facts About Sugar, *33* (No. 3), (1938).

Chapin, E. E. & King, J. A., "Bonechar and Vegetable Carbon," Int. Sug. J., *41*, 427-29 (1939).

Irazoqui, J. T., "The New Sucrest Refinery." Facts About Sugar, *32* (No. 6), 225-230 (1937).

Wickenden, L. & Anderson, S. W., "Sugar Refining," Int. Sug. J., *41*, 460-462 (1939).

POWER

Coyle, A., "Utilization of Electrical Power in Sugar Mills." Proc. Queensland Soc. Sugar Cane Tech. 11 Conf., 65-69 (1940).

Dennis, E. L., "Power Problem at Reserve Refinery Solved by Superposition." Facts About Sugar, *33* (No. 11), 41-48 (1938).

Forbess, A. J. & Kloster, W. W., "Electric Power in Today's Beet Sugar Factory." Facts About Sugar, *34* (No. 1), 51-53 (1939).

Gutleben, D., "Pennsylvania Refinery's Modern Steam Plant." Facts About Sugar, *27* (No. 8), 337-341 (1932).

Jenkins, G. H., "Surplus Power from Surplus Bagasse," Int. Sug. J., *42*, 18-20 (1940).

Johnson, R. B., "Ewa Plantation's New Power Unit." Facts About Sugar, *30* (No. 4), 131-135 (1935).

O'Neill, H. & Dillard, J. M., "Sugar Land's Outdoor Steam Plant." Facts About Sugar, *33* (No. 5), 25-31 (1938).

Tromp, L. A., "Standard Heat Balance in Cane Sugar Factory," Int. Sug. J., *40*, 175-179, 224-228 (1938).

"Steam Pressure Fluctuation," Int. Sugar J., *41*, 301-304, 340-345, 418-421 (1939).

Tromp, L. A., "Partial or Total Electrification of Cane Sugar Factories," Int. Sug. J., *42*, 241-244, 277-282 (1940).

Whitaker, L. B., "Totally Electrified Sugar Factory," Int. Sug. J., *42*, 167-171, 202-206 (1940).

MODERNIZATION

Kopke, E. W., "Observations on the Sugar Industry in La." Facts About Sugar, *33* (No. 10), 46-47 (1938).

"Improved Factory Earnings Through Technical Modernization." Facts About Sugar, *34* (No. 10), 36-37 (1939).

Shafor, R. W., "Process Economy in Recent Beet Sugar Developments," Chem. & Met., *47*, 464-467 (1940).

Smith, E. C., "Machinery Maintenance in a Cane Sugar Factory," Int. Sug. J., *40*, 352-355 (1938).

Tromp, L. A., "Recent Improvements in Mechanical Engineering in the Cuban Sugar Industry," Int. Sug. J., *41*, 135-140 (1939).

DESIGN AND OPERATION OF SOME MODERN FACTORIES

Anon., "The New Woodland Sugar Factory." Facts About Sugar, *32* (No. 12), 467-470 (1937); *35* (No. 5), 23-27 (1940).

"Hardin: Montana's Newest Factory." Facts About Sugar, *33* (No. 1), 31-34 (1938).

"Mexico's New Cooperative Factory Ingenio Central Emiliano Zapata." Facts About Sugar, *33* (No. 3) (1938).

"The Iberia Sugar Cooperative Mill." Facts About Sugar, *33* (No. 10), 50-57 (1938).

"Amalgamated Sugar Company New Factory in Oregon. The Nyssa Plant." Facts About Sugar, *33* (No. 12), 25-28 (1938); *35* (No. 9), 22-26 (1940).

"Breaux Bridge: La's. Latest Cooperative Factory." Facts About Sugar, *34* (No. 1), 31-35 (1939).

Buffum, W. H., "Ledesma, A Great Argentine Factory." Facts About Sugar, *35* (No. 7), 24-27 (1940).

Ormond, A. M., "Savannah Refinery Modernizes Plant." Facts About Sugar, *31* (No. 11), 413-418 (1936).

CHAPTER 36

STARCH: ITS SOURCES, MANUFACTURE AND PRODUCTS

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HISTORICAL

The use and preparation of starch is extremely old, having been known from early times. The earliest description of its use being reported by Pliny in 130 B.C. in which he described a paste made from a white flour boiled with a weak solution of vinegar as being used in sizing papyrus. Its preparation was recorded by Marcus Porcius Cato in 184 B.C. in which he described the preparation of starch from cereal grains, the highest grades of which he reported as coming from the Island of Chios while inferior products came from Crete and Egypt.

Early in the sixteenth century laundry starch was introduced into England and according to the book of H. A. Auden, during the reign of Queen Elizabeth, tubs and other utensils necessary to the making of starch were to be seen in the most aristocratic residences of England and washing and drying of clothes was performed in the presence of nobles.

However, it was not until early in the nineteenth century that the manufacture of starch was begun in the United States. The first material used for the purpose was the potato, but with the increase of grain, production was soon also undertaken from corn. The new industry grew rapidly and soon became much more important than the potato starch industry, so that today the potato starch industry, which has declined, is now practically entirely confined to the county of Aroostook, Maine, while the production from corn comprises the major source of our supply.

OCCURRENCE AND PHYSICAL CHARACTERISTICS

Starch is a carbohydrate substance of wide occurrence in the plant kingdom formed by the action of sunlight upon green leaves in the presence of air and moisture. It is found as stored food in the tissues of the higher plants and comprises the larger part of the solids of grains and tubers. In the pure state [1] it is a white, soft, amorphous powder, density 1.6, insoluble at ordinary tem-

[1] Rolfe, G. W., "Manual of Industrial Chemistry—Rogers," 5th Edition, Vol. II, pp. 1209-1228, D. Van Nostrand Co., Inc. (1931).

perature in water, alcohol, ether or other common solvents. Under the microscope it appears as minute, white translucent grains varying greatly in size and shape but so characteristic that it is usually comparatively easy to determine its botanic origin, it[2] appearing as though the starch molecules were packed into a sack and this sack were of different shape for different starches. Thus corn starch granules[3] appear in a polyhedral form with some small cylindrical granules. The hilum, that is, the nucleus around which the granule has developed, being centrally located and star-shaped, ranges in size from 14 to 18 microns. Potato starch appears oval or egg-shaped with some small round granules, the hilum being usually at the smaller end of the granule from which concentric rings covering the granule have their beginning, and ranging in size from 15 to 100 microns. Wheat starch granules appear practically cylindrical and vary widely in size. The hilum, while centric, is rarely distinct and ranges from 20 to 40 microns in size. Tapioca appears fairly round with some granules with a flattened side while others are slightly urn-shaped or hemispherical. The hilum appears in star-shaped form or as a crack, ranging in size from 5 to 30 microns. Sago appears oval or in the shape of an Irish potato with some urn-shaped and some small practically round granules. The hilum is quite distinct and is usually observed at the rounded end of the granule, ranging in size from 10 to 60 microns. Rice is similar to corn starch only much smaller in size while the hilum, centric and not always discernible, ranges in size from 3 to 5 microns.

In general, starch granules[1] can be divided morphologically into the following groups:

1. Large oval granules showing concentric rings and a nucleus or hilum, placed eccentrically, such as the various arrowroot and potato starches, *the potato group.*
2. Round or oval granules usually showing the concentric rings and having the hilum irregular, as those from peas, beans and lentils, the so-called *leguminous starches.*
3. Round or oval granules showing hilum in center. This includes starches from wheat, barley, rye, acorns and many medicinal plants, the so-called *wheat group.*
4. Granules truncated at one end, such as sago, tapioca and cinnamon starches, the so-called *sago group.*
5. Small angular grains, often polygonal, such as maize, rice, buckwheat and pepper starches, the so-called *rice group.*

Chemically all starches are similar, their empirical composition being ($C_6H_{10}O_5$) but their physical characteristics vary with their plant sources. Their structure is quite complex and is not yet completely known but the starch granules are believed to contain at least two different substances upon which the physical behavior of the starch depends: (1) an envelope (80 per cent) of amylopection, a-amylose or a starch which is less soluble and contains a phosphoric acid ester, yields a paste and forms a violet color with iodine; (2) an

[2] Bryant, A. P., "The Candy Manufacture," Sept., pp. 44-56 (1921).
[3] Stallings, J. W., "American Dyestuff Reporter," July, pp. 251-253 (1935).

inner substance, amylose, B-amylose, granulose or B-starch which is more soluble and free of phosphorous, does not yield a paste and turns blue with iodine; and (3) a third substance, amylo-hemicelluose, found in cereal starches but not yet proven to be an actual constituent of the granule. Samec[4] has shown that the phosphorous is in combination as an amylo-phosphoric ester indicating that in the cereal starches it contains nitrogen, being a protein amylo-phosphoric ester. Non-carbohydrates found in small amounts, such as fatty acids may, as Taylor and Iddles[5] have shown, be actually esterified or possibly be due to the marked absorbent property of the granules and the particular conditions of manufacture.

When starch is acted upon by hot water, the exact temperature varying somewhat according to its nature and origin, the granules swell, burst and form a paste or thick sticky liquid varying widely in gel characteristics and viscosity. A starch paste as usually made, therefore, consists of granules in various phases, some partially swollen, some burst, some soluble material and some debris of the outer portions of the burst granules. The pastes[1] therefore as generally prepared are not homogeneous. The work of Alsberg and Taylor and Beckmann tends to show that their viscosity is more a physical than chemical characteristic, dependent on the amount and condition of swollen granules present. The knowledge and study of the physical properties and behavior of starch have accounted for many of its successfully developed methods of production and commercial utilization.

CHEMICAL CHARACTERISTICS

Much has been done on the study of the chemical structure and investigation is still proceeding vigorously. Two fundamentally different theories[6] have been advanced to explain its chemical constitution. One considers starch as built up of low-molecular units joined together by forces other than normal valencies to "micelles," the size of which accounts for the characteristics of starch; whereas according to the other theory, starch is a macromolecular substance in which the units that determine colloidal and other properties are in fact the true molecules. The first theory is today practically abandoned and most investigators agree that starch is a true macromolecular substance, the molecules of which are composed of a great number of hexoses united to chains of some sort. Haworth[7] looks upon the starch molecules as a chain of glucose molecules linked together by glucosidic bonds exclusively, while Staudinger[8] concludes that the molecules are branched chains.

According to Lintner[9] and Düll, diastatic hydrolysis, by separating the substances found in successive stages by fractional precipitation with alcohol, yields soluble starch → erythrodextrin I → achroodextrin I → achroodextrin II → isomaltose → maltose, where acid (oxalic) hydrolysis yields soluble starch → erythro-

[4] Samec, M., "Kolloidchemie der Starke," T. Steinkopff, Dresden and Leipzig (1927).
[5] Taylor, T. C., and Iddles, H. A., Ind. and Eng. Chem., *18*, 713 (1926).
[6] Myrback, Karl, Current Science, No. 2, pp. 47-50 (1937).
[7] Haworth, W. N., "The Constitution of Sugars," Arnold, London (1929).
[8] Staudinger, H., Ber. *69b*, 819 (1936).
[9] Lintner, C. J., and Düll, Ber, *26-28*, 2533-1522 (1893-1895).

dextrin I → erythrodextrin IIA → erythrodextrin IIB → achroodextrin I → achroodextrin II → ismomaltose → dextrose. Lintner's isomaltose is reported by A. R. Ling [10] to be a mixture of maltose and dihexosan.

Alkalis, salts and oxidizing agents act on starch to produce a wide range of varying type property pastes of differing gel and viscosity characteristics.

Starch forms a series of ethers and esters [11] of a wide variety of characteristics, many by fairly simple reactions. All starches regardless of source give a blue test with iodine when in the gelatinized state and the basic granular property of its structure imparts the optical property known as anisotropy. They have approximately the same density in the dry state, the same refractive indices, the same optical rotation and because of their common chemical and physical characteristics, starches obtained from different sources (plant organs or plant species) can in many instances be put to essentially the same trade and industrial uses. Being plentiful, starch is consumed in larger amount than any other basic substance and finds essential use both as a food and for industrial purposes. The amount consumed as food is about one-fourth of the total manufactured, arrowroot being the only starch still used almost entirely as food.

Many different starches [12] are used for food and industrial purposes including corn starch, tapioca, sago, arrowroot, wheat, rice, potato (Irish) and sweet potato starches. Of these the first three are the most important in volume and value. For conversion into sugar (dextrose) any starch may be used, but for certain industrial purposes only particular kinds of starch which have some distinctive and especially desired physical property are used. Because of the difference in their properties, starches are not always easily interchangeable and, as a result, for some purposes one starch cannot be readily substituted for another, while for other purposes one need only select one or another solely on the basis of its lower price.

STARCH CONSUMPTION

The United States Tariff Commission [12] reported 2,684,000,000 pounds of starch consumed in the United States in 1939 and although its consumption for all purposes amounted to about the same as in 1927 and 1929 and appreciably greater than for most of the intervening period, the production had declined while there was a marked increase in imports. Of all the domestically produced starch, about 98 per cent is corn starch, the remainder being white potato, sweet potato, rice and wheat starch; corn, rice and wheat starches being produced in the middle west, white potato starch in Maine and sweet potato starch in Mississippi and Louisiana. About two-thirds of the corn starch produced is converted into sirup, sugar and dextrine and one-third is sold in the form of starch. Imported starches comprise principally tapioca flour from the Netherlands Indies with relatively small amounts of sago, arrowroot and potato starches with an insignificant amount of wheat and rice starch.

[10] Ling, A. R., J. Inst. Brew., *44*, 419 (1938).
[11] Worden, E. C., "Technology of the Cellulose Esters," I, Part 1, Eschenbach Printing Co., Easton, Pa. (1921).
[12] United States Tariff Commission, Rep. No. 138 (1940).

The manufacture of corn starch is a typical American industry and, until relatively a few years ago, was confined entirely to this country. Production, according to the Department of Commerce, increased from 311,140,814 pounds in 1904 to 1,046,435,117 pounds in 1929, the largest output in the history of the industry. Since 1929 production has declined and in 1937 was reported as 730,859,806 pounds, although the total consumption of starch for all purposes was about the same. The decline in production was accompanied by a marked increase in imported starches, the imports of duty-free starches approximating 500,000,000 pounds. The importation of these duty-free starches still remains one of the unsolved farm problems of particular interest to corn belt agriculture.

The imports, increasing at the rate of about 10 per cent per year, produced in the tropics with coolie labor, limited capital investment and imported free of any duty, make up about one-third of the domestic starch supply. This leaves these low cost duty-free starches competing unequalized with starch produced from our own agricultural crops, although an import duty is imposed on every foreign product competitive with domestically produced corn and corn products, wheat, rice and potatoes or their starches. The United States is the "dumping ground" for the world's surplus of tapioca and sago starches. This increasing competition from these duty-free starches prevents by its restriction the efficient and effective operation of the domestic starch industry.

PROCESSES OF MANUFACTURE—GENERAL

Starch being the same regardless of the raw material source from which it is obtained is produced by physically separating it from other substances in grains or roots by essentially the same general procedures. The operations comprise mechanically breaking down the plant tissues in the presence of water and loosening the starch granules from the surrounding substances. The starch is settled out of the mixture and where it is desired as such, washed and dried, while if it is to be converted into sirup or sugar, it is used in the wet state. In general the procedures are:

1. Disintegrating the plant tissue so that the starch grains or, in the instance where the germ is to be recovered as in corn, the starch grains and germ are set free without breaking.
2. Separating the heavy starch, or as in corn the germ and hull, and further distintegrating the separated endosperm and then separating the heavy starch by settling or centrifuging.
3. Washing the starch by dilution, agitation and mechanical filtration.
4. Recovery of the starch by filtration or centrifuging.
5. Drying the starch in kilns or mechanical dryers.

The process is simplest in the manufacture of root starches as cassava or potato and more complicated when grain is the raw material, particularly where other substances as oil and gluten are recovered, as in the case of corn. Continued heating of starch with an acid entirely destroys the starch granule and changes the chemical properties of the resulting substance, the final product of the conversion being dextrose or a sirup containing dextrose. The sirupy solution of dextrose along with its other ingredients is known commercially as glucose. Dextrine is the intermediate product in the conversion of starch to dextrose.

The common names for the starch conversion products are usually taken from the name of the plant from which the starch was derived—"corn sirup," "tapioca," "dextrine," etc.

PROCESS OF MANUFACTURE OF CORN STARCH

The corn kernel[13] is comprised of five parts (see Figure 1). The hull, or thin outer skin, is fibre; next to the hull is a shallow layer of gluten, a sub-

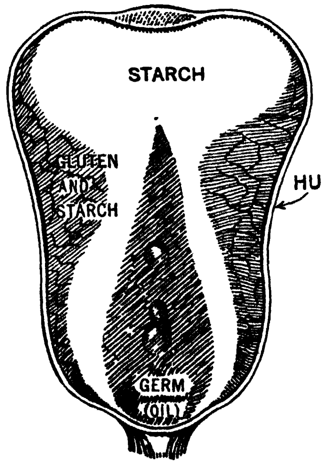

FIG. 1. Corn Kernels. (Courtesy Corn Industries Research Foundation)

stance rich in protein; on the sides and back of the kernel, inside the layer of gluten, a mixture of starch and gluten bulges in towards the center, filling the upper part of the kernel and extending downward partly to surround the germ in the white starchy part of the kernel. The germ itself is level with the flat "front" of the kernel. It contains protein, most of the oil and a large share of the minerals.

Chemically, from 15 to 20 per cent of the kernel is water and the remainder made up of:

	Per Cent
Starch (and other carbohydrates)	80.0
Protein	10.0
Oil	4.5
Fibre	3.5
Ash (mineral content)	2.0

Corn processed by the industry is principally of the Flint and Dent types purchased on the basis of their classification by established grades on a moisture

[13] Corn Industries Research Foundation, Handbook, "Corn in Industry," (1938).

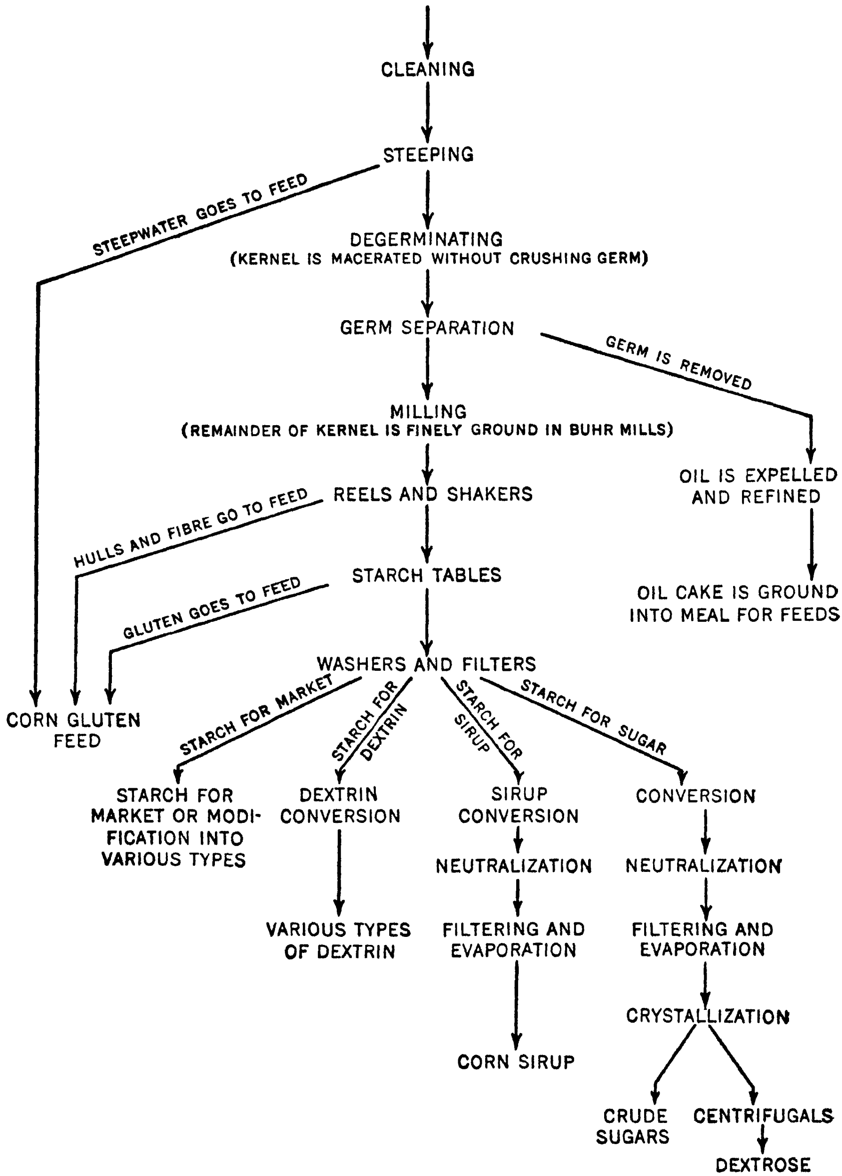

FIG. 2. Simplified Diagram of the Corn-refining Processes. (Courtesy Corn Industries Research Foundation)

and damage content basis. The dried grades 1, 2, 3, yellow, white and mixed, are deemed of greatest value because they contain a larger amount of dry substance and yield a larger amount of starch per bushel processed. The cost of corn is based on the legal weight of 56 pounds per bushel and conforms with the official grain standards of the United States.[14]

Receiving the Corn—The shelled corn is delivered to the plant in carload lots of from 1200 to 1500 bushels. It is elevated into storage bins or tanks from which machinery and equipment handle it in successive stages to the process (see Figure 2), passing first through cleaners which remove light ma-

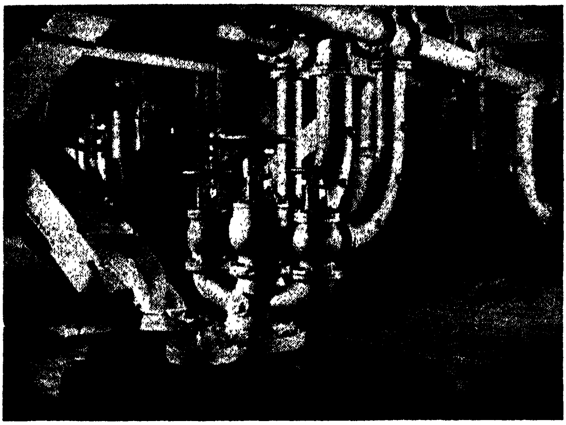

FIG. 3. Filling Modern Steep Tanks. The tanks go down through the next floor. (Courtesy Corn Industries Research Foundation)

terial by blowing it out with a strong current of air and the heavier foreign material by sifting; electro-magnets drawing out any metal particles.

Steeping—The cleaned corn then goes to large tanks (see Figure 3) and is soaked or steeped[15] for about 48 hours in warm water (about 115° to 125° F.) containing a small amount of sulfur dioxide (about .2 per cent). The steeping prevents undesirable fermentation changes, removing much of the mineral matter of the kernels, loosening the hull and softening the gluten. The steep waters are circulated through the corn in a countercurrent system, being finally drained from the steeps, concentrated by vacuum evaporation and recovered by addition to the gluten and fibre as cattle feed. The thoroughly softened grain from the "steeps" is passed through "attrition" or "degerminating" mills (see Figure 4), which consist of two parallel vertical plates, rapidly revolving in opposite directions, studs which project between each other rupturing the kernel in a manner that frees the germ but does not crush it.

Separating the Constituents—The macerated corn from the degerminating mills is washed into tanks called "germ separators" (see Figure 5). The germ,

[14] U. S. Dept. of Agriculture, "Handbook of Official Grain Standards," January (1929).

[15] Bartling, F. W., "Wet Process Corn Milling," American Miller, Aug. pp. 40-42 (1940).

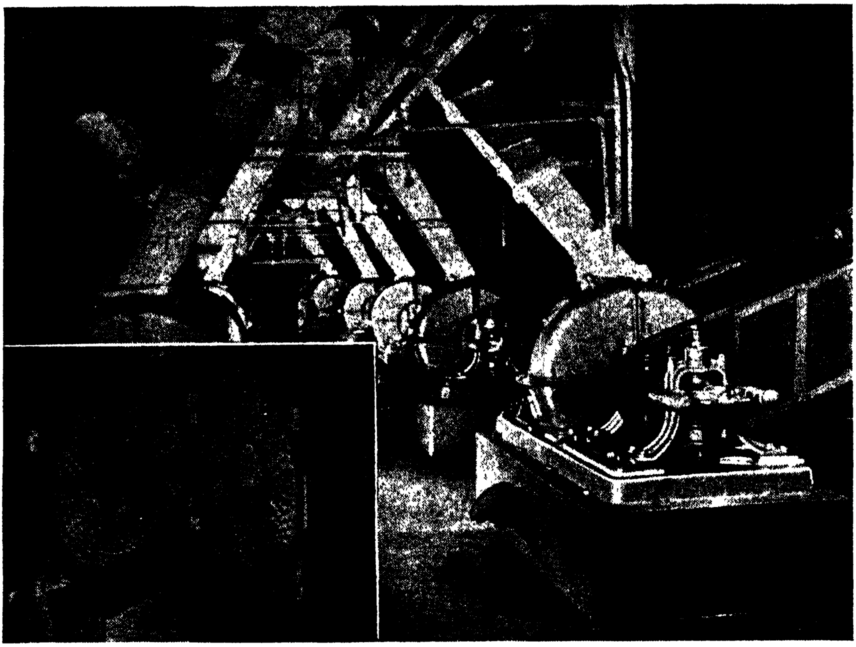

FIG. 4. Degerminating Mills. (Courtesy Corn Industries Research Foundation)

View of open mill at left shows the studded rotary plates which turn in opposite directions and tear the kernel apart without crushing the germ.

FIG. 5. Germ Separator. (Courtesy Corn Industries Research Foundation)

The germ is skimmed off at the top and the heavier parts of the kernel sink to the bottom. The man is reading the temperature.

because of its oil content, is lighter than the rest of the kernel. Agitation loosens the parts of the macerated kernel and the germ floats up to the top of the tank and is skimmed off while the heavier parts of the grain pass off from below.

The germ is washed in hexagonal copper or Monel metal cloth covered reels in which it is freed of adhering starch and excess liquor. It then passes to the squeezers for further removal of the water, is then dried and the oil recovered by extraction or in conventional expellers (see Figure 6). The heavier

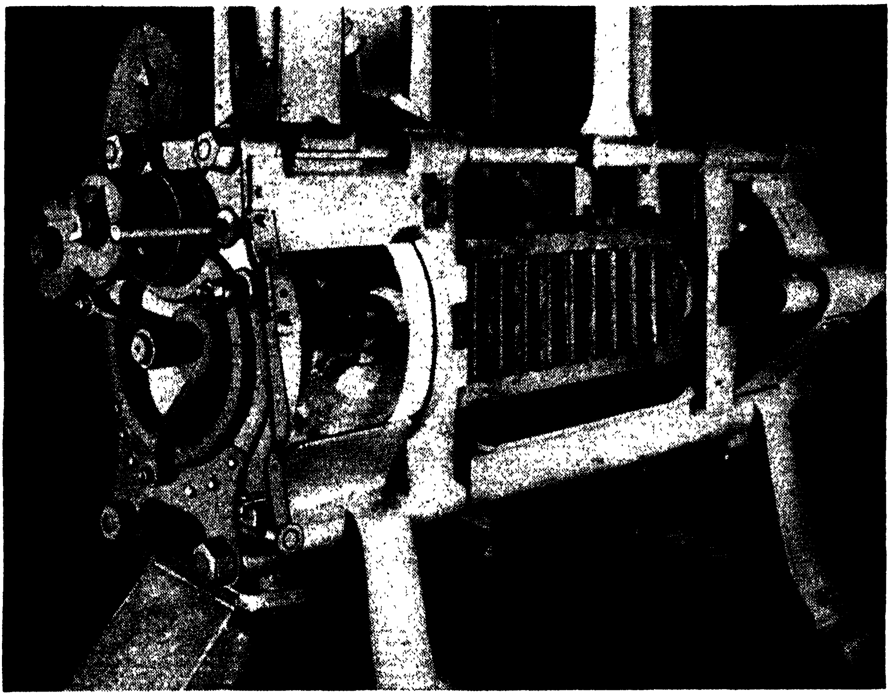

Fig. 6. Oil Expeller. (Courtesy Corn Industries Research Foundation)

parts of the kernel from the lower section of the germ separators are ground between millstones in order to separate the granules of starch and gluten from the fragments of fibre and hull, the grinding being done in special mills called Buhr mills [16] (see Figure 7).

The ground mash is then washed through a series of reels (see Figure 8) and shakers (see Figure 9), the reels being long hexagonal tubes, covered with bolting silk, open at each end, slightly inclined and rotated by a centrally located shaft. The mash is washed in at the upper end and as the reels revolve is constantly picked up and dropped as it passes through, the water washing the gluten and starch through the silk covering of the reel, while the particles of hull and fibre advance toward the lower end.

The shakers are rectangular, slightly inclined sieves with bottoms of fine bolting silk and are shaken rapidly back and forth, further to remove bits of hull

[16] See also Chapter 2.

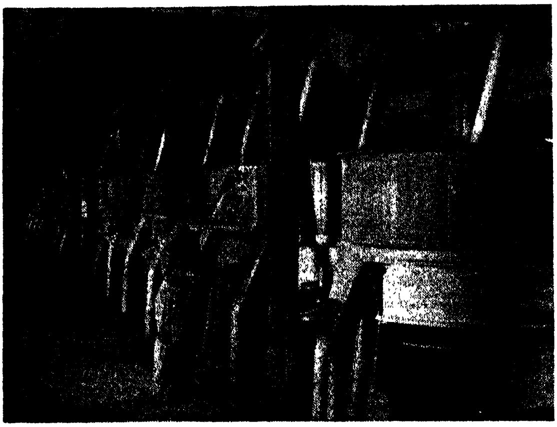

FIG. 7. Buhr Mills. (Courtesy Corn Industries Research Foundation)
These mills grind the corn into fine particles after the germ has been removed.

FIG. 8. Reels. (Courtesy Corn Industries Research Foundation)
Silk, stretched tight on frames, forms the sides. The particles that cannot pass through the silk are tumbled out at the lower end.

and fibre. The mixture of starch and gluten from the shakers is adjusted to proper density (from 4 to 12° Be.), the heavier concentration being used in so-called heavy table practice or where centrifugal separation is used, is passed onto the starch tables (see Figure 10) for separation of the starch. The starch granules being heavier than the gluten, are freed from gluten particles which flow off at the end, as they are rolled over and over down the tables, leaving the starch deposited on the tables. The tables are flat-bottomed troughs, about 2 feet wide, 120 feet long, slightly inclined (about 4 to 6 inches per 100 feet) so that the mixture will flow slowly towards the far end.

FIG. 9. Shakers. (Courtesy Corn Industries Research Foundation)

As the name suggests, they shake back and forth and particles of fiber and hull are caught on the bolting silk bottoms.

The surface of the deposited starch is kept smooth to prevent loss through any cutting action that might be caused by irregular depositing or accidental obstruction. The deposited starch which extends in a layer over the length of the table to a thickness of about 6 to 8 inches at the upper end of the run is worked free of surface gluten and flushed from the tables by a heavy stream of water. The gluten liquors from the tables, which contains considerable starch, is concentrated by settling and passed through centrifugals and returned to processing for further recovery of starch. Continuous settlers[17] of the Dorr type and Merco centrifugals are used.

The flushed starch from the tables is washed on mechanical filters[18] (see Figure 11) until it is substantially free of associated soluble matters and it is then ready for drying, where dried starch or dextrine is desired, or for further treatment if it is to be chemically modified or converted to sirup or sugar. The gluten liquor from the centrifugals or from the gluten settlers is passed through plate and frame filter presses (see Figure 12) and the cake thus formed is used to supplement corn bran, destarched for production of whole corn proteins,

[17] See also Chapter 2.
[18] See also Chapter 2.

FIG. 10. Starch Tables.

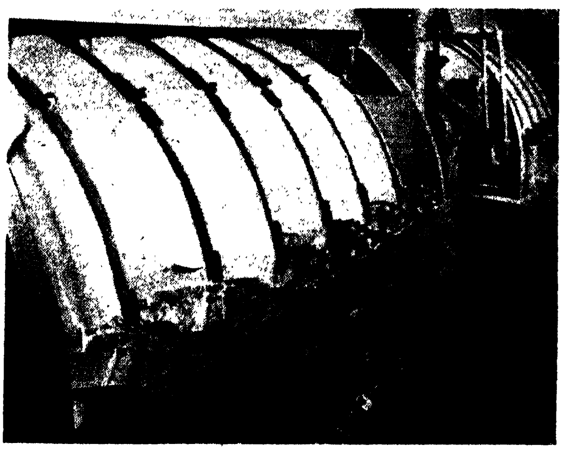

FIG. 11. American Starch Filters. (Courtesy Corn Industries Research Foundation)

extracted for the production of zein[19] (the prolamin of corn) or dried, ground and sold as gluten meal.

Drying—Starch, either directly from the process or following modification and/or final washing from mechanical filters or centrifuges, is dried on trays

FIG. 12. A Gluten Press. (Courtesy Corn Industries Research Foundation) The pressed gluten is pried free and drops to a conveyor belt below.

in kiln dryers[20] (see Figure 13) or in continuous mechanical dryers of the belt, flash or rotating shelf types such as the Proctor and Schwartz, Raymond or Beuhl type dryers.

Pearl starch constitutes agglomerates of the granules from the dryers or the kilns, belt or shelf types, whereas powdered starch is the ground starch from the dryers or that resulting directly from flash drying in which it is disintegrated in the process of drying.

[19] For a discussion of zein in plastics, see Chapter 44.
[20] See also Chapter 2.

FIG. 13. Starch Kilns. (Courtesy Corn Industries Research Foundation)

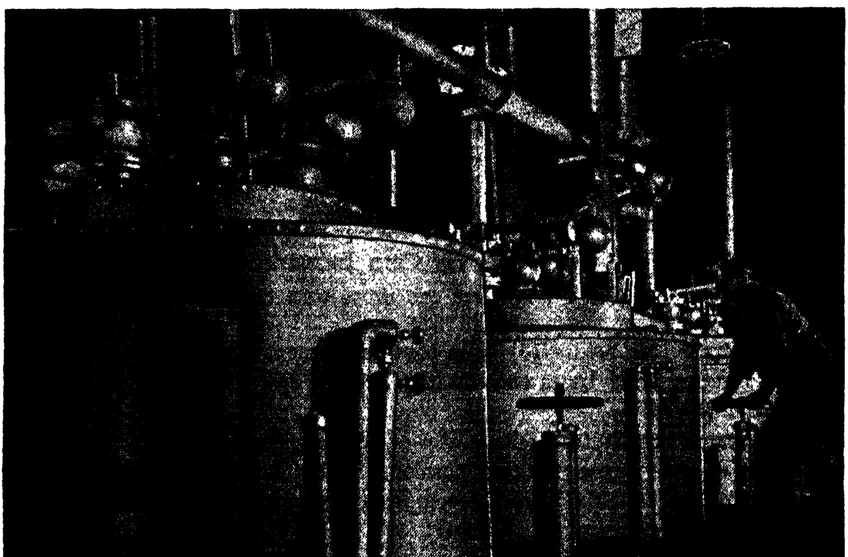

FIG. 14. Syrup or Sugar Converters, Upper Part. (Courtesy Corn Industries Research Foundation)

COMMERCIAL GLUCOSE, DEXTROSE AND OTHER CONVERSION PRODUCTS

Starch mixed with water and heated in the presence of water and acid breaks down chemically into different and simpler substances, the final product being dextrose, the same sugar that is found in the blood stream. The characteristics of the resulting product depend on the degree of conversion, as expressed as dextrose equivalent (total reducing sugars as anhydrous dextrose on the basis of the dry substance). The lower degrees of conversion products are corn

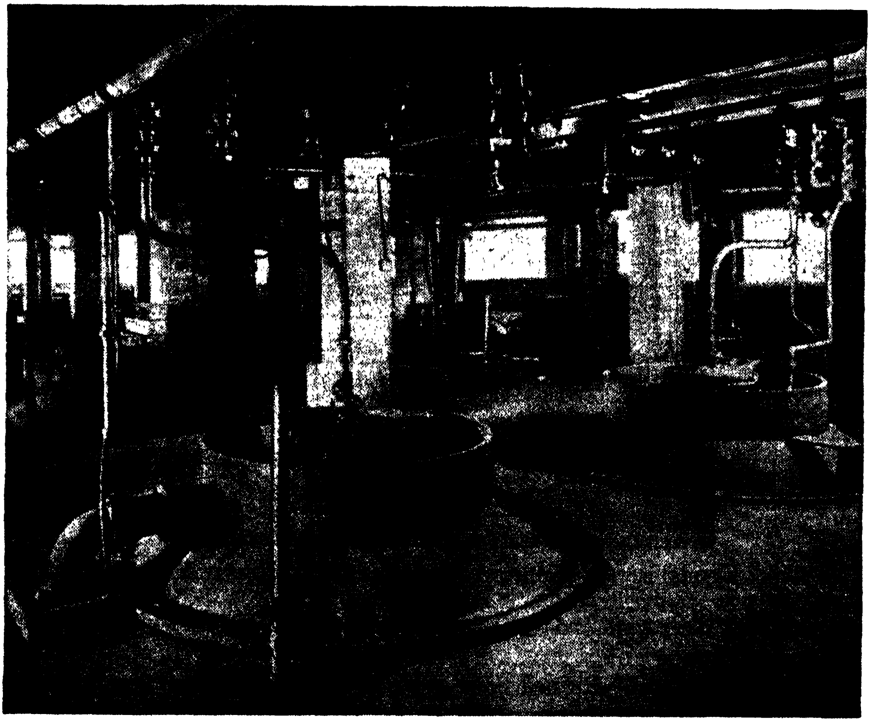

FIG. 15. Decolorizers. (Courtesy Corn Industries Research Foundation)

sirup while those of the higher ranges are commercial corn sugar and sirup from which dextrose is isolated by crystallization.

Conversion—The conversion (see Figure 14) is carried out with a dilute acid (generally hydrochloric acid), under heat and pressure and usually by direct steam. When the conversion has reached the desired degree it is stopped by releasing the pressure, and the resultant liquor is discharged to a neutralizing tank where the reaction is stopped by neutralization of the acidity by the required amount of alkali—sodium carbonate or soda ash. In addition to neutralizing the acid and stopping the conversion reaction, the soda ash acts to assist the coagulation of the proteins and separation of the fats and fatty acids resulting from the conversion. The converted, neutralized (pH adjusted 4.5-5.5) liquor is then refined by removing the coagulated proteins, fats, fatty acids and colloidal material by filtration with filter aid decolorized by treatment with bone black (see Figure 15) or activated carbon and concentrated to the required degree for finished sirups, solidification for commercial corn sugar or crystallization for production of dextrose. Corn sirup or glucose usually range from 31 to 55 dextrose equivalent while the commercial types of sugars range from 70 to 80 depending on the per cent of residual water and dextrines to substantially pure crystallized dextrose. Pressed sugars are obtained by pressing out the mother liquor from the crystallization in hydraulic presses. The pressing sepa-

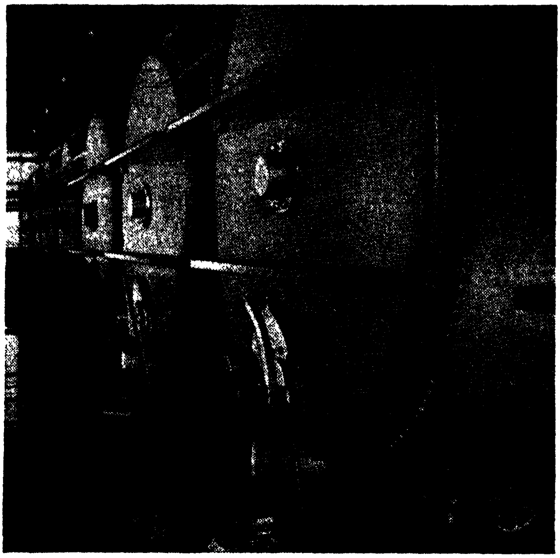

FIG. 16. Crystallizers. (Courtesy Corn Industries Research Foundation)

rates most of the sugars and forces out an uncrystallizable dark-colored liquid or corn molasses.

Refined Dextrose—Refined corn sugar or dextrose is generally produced in accordance with the processes of Newkirk[21, 22] in which the refined concentrated conversion sirup is crystallized in specially designed cylindrical horizontal crystallizers (see Figure 16) equipped with spiral agitators and cooling facilities to allow regulated, controlled crystallization in order that the resulting crystallized dextrose may be easily and readily purged and washed free of its mother liquor. The crystallizers are seeded with previously formed crystals and require from three to six days for proper crystallization. The crystallized liquor is placed in centrifugals (see Figure 17) to remove and free the corn molasses from the crystallized dextrose, leaving a white refined dextrose of 99.5 to 99.9 dextrose equivalent. The isolated dextrose is then dried, screened and bagged. Where anhydrous, beta dextrose or more highly refined dextrose hydrate is required, it is produced by recrystallization.

[21] Newkirk, W. B., U. S. Patents 1,471,347 and 1,508,569.
[22] Newkirk, W. B., Ind. and Eng. Chem. (Manufacture and Uses of Refined Dextrose), *16*, 1173 (1924).

Characteristics of Conversion—The progress of the hydrolysis or conversion manifests itself by characteristic chemical and physical changes. The thick paste loses its colloidal nature, becoming more limpid as the concentration increases, while the carbohydrates become specifically lighter and the solution acquires a sweeter taste. Tested with a weak iodine solution, the deep sapphire blue given by the original starch paste changes as the hydrolysis proceeds, passing into violet, to a rose red, which in turn changes to a reddish brown growing steadily lighter, until just preceding complete hydrolysis, it disappears alto-

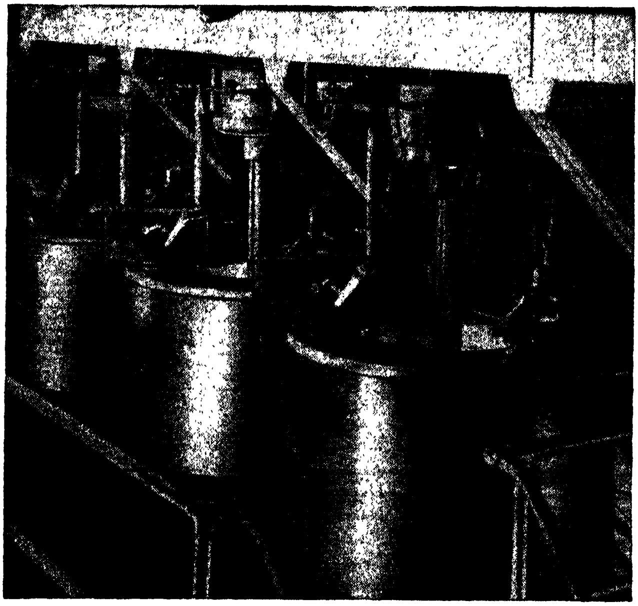

FIG. 17. Centrifugals. (Courtesy Corn Industries Research Foundation)

gether. During the early stages of conversion, the solution when poured into alcohol gives a copious white precipitate and as the conversion continues becomes less until toward the end no precipitate is produced.

Tested polariscopically conversion products show a progressive fall in specific rotation values from that of starch paste (202°) to that of dextrose (52.7°). Special type sirups are made by combined acid and enzyme conversion and are lower in viscosity and higher in total sugar content than corresponding acid-converted sirups. The diagram (Figure 18) gives the variation in percentage of the three primary constituents, dextrine, dextrose and maltose present in the carbohydrate matter as acid hydrolysis proceeds. The progress of the hydrolysis is shown by the change in optical rotation from that of starch paste to that of dextrose.

The rate of hydrolysis depends on the pressure, nature and amount of acid used and the temperature during conversion. Hydrochloric acid is almost universally used as the hydrolyte owing to its greater converting power and the fact that its resultant products can be more easily refined. The modern type converters are of the vertical type, constructed of acid-resisting bronze and capable of withstanding pressures up to 150 to 250 pounds, the conversions usually being

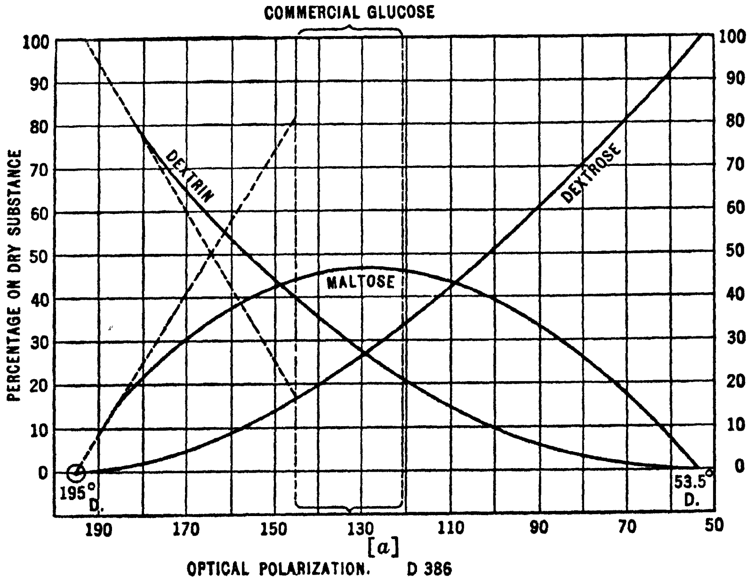

FIG. 18. Specific Rotation of Converted Materials.

The diagonal dotted lines show the respective dextrin and maltose percentages obtained in starch products hydrolyzed by diastase (malt) conversion for the corresponding rotation values. These are corrected for the polarization influence of carbohydrates introduced in the malt, which do not come from starch hydrolysis.

These curves represent the progress and state of a normal hydrolysis of starch, interpreted in terms of its three primary constituents as previously explained. It should be emphasized that they apply only to a product resulting from normal hydrolysis, that is: to a commercial glucose which has been made from a single batch of starch carried to a definite point of conversion. Formerly, such samples of glucose were common, but now glucoses are often blends or mixtures of different batches containing highly converted liquors worked back into those low converted. The large scale production of today and factory economics have, no doubt, much to do with such products.

Such glucose mixtures will not conform to values shown by the hydrolytic curves. A simple calculation of the optical and reducing constants of two normally hydrolyzed glucoses when mixed will show that the resultant reduction value will always be lower than called for by the corresponding optical rotation for a normal hydrolysis. A group of reduction values of such glucose mixtures, plotted against their optical rotations, will often fall closely on a straight line instead of on the normal curve. Hence, tests made on such glucoses may be the cause of erroneous statements that dextrose is the only reducing constituent of commercial glucose. Iodine tests on such glucoses will often show a conversion point much lower than that required by the rotation.

It should not be inferred that such glucoses are in any way inferior for the purposes intended. Addition of dextrose, for instance, seems to be an advantage in glucoses designed for hard candies.

carried out at pressures ranging from 30 to 60 pounds. They are heated by live high pressure steam. The last few years have witnessed the introduction of precoat filters, use of activated carbon[23] and "organolites"[24] and various improved

[23] See Chapter 18. [24] See Chapter 6.

LIST OF PRODUCTS MADE FROM THE CORN KERNEL

Starches	*Dextrins*	*Sirups*	*Sugars*	*Corn Oil*	*Feeds*	*Miscellaneous*
Pearl	Canary Dextrin	Mixing Corn Sirup	Dextrose, Chemically Pure	Corn Oil, Crude	Corn Gluten Feed	Lactic Acid
Powdered	White Dextrin	Special Tanners' Corn Sirup	Refined Corn Sugar	Corn Oil, Refined	Corn Gluten Meal	Zein
Soluble	Special Dextrins	Brewers' Corn Sirup	Refined Hydrate Corn Sugar	Corn Oil, Solidified	Corn Oil Cake	Calcium Lactate
Thick Boiling	British Gum		Refined Bread Sugar	Soap Stock	Corn Oil Cake Meal	Sodium Lactate
Thin Boiling	Special Gums		Corn Sugar Seventy	Black Grease	Corn Bran	Pudding Powders
Alkaline	Founders' Mixture		Corn Sugar Eighty	Solid Soap		Corn Sugar Molasses (Hydrol)
Chlorinated						Yeast
Non-Congealing						
Gelatinized						
Binder						
Crystal						
Lump						
Bakers'						
Boraxed						
Confectioners'						
Brewers' Grits						

AND THEIR USES

Textiles	Textiles	Confectionery	Caramel	Textiles	Beef Cattle	Dietary
Paper	Paper	Ice Cream	Sugar Color	Salad and Cooking Oil	Dairy Cattle	Medical
Confectionery	Colors	Preserves	Brewing	Soaps	Sheep	Experimental
Household	Carpets	Table Sirups	Vinegar	Commercial Baking	Poultry	Foods
Baking	Twine	Food Sauces	Ice Cream	Pharmaceuticals	Other Domestic Animals	Tanning
Baking Powders	Window Shades	Canned Meats	Dietetics			
Brewing	Pastes	Jams, Jellies	Pharmaceuticals			
Asbestos	Sizings	Baking	Fiber Silk (Rayon)			
Explosives	Gums	Beverages				
Laundry	Glues	Brewing				
Pastes	Mucilage	Tobacco				
Sizings	Leather	Pharmaceuticals				
Soaps	Fireworks	Infant Feeding				
Cosmetics						
Pharmaceuticals						

FIG. 19. Products of Corn and Their Uses. (Courtesy Corn Industries Research Foundation)

processing techniques in the manufacture of sirups and sugars which have been manifest in improved recoveries and quality of finished products.

In the refining of starch, Merco centrifugals, in primary separation as well as in the recovery of starch from gluten, improved mechanical filters washing and concentrations and continuous settlers have found increasing application in the processes.

By-products—Products of the process (see Figure 19), other than starch, dextrines, corn sirups, corn sugar and dextrose are crude and refined corn oil, oil meal, gluten and mixed feed of the bran (Figure 20), steep water solids and

FIG. 20. Rotary Feed Drier. (Courtesy Corn Industries Research Foundation)

gluten as cattle feeds and industrial proteins[25] from gluten, zein, the alcohol soluble protein, and destarched gluten containing glutelins, globulins and zein with associated fibre, fats and fatty acids used in coatings, adhesives and plastic compositions. Also some amino acids and their salts are produced from corn gluten while some prospectively interesting products of the components and their derivatives have been prepared from the solids of steep water.

THE CROP AND THE INDUSTRY

Our nation annually sows about 100,000,000 acres[12] in corn. It is one of our most fertile crops, producing about twice the yield of wheat from one-eighth the amount of seed in one-half the time. It can be picked sixteen weeks after planting, its cultivation and harvesting are relatively simple, compared to the harvesting of the small grains. Although the crop is large, only a small amount (about 2.7 per cent) of it is used by the wet corn-milling industry. The industry comprises eleven companies with thirteen factories, all located in the corn-raising states of the middle west: Illinois, Iowa, Indiana, Michigan, Missouri and Ohio. Eight of the companies, including all of the larger ones, manufacture starch and also convert it into sirup, sugar or other products. The three

[25] Walsh, J. F., Ind. and Eng. Chem., *29,* 673 (1937).

smaller companies sell starch only and usually do not grind corn but process and package corn starch which they purchase from other companies.

The following tables from U. S. Tariff Commission, Report No. 138 show the location of plants, the names of companies and the kinds of products sold and the total sales of the industry.

The total investment in the wet corn-milling industry in the United States was reported in 1936 as about 100 million dollars. About one-half the amount is invested in land, buildings and equipment, about one-fifth in inventories of

TABLE 1—NAMES OF COMPANIES, LOCATION OF PLANTS AND PRODUCTS SOLD—1938

Name and Address of Company	*Location of Plant*	*Products Sold (indicated by X)*			*Remarks*
		Corn Starch	*Dextrine*	*Sirup or Sugar, or both*	
American Maize-Products Co., New York, N. Y.	Roby, Ind	X	X	X	
Anheuser-Busch, Inc., St. Louis, Mo.	St. Louis, Mo .	(*)		X	Principal business of this company is the manufacture of beer.
Clinton Co., Clinton, Iowa.	Clinton, Iowa ..	X	...	X	Also produces oil and meal from soybeans.
Corn Products Refining Co., New York, N. Y.†	Edgewater, N. J. Argo, Ill ..... Pekin, Ill ..... Kansas City, Mo	X X X X	X X X X	X X X X	Edgewater plant does not grind corn. It processes corn starch transferred from other plants of the same company.
The Hubinger Co., Keokuk, Iowa.	Keokuk, Iowa .	X	..	X	
The Huron Milling Co., Harbor Beach, Mich.	Harbor Beach, Mich	X	....	.	Does not grind corn but obtains corn starch from other companies. Also produces wheat starch.
The Keever Starch Co., Columbus, Ohio	Columbus, Ohio	X	...	....	Does not grind corn but obtains corn starch from other companies. Also produces wheat starch and rice starch.
Penick & Ford, Ltd., Inc., New York, N. Y.	Cedar Rapids, Iowa	X	X	X	Owns other plants which produce sirups other than corn sirup.
Piel Bros. Starch Co., Indianapolis, Ind.	Indianapolis, Ind	X		.....	In recent years has also at times purchased corn starch for reprocessing and resale.
A. E. Staley Manufacturing Co., Decatur, Ill.	Decatur, Ill	X	...	X	Also produces oil and oil cake from soybeans and carries on a grain-merchandising business.
Union Starch & Refining Co., Columbus, Ind.	Granite City, Ill	......	....	X	

* Sold some cornstarch in 1937.
† Owns interest in 13 plants in foreign countries.

TABLE 2—COMPUTED VALUES OF PRODUCTS—1937

Product	*Quantity*	*Average Quoted Price*	*Value*	*Per Cent of Total Value*
	1,000 pounds	*Cents per pound*	*1,000 dollars*	
Starch products sold:				
Corn starch	730,860	3.91	28,577	23.5
Miscellaneous starch products	50,501	(*)	(*)	....
Total	781,361	....	28,577	23.5
Starch derivatives:				
Dextrine	83,314	4.38	3,649	3.0
Sirup (unmixed)	1,033,468	4.00	41,339	34.0
Sugar, crystallized	417,849	4.18	17,466	14.3
Miscellaneous refinery products	14,121	(*)	(*)	....
Total	1,548,752	....	62,454	51.3
By-products:				
Corn oil:				
Crude	19,599	8.50	1,666	1.4
Refined	113,357	11.47	13,002	10.6
Miscellaneous-oil (soap stocks, etc.)	10,663	(*)	(*)	....
Corn-oil cake and oil-cake meal	57,696	(*)	(*)	....
Gluten feed and meal	1,084,914	1.48	16,057	13.2
Total	1,285,619	....	30,725	25.2
Total, all products	3,615,732	....	121,756	100.0

* For some classes of products, small in comparison with the total, average prices are not available and values are not included in totals.

Source: Computed from quantities reported by the Corn Refiners Statistical Bureau and published quoted prices.

corn and finished products and about one-fifth in other assets; the total grinding capacity of the industry is about 92 million bushels per year, equivalent to 2,700 million pounds of corn starch.

According to the Report of United States Tariff Commission No. 138, the cost of corn constitutes the largest and most variable cost element of the process of manufacture, usually ranging from 50 to 60 per cent of the cost of all products including selling costs. Wages average about 8 per cent of the total cost. Fixed charges are comparatively low, with inventories running from 15 to 20 per cent of the annual output. Profits vary considerably from year to year but on an average compare favorably with profits of other industries.

POTATO STARCH INDUSTRY

Although during the first half of the nineteenth century a large part of the starch produced in the United States was made from white potatoes, today it comprises only a small portion of our domestic starch production and is produced almost entirely from cull potatoes.

The industry[12] consists of twenty-four factories located in Aroostook County, Maine, and one in Minnesota. Most of the factories are small and equipped with relatively simple machinery. They usually derive their heat and power from coal or wood, although electric power is used in some plants. The combined capacity of the industry is about 250,000 pounds per day or about 25,000,000 pounds per year, the production being largest when the potato crops are large in all producing states. Table potatoes are supplied from nearby sources, thus requiring disposal of marketable grades as well as culls to the starch factories.

New Plants—G. H. Muller [26] in an article "Potato Starch Technology Modernized" reports and describes (see Figure 21) the operation of one of two

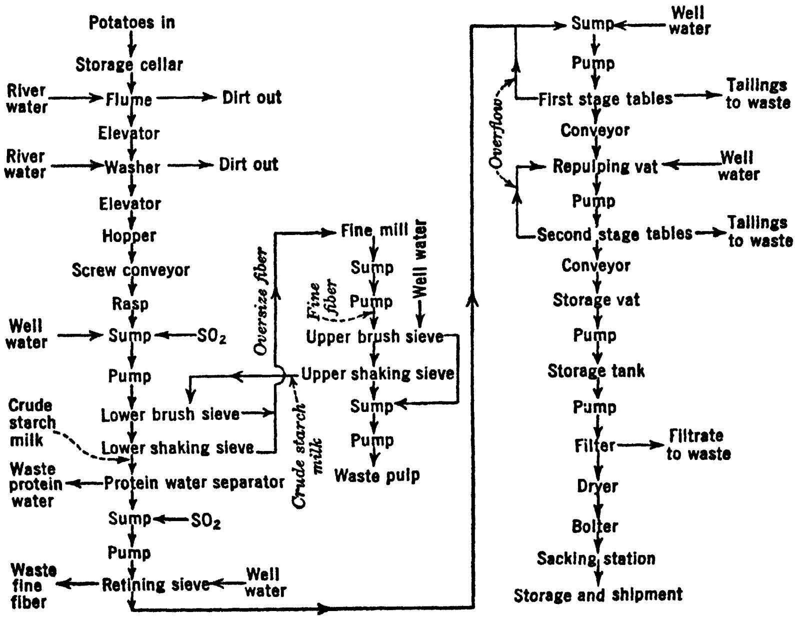

FIG. 21. Flow Diagram of White Potato Starch Process Used in Plant of Aroostook Potato Products, Inc., Houlton, Maine. (From "Potato Starch Technology Modernized" by G. J. Muller. Courtesy Chem. and Met. Eng.)

modernized plants of ten and sixteen tons capacity respectively in Maine in 1938 and 1939. The process is more effectively laid out, more completely mechanized than in the older units, full advantage being taken of modern centrifugals, mechanical filters and drying equipment. Yields are reported as about 90 per cent recovery of the starch of the potatoes as against 50 to 70 per cent in the instances of the old type plants. The steps of the process are: washing the potatoes to remove the dirt, rasping to dissociate the starch cells from each other and from the two skin layers, and a series of sieving and settling operations to separate the starchy and non-starchy portions. As the operations are carried out in water suspension, the soluble constituents are removed with the water. The final operations, the filtering, drying, bolting and packaging of the purified starch, are carried out in conventional equipment. The potatoes contain from 14 to 17 per cent starch, 70 to 80 per cent water, the balance

[26] Muller, G. H., Chem. and Met., *48*, 78 (1941).

being proteins, fat, sugars, cellulose, organic acids and small quantities of other substances. On processing they yield from 10 to 12 per cent or about 20 pounds of starch per 165-pound barrel of potatoes.

White potato starch is chiefly used in the textile industry for finishing, warp sizing and textile printing pastes, in laundering, in some adhesives, in plywood, in wall-paper paste, in making nitrostarch, in cosmetics and fields of use where it does not have to compete with corn starch on a price basis and to a limited extent in specialized foods.

SWEET POTATO STARCH

In 1934 and 1935 the Federal Emergency Relief Administration built a factory at Laurel, Mississippi, to provide work relief, a better local market for the sweet potato crop in Mississippi and Alabama and an opportunity to study the possibilities of establishing an industry to benefit southern agriculture. The process is fully described in an article by Paine, Thurber, Balch and Ritchie.[27] In 1938 a production of 1,599,085 pounds was attained, finding principal use in the southern cotton mills and laundries in Mississippi, Alabama and Louisiana. It has been concluded that as a starch material, sweet potatoes compare favorably with white potatoes. The starch content ranges from about 14 to 28 per cent depending on the variety of sweet potatoes. A bushel of sweet potatoes (60 pounds) yields from 10 to 12 pounds of starch and 5 pounds of pulp.

The manufacturing process is relatively simple and lends itself to production on a moderate scale, the process being similar to that for other root starches. The sweet potatoes are washed and then ground and screened. The pulp is passed through a de-watering process and is sold for stock feed. The starch milk from the screens is passed over tables for the purpose of recovering the starch. After the color has been removed by bleaching, the starch is dried and pulverized. The starch is of high quality and has found reasonably ready outlets. Satisfactory results have been reported on the experimental production of a sirup from sweet potato starch by hydrolysis [28] but its commercial production has not as yet been undertaken.

TAPIOCA, ARROWROOT AND SAGO

Cassava (tapioca) and arrowroot starches are made from roots or tubers by processes similar to those used in the manufacture of potato starch. However, when produced in tropical areas, their costs of production are much less than that of any of the domestic starches. Their yield of starch per acre,[29] 1500 to 1750 pounds, is greater than that of corn (1050 pounds), labor being exceedingly cheap and the tropical sun being substituted for coal and oil. Certain varieties of the cassava plant contain large amounts of prussic acid [1] and, as such starches are used extensively for food, it is necessary that they undergo

[27] Paine, H. S., Thurber, F. H., Balch, R. T., Ind. and Eng. Chem., *30*, 1331-1348 (1938).

[28] Stout, L. E., and Ryberg, C. G., Jr., Ind. and Eng. Chem., *31*, 1451-1454 (1939).

[29] Hosking, F. J., Starch Economics, National Association of Commissioners Secretaries and Directors of Agriculture, Nov. 15, (1938).

a special fermentation and thorough washing to remove this highly poisonous material. Practically all of the tapioca and a large part of the sago comes from the Netherlands East Indies. The United States Tariff Commission reported tapioca constituting 90 per cent and sago 5.3 per cent of our total imports of starch in 1939. More than 90 per cent of the tapioca is in the form of flour which consists almost entirely of starch and is suitable for most uses without further processing. The remainder is in the form of pearls, seeds, flakes and siftings and crude tapioca. The average value for 1939 was 1.4¢ per pound.

Sago—Sago is derived principally from wild growing trees in Sumatra and the outer provinces. The flour from which the starch is made is obtained by grating the palm to a fine powder and kneading it with water through strainers through which the starch passes, leaving the woody fibres behind. The starch is then processed much the same as in the case of tapioca.

The imports of sago, practically all flour, crude and pearl sago being very small, are much less than tapioca but, as in the case of tapioca, have been on the increase since 1931, reaching 23 million pounds in 1939 at an average value of 1.3¢ per pound. Preceding the present world war, these imported duty-free starch products were attaining serious proportions in the economic relationships and development of our domestic starch industry.

WHEAT STARCH

Wheat starch, although its production is the oldest branch of the starch industry, has declined in importance relative to other starches, so today it is produced on only a rather small scale. The United States Tariff Commission reports only two wet-milling companies producing wheat starch, both using purchased wheat flour as their raw material from which they produce wheat starch and gluten. Wheat flour is produced from soft wheat which contains about one-half starch and yields about 22 pounds of starch per bushel of wheat, based on 42.5 pounds of flour per bushel.

Two methods [12] of manufacture are in use, the fermentation process and the Martin process. In the fermentation process the glutenous matter is decomposed, releasing the starch granules which are washed by sedimentation and decantation and then isolated and dried. In the Martin process, the flour is made into a dough by moistening the flour, kneaded in grooved rolls, where the starch is worked out with jets of water, the starch recovered by sedimentation and decantation, finally purified by treatment with caustic soda further to remove gluten, and finally washed and dried. The fermentation process yields a thin boiling starch whereas the Martin processes produce a thick boiling starch. The gluten is marketed as such or converted for use as a condiment or flavoring or in bouillon cubes, gravies, etc.

RICE STARCH

Rice starch is of negligible importance in relation to other starches in the United States, although it is produced in substantial quantities in several

European countries and in the Orient. There is only one company[12] producing it in the United States.

The processes of producing rice starch, in general, depend on destruction of the glutenous matter by fermentation, by alkali or by both and subsequent purification of the starch by sedimentation, decantation, washing and drying of the starch. Rice, although it contains more starch than any other starch-producing materials, has its cells and starch granules so bound together by a very resistant gluten, that separation by usual methods is difficult.

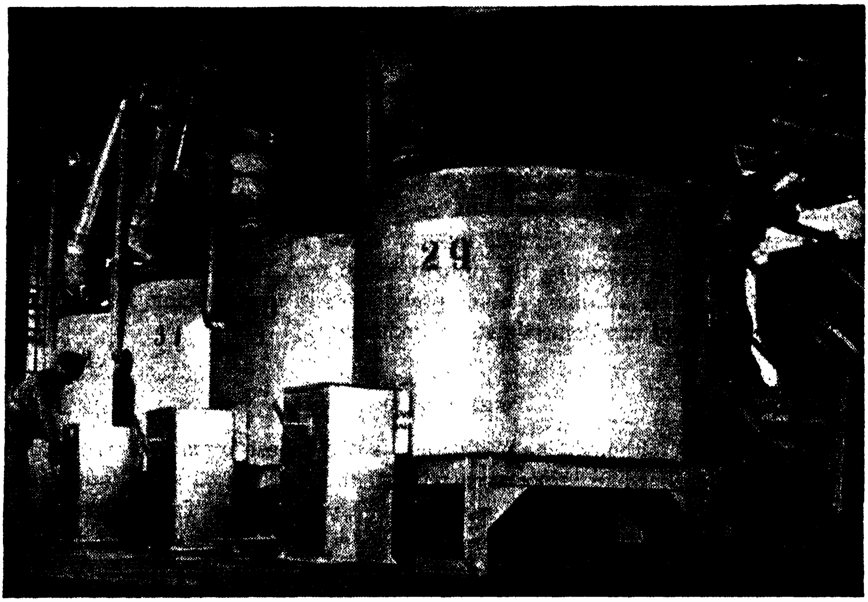

FIG. 22. Dextrin Converters. (Courtesy Corn Industries Research Foundation)

DEXTRINES AND GUMS[30]

Dried starch or starch in the process of drying, when subjected to the action of heat and/or acids and alkali, yields dextrines or gums varying in their chemical complexity and physical characteristics and intermediate between starch and sirups and sugar. Many grades of dextrines and gums are made from starch, varying in their physical and chemical characteristics from true dextrines to some partially converted to others that still contain a percentage of unconverted starch. The operation is usually carried out in jacketed cookers (see Figure 22) provided with mechanical agitators and heated by oil or steam. The chemicals used, their amount, time and temperature of heating are varied according to the requirements that are desired in the finished product. The time of conversion ranges from a matter of minutes to several hours or more if a gum is to be made. To stop conversion at the desired point, the dextrine or gum is quickly cooled. After cooling, it is powdered and bolted. The finished dex-

[30] See also Chapter 40.

trines and gums vary widely in their physical and chemical characteristics, depending on the starch used, the kind of acid or alkali, and time and temperature of the treatment.

There are no recognized general standards for dextrines and gums; color, solubility characteristics and body of their pastes usually being the best means of their evaluation. They are not definite chemical compounds, neither are they made according to fixed methods of procedure. Often they are blends of different products to give the desired properties. Although little is known of their actual chemical constitution and much has been assumed, they do contain some products of acid hydrolysis.

Other processes comprise cooking starch in water containing a small amount of acid or alkali until the desired degree of conversion is attained, treating a starch solution with diastase and holding it at the proper temperature until the desired degree of conversion is obtained and by subjecting pH adjusted wet starch to drying under controlled temperature conditions, the pH, time and temperature of drying determining the degree of conversion. Dextrine and gums produced in the United States are made principally from corn starch, lesser amounts being made from potato, tapioca and sago starches.

MODIFIED STARCHES

Modified starches comprise as a whole starches modified in one way or another so that in their dried finished state on subsequent dispersion as a gel or in paste form yield products of varied chemical and physical characteristics. The so-called alkali or pH adjusted starches yield thick-bodied starches, while those subjected to treatment with dilute acids below the bursting or pasting point of the granule yield thin-bodied or low viscosity starches. Further modifications are produced by treating the starches in suspension or in the process of drying with various oxidizing agents and salts, resulting in clear and more elastic gels and films. It is practically impossible to subject commercial starch to any action of water, chemicals, heat or mechanical treatment without subjecting it to more or less incipient changes which can be recognized by suitable physical and chemical tests. This has resulted in the production of a wide variety of types [31] of modified starches. Some are produced by heat; others by chemical treatment. There are numerous patented and published results of studies of treatment of starch with various salts, oxidizing and reducing agents, treatments under heat and reactions with various chemicals as well as the effect of mechanical disintegration of the starch granule on its resultant physical and chemical characteristics. However, numerous as these modified starches are, there is a clear distinction between them in the trade, based primarily on their behavior under various tests of their properties as they are applied in the industries.

INDUSTRIAL USES

Starches, as such, are consumed for food, in textiles, paper, for laundry purposes, in plywood and veneer and in the manufacture of dextrines and adhesives

[31] Sjostron, O. A., Ind. and Eng. Chem., *28*, 63 (1936).

In each of these uses, substitution of one starch for another varies within wide limits, depending largely upon the relative prices of the starches and upon their physical properties. The United States Tariff Commission reports that in 1937 a total of 794,034,000 pounds of domestically produced starch was sold and used as such for various industrial purposes, foods using 238,974,000 pounds; textiles 153,970,000; dextrines and adhesives 92,974,000; laundries 137,191,000; paper making 89,554,000, and miscellaneous 81,371,000 pounds.

The starch consumed by food manufacturers is used in beer, baking powder, bakery products, confectionery and starch for use in the household, in the textile industry, in sizing the warp preparatory to weaving and in finishing the cloth, in dextrines and adhesives for the manufacture of sizings and adhesives for various purposes, in laundries as such, modified and some chlorinated for starching and sizing of washed fabrics, and in paper making as a sizing material,[32, 33] in finishing as a coating, and as an adhesive in laminated paper and fibre-board.

Starch conversion products find wide use in foods, the fermentation industries, the production of rayon, tanning, pharmaceuticals and the production of caramel and numerous other less familiar uses.

Starch can rightfully be considered one of the most abundant, relatively high in purity, low cost raw materials available to the chemical industry, either as such or in one or another of its manifold conversion modifications. Although its present uses are many, there is little doubt that as compared to its ultimate prospective possible application, they constitute little more than a beginning.

READING LIST

GENERAL

Radley, J. A., "Starch and Its Derivatives," D. Van Nostrand Co., Inc., New York (1940).

Allen, P. M., "Industrial Fermentations," Chapter 16, (1926).

Walton, R. P., "A Comprehensive Study of Starch Chemistry," The Chemical Catalog Co., Inc., New York (1928).

Spicer, Ruth, Dept. of Commerce, Bureau of Foreign and Domestic Commerce, Starch, (1938).

TECHNICAL

Caesar, G. V., and Moore, E. E., Ind. and Eng. Chem., Consistency Changes in Starch Pastes, *27*, 1447 (1935).

Brunhall, B., and Hixon, R. M., Ind. and Eng. Chem., The Rigidity of Starch Pastes, *11*, 358 (1939).

Bartling, F. W., American Miller, Wet Process Corn Milling—Series of Articles —Starting Dec. (1939).

Haworth, W. N., Chemistry and Industry, The Molecular Structure of Carbohydrates, Sept. p. 859 (1935).

Vollrath, H. B., Rayon and Melliand Textile Monthly, The Use of Corn Sugar in Viscose Rayon Manufacture Apr. p. 244 (1936).

Hansen, D. W., Bibliography on Chemistry of Starch, Corn Industries Research Foundation, (1940).

[32] Bolton, P. S., The Paper Mill and Wood Pulp News, June 27, p. 80 (1936).
[33] Saxl, I. J., Paper Trade Journal, Sept. 23, p. 46 (1937).

CHAPTER 37

THE PULP AND PAPER INDUSTRY

ALLEN ABRAMS
Vice President, Marathon Paper Mills Company

HISTORY

The transmission of thought by means of symbols was practiced for thousands of years prior to the Christian era. Primitive people used stones, clay, palm leaves, shells and the bark of plants on which to inscribe information. Then in Egypt, about 3500 B.C.,[1] men began to strip off the inner bark of the papyrus reed, spread it out in pieces and combine several of these to form a sheet on which to make their marks. Later on they pounded the bark into fibrous masses and formed crude sheets. These materials were employed extensively until the 9th or 10th century A.D. when they were supplanted by the product of the paper manufacturer. Curiously enough, Egypt, the country where paper originated, does not produce any paper today.

About 180 B.C. another medium was developed for receiving inscriptions. Parchment sheeting was produced from the skins of animals, such as sheep, goats and calves, by removing the hair, cleaning, stretching and drying the skin. This sheet did not compete seriously with papyrus until the 2nd century A.D., but thereafter it seems to have been used extensively until the 13th or 14th century.

In China about 200 B.C. there appeared the first sheet material which might be considered the forerunner of modern paper.[2] The Chinese soaked short lengths of bamboo until they were soft, then beat them into pulp with stamps. The pulp was placed in a vat and diluted with water; sheets were made by dipping some of the pulp onto a mold consisting of a shallow tray with a removable side and a bottom of woven reeds. For many years the Chinese were the only producers of paper. Then in 700 A.D. the Arabs captured Chinese paper makers at Samarkand, thereby learning the secrets of manufacture, which they used extensively and passed on to the rest of the world.[2] At first the Arabs employed linen rags, but later on they used cotton rags, flax or any other vegetable growth which would yield suitable fiber.

The interdependence of inventions is illustrated by the development of the printing press and the large-scale manufacture of paper. Printing first started in China, where the oldest known manuscript appeared in 868 A.D. The evolution of printing presses created an increasing need for a cheap, uniform sheet

[1] Jerrold, W., Paper, *21*, No. 21:15 (Jan. 30, 1918).
[2] *Encyclopædia Britannica*, fourteenth edition, V. 17:228 (1937).

which could be produced in large quantities. The use of movable type, ascribed first to Gutenberg in 1440, materially accelerated this development.

The earliest recorded use of rag paper was in Europe during the first part of the 12th century. However, the supply of rags later became inadequate, due partially to the increasing production of paper and in more recent years to the changing styles in cloth. Cotton and linen rags make good pulp and paper, but natural and artificial silk are not suitable for such use. Yet it was not until the 19th century that serious work was undertaken to secure fiber from wood, the most important known potential source of this raw material in the world. In 1840 [3] a German named Keller set about to emulate the process by which wasps break down wood fiber for use in their nests. From this experimentation came a method of grinding wood into pulp suitable for the manufacture of paper.

When the whole wood fiber was used, pulp was obtained which had certain deficiencies in color and strength. Naturally attempts were then made to improve the quality of fiber by removing certain of the incrusting materials from the wood. Two Englishmen, Burgess and Watt, found that they could cook wood in caustic soda at high temperatures and obtain a good quality of pulp.[4] Their early work in 1851 gave only discouraging results, but Burgess came to Gray's Ferry, Pennsylvania, in 1854,[5] carried on further work and subsequently patented the soda process in this country. It is worthy of note that his efforts were openly derided by newspapers of the time—but such is the price of progress!

The next and most important development in pulp making took place at Manayunk, Pennsylvania, when an American chemist, Tilghman, produced chemical wood pulp by the acid sulfite process. After taking out a patent in 1867, Tilghman [6] abandoned his efforts because of mechanical difficulties; whereupon Fry and Ekman took up the work in Sweden about 1870 and later put the system into commercial operation. Subsequently Charles Wheelwright built a mill in Rhode Island, and gradually the sulfite industry assumed a dominant position in this country.

Now, in Europe, the growing sulfite industry began to create serious competition for the Scandinavian soda pulp manufacturers. The Scandinavians watched with interest, then promptly commercialized the sulfate process, a modification of the soda process, developed in Sweden about 1879 by C. F. Dahl.[7] This sulfate, or kraft, treatment was applicable to a greater variety of woods and yielded a stronger, cheaper wood pulp than that obtained by other processes. Despite this fact, the sulfate process did not reach North America until 1903, but thereafter its use expanded rapidly. Further modifications of the cooking and bleaching processes have brought kraft pulp into an important economic position.

All of these improvements in the quantity and quality of pulp production have demanded constantly more and better equipment for making the pulp into paper.

[3] Studley, J. D., "United States Pulp and Paper Industry," p. 3, U. S. Department of Commerce (1938).

[4] Everest, D. C., Paper Trade J., *82*, No. 1:38 (Jan. 7, 1926).

[5] Weeks, L. H., "A History of Paper Manufacturing in the United States, 1690-1916," p. 227, Lockwood Trade Journal, Inc. (1916).

[6] Anon., "Two Hundred and Fifty Years of Paper Making in the United States," Paper Trade J., *111*, No. 22, Section II:27-28 (Nov. 28, 1940).

[7] Stevenson, L. T., "The Background and Economics of American Papermaking," p. 25, Harper (1940).

The crude hand methods of the early Christian era required a tedious process of pounding fibrous materials into pulp, dipping sheets from a vat and then squeezing water out in a screw press. Considerable improvement in the maceration of fibrous materials was made in Holland about 1750 when the Hollander beater was introduced.[8] This speeding up of beating, an important step in paper making, was a forerunner of the next major mechanical development in the industry. In 1799 Louis Robert, a Frenchman, patented the idea of matting the fibers into a sheet on a moving wire belt through which the excess water could drain.[9] This principle was taken up by the Fourdrinier brothers in England, and it is to them that much credit should be given for commercializing the paper machine which bears their name and which is today the most important piece of equipment in the paper mill.

Paper Making in the United States—William Rittenhouse, a Dutch paper maker and Mennonite clergyman, arrived in the United States in 1688.[10] Finding that there was no paper industry here, he promptly made connections with William Bradford, a printer, whereupon the two men built a paper mill near Philadelphia in 1690. A number of other mills were built in that vicinity, and later in New England. By the year 1800 there were 100 mills in the United States; by 1810 there were nearly 200 mills.

During this early period of American paper making, rags were the principal source of raw material for pulp. There seemed to be a continual dearth of this material. During the Revolutionary War rags went to such a high price that the search for other raw materials was intensified. Mathias Koops, working in England, had developed methods for making pulp from straw, waste paper and at least one kind of wood. In 1800 he wrote a book which was printed on straw paper and which also contained sample pages of wood paper.[11] In 1827 Magaw erected a mill in Meadville, Pennsylvania, where he employed a process for making straw pulp similar to that of Koops', but of his own invention.[12]

Early in the 19th century two other interesting developments occurred. Joshua Gilpin built a mill which might be called the first efficient mechanical paper plant in the United States.[13] Here he employed his own cylinder machine, which attained considerable popularity, and which was copied later by other mills. The Ames brothers, near Springfield, Massachusetts, took material from an old gypsum mine near their plant, crushed the gypsum and used it as a filler in paper. This was the beginning of efforts to improve certain qualities of paper by the addition of inorganic materials.

Perhaps the outstanding development of the American paper industry in the 19th century was the installation of the first Fourdrinier paper machine in a mill at Saugerties, New York.[14] Not long afterward, the manufacture of this

[8] Studley, J. D., "United States Pulp and Paper Industry," p. 3, U. S. Department of Commerce (1938).

[9] Ibid., p. 3.

[10] "Two Hundred and Fifty Years of Paper Making in the United States," pp. 6-7.

[11] Koops, Mathias, "Historical Account of the Substances Which Have Been Used to Describe Events, and to Convey Ideas from the Earliest Date to the Invention of Paper," T. Burton, London (1800).

[12] "Two Hundred and Fifty Years of Paper Making in the United States," p. 8.

[13] Ibid., p. 17.

[14] Weeks, L. H., "A History of Paper Manufacturing in the United States, 1690-1916," p. 179.

machine was started in Connecticut, and from that time forward there was rapid development in its use.

In 1866 the Pagenstechers of Stockbridge, Massachusetts, imported two Keller-Voelter machines for the production of groundwood pulp.[15] Other groundwood mills were soon built and from then on this type of pulp became an important factor in the industry.

Perhaps no industry in the United States has been more fortunate in its pioneers. Many famous names have been carried down through generations and are still well-known in this industry—Crane, Parsons, Crocker, Warren, Mead, Kimberly. It was their courage and appreciation of new materials and methods which brought about increased production, reduced costs, and better products. These improvements enabled the pulp and paper industry to expand geographically as new raw materials were made available for use. The industry also grew as old markets were expanded and as new markets were created by the progressively reduced price of paper, together with an increasing consumer purchasing power and a growing population.

RAW MATERIALS

The raw materials employed in the pulp and paper industry are of the fiber-yielding type such as wood, rags, straw, bagasse; and of the nonfibrous type such as sulfur, limestone, rosin, alum, soda ash, salt cake and clay. The United States is fortunate in having within her borders practically all of these essential materials for producing pulp and paper.

Fibrous Raw Materials—Almost every known fibrous material has been tried for the manufacture of pulp and paper; nearly every one will make a product having some desirable properties. Hence the use of the raw material is determined by its economic, as well as its technical, suitability. Is there an ample supply of the raw material? Is it available in all seasons of the year? Does it deteriorate in storage? What yield and quality of fiber does it give? What are the costs of collecting and transporting the material to the pulp mill; of converting it into pulp and paper?

Wood—When these criteria are applied to all fiber-yielding plants, it becomes evident that wood is the outstanding source of cellulose fiber—in fact more than 90% of the paper consumed in the world is made from wood fiber. As of 1937, in the United States more than 10,000,000 cords of wood were employed for the production of pulp.[16] (See Figure 1.) Eighty-five percent of this wood was cut in the United States, the remainder imported from Canada. It will be noted that the price of pulpwood declined steadily from 1921 to 1933, since which time it has increased slightly. In addition to our wood imports, we brought in the equivalent of 5,000,000 cords in the form of pulp and another 4,000,000 cords in the form of newsprint paper. Our total annual usage was therefore equivalent to about 19,000,000 cords of wood, approximately half of which was produced in this country.

The United States has the greatest timber resources of any country in the

[15] "Two Hundred and Fifty Years of Paper Making in the United States," p. 22.

[16] Pacific Northwest Regional Planning Commission, Pacific Pulp and Paper Ind., *12*, No. 8:41-43 (August, 1938).

world, except Russia. The North American continent possesses 40% of the world supply of softwood, the most important source of pulp fiber. Despite the fact that the paper industry uses less than 5% of the total annual cut of wood,[17] it is recognized that intelligent conservation based on wise use and scientific forestry is needed to assure a continuous supply of this raw material for the future.

Wood pulp production and consumption in the United States have been in proportion during recent years, indicating that our wood pulp imports and ex-

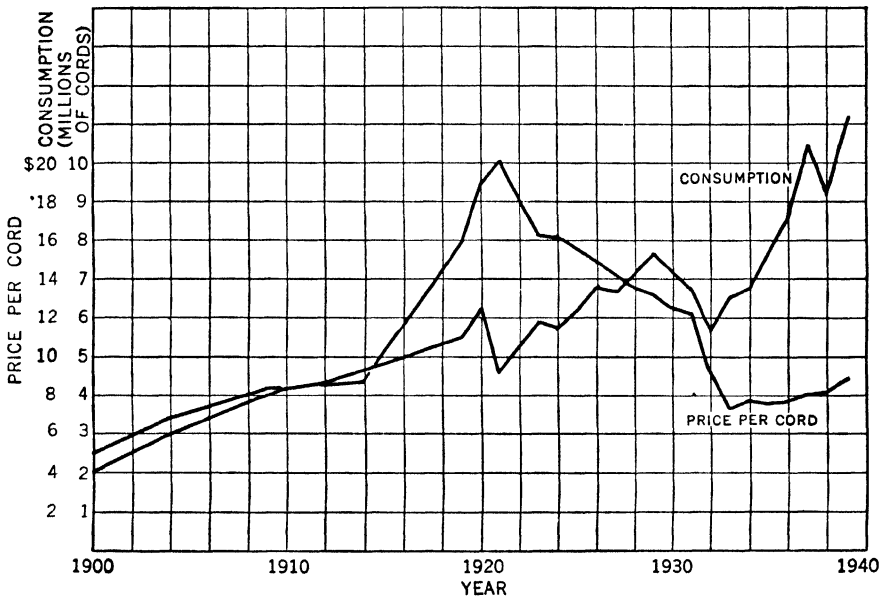

FIG. 1. U. S. Pulpwood Consumption and Price Per Cord. [U. S. Bureau of Census (1899-1938); Amer. Pulp and Paper Assn. Estimate (1939)]

ports have been fairly constant. (See Figure 2.) The production of mechanical pulp has declined in recent years, sulfite pulp has increased somewhat and sulfate pulp has grown very markedly. (See Figure 3.) (The different kinds of pulp will be explained later in the chapter.)

Conservation of Wood. In recent years there have been efforts to conserve raw material by decreasing waste, using new species and increasing yields. Many pulp mills now operate on the slabs and edgings from sawmills. The explosion process commercialized by Mason in 1924 employs waste wood, exposing the pieces to a steam pressure of about 1000 pounds for a few seconds, releasing the pressure and thus blowing the chips into masses of fiber.[18] Shorter chemical cooking periods, followed by mechanical disintegration, lead to a higher yield of pulp, although it is of inferior cleanliness, color and strength. In the South, pine stumps are shredded to small size; the wood rosin is removed by a sol-

[17] *Encyclopædia Britannica,* V. 17:235.
[18] Boehm, R. M., Ind. Eng. Chem., *22,* No. 5:493-497 (May, 1930).

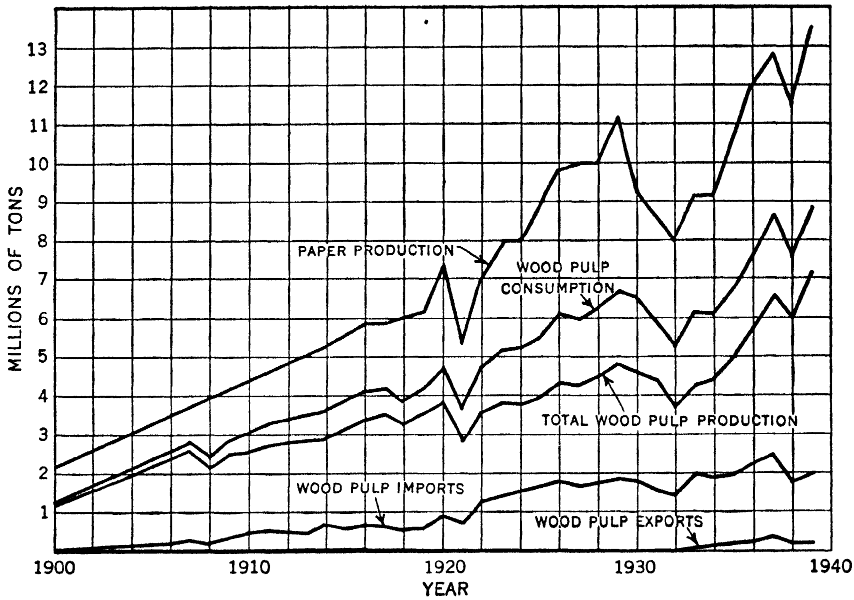

FIG. 2. U. S. Total Wood Pulp Production, Consumption, Imports, Exports and Total Paper Production. ["Wood Pulp Statistics" (1940), U. S. Pulp Producers Association]

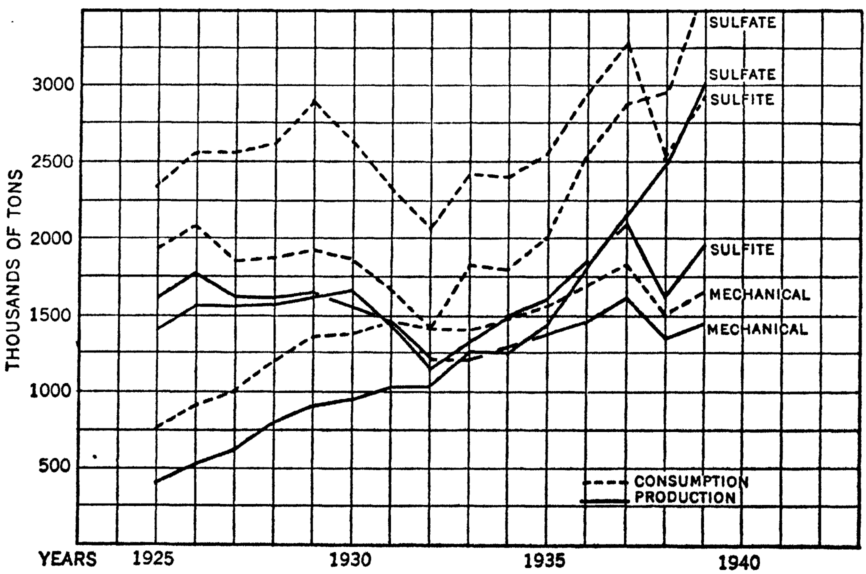

FIG. 3. U. S. Production and Consumption of Wood Pulp by Kinds. ["Wood Pulp Statistics" (1940), U. S. Pulp Producers Association]

vent;[19] and the wood is then used for the production of pulp for wallboard. As a result of extensive government studies, the loss of pulpwood by decay, and of pulp through the attack of molds and fungi, has been reduced considerably. Broadleaf woods and semi-pitchy coniferous woods are now being cooked by the sulfite process. Herty's work showed that southern pines do not develop high pitch content until heartwood forms; therefore groundwood and sulfite pulps may be obtained from these species by suitable procedures.[20]

Surveys of the available amounts of the various species of wood and their characteristics for pulp making are being made constantly. Spruce, the most valuable of all pulpwoods, constituted 75% of the total usage in 1900; yet, despite an actual increase in its consumption, spruce in 1939 constituted only 23% of the usage. Southern yellow pine was a close second, followed by hemlock from the North Central and Western states. Jackpine, firs and the broadleaf woods, of which poplar is most important, constituted 25% of the total usage.

Other Fibrous Raw Materials—Since 1860, when wood was first employed intensively for the manufacture of pulp, no new fibrous raw material of *major* importance has appeared. No other growth has been found which approaches the tree as a commercial producer of cellulose. Whereas the cotton plant yields about 160 pounds of fiber per acre annually, well-managed woodland will produce about 2000 pounds per acre-year.[21] The re-use of waste paper has become of such importance in recent years that it now constitutes approximately one-third of our total pulp consumption.

A few other fibrous raw materials are worthy of note. About 500,000 tons of rags are employed annually in the United States for the production of pulp. Nearly one-third of this amount is imported, principally from Japan, France, Spain and other foreign countries. With the introduction of strong wood pulp, having improved permanence or aging characteristics, there has been a decrease in the consumption of rags. Straw, largely of wheat or rye, furnishes an additional 500,000 tons of raw material annually, principally for the production of various kinds of boxes. Manila stock, much of which is imported, supplies approximately 100,000 tons of fiber each year.

Nonfibrous Raw Materials—The pulp and paper industry consumes annually about 200,000 tons of sulfur.[22] Formerly this element was imported, but today most of it is produced in Texas and Louisiana.[23] Aside from extensive use in the sulfite pulp industry, sulfur is now being used for the manufacture of synthetic salt cake.[24] This is a step of great importance to the kraft industry, which consumes 400,000 tons of cake a year, of which over half was imported in the past, largely from Germany.

The alkalis, caustic soda and soda ash,[25] are employed for cooking fibrous raw materials, to make rosin size, in bleaching processes and for other conversion operations. 150,000 tons are used each year by the pulp and paper industry. The amount of lime consumed is nearly three times as great as this, representing

[19] See Chapter 17.
[20] Herty, C. H., Paper Mill, *58*, No. 1-3 (Jan. 5, 12, and 19, 1935).
[21] Schorger, A. W., Paper Trade J., *89*, No. 23:66 (Dec. 5, 1929).
[22] Hanson, H. H. and Poore, E. N., Tech. Assoc. Papers, *23*:435-439 (1940).
[23] See Chapter 7.
[24] See Chapter 9.
[25] See Chapter 10.

15% of the total usage of the country for all purposes. Lime is employed for the production of sulfite cooking liquors and bleach liquors.

Loading and filling agents are materials which impart brightness, smoothness and opacity to papers. Many of these are natural mineral substances such as clay, talc and chalk; others are manufactured substances as barytes, crown filler, zinc compounds and titanium compounds. Despite its high cost, titanium dioxide and its blends with other minerals have come into extensive use lately, largely on account of the high opacity and brightness which they add to paper. All of these filling materials are suitably graded for particle size and color, then supplied to the industry under well-defined specifications.

In the sizing or waterproofing of paper fibers, two principal materials are used—rosin and alum. Rosin of suitable color is cooked with soda ash to make a rosin soap or size. This rosin, obtained from southern pines, may be of the gum type produced from the living tree; or it may be of the wood type as extracted from stumps.[26] When rosin size is used in papermaking, it is set or coagulated on the fibers by means of paper makers' alum or aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] a material made principally by the treatment of clay with sulfuric acid. About 100,000 tons each of rosin and alum are used annually in pulp and paper manufacture.

Prior to 1920, pulp bleaching was accomplished principally with calcium hypochlorite or bleaching powder. Then came a development whereby most companies made their own bleach liquor from liquid chlorine and lime. In recent years chlorine is used alone for some stages of the process. While the present consumption of liquid chlorine is about 200,000 tons a year, this amount is increasing rapidly with the development of bleached kraft in the South.

Dyestuffs employed for paper are principally of the aniline type,[27] rather than pigments or natural organic dyes. Aniline dyes are obtainable in a wide variety of shades, are usually reasonable in cost and may be obtained with good resistance to light, heat and chemical action.

MANUFACTURE OF PULP

Wood Pulp—Most wood comes to the mill in the form of logs. Some mills, especially those operating on alkaline processes, use slabs and edgings, the waste material from sawmills. In general, the wood is delivered in 4- or 5-foot lengths, although the 8-foot length is also commonly supplied. Logs may have the bark on them, or they may have been barked previously or peeled in the woods. In the northern part of the United States, the wood is often stored for a period, up to several years; in the South, wood is used up rapidly on account of the possibility of fungus attack. If the wood is unbarked, the logs are cut into short lengths and then run through mechanical barkers to remove the bark.

The processes employed in the preparation of pulp from wood are mechanical (i.e., groundwood), chemical (sulfite, sulfate, and soda), and a combination of mechanical and chemical known as "semichemical." The object of the pulping processes is to separate the wood into its fibrous elements. The original wood

[26] See Chapter 17.
[27] See Chapter 28.

contains approximately 50% of fibrous or cellulosic material and about 50% of nonfibrous matter consisting of lignin, hemicelluloses, extractives and inorganic matter. The lignin is incrusting matter which serves to cement the fibers together into a strong, rigid mass.

The mechanical process tears the fibers apart; the chemical processes soften and dissolve the binding matter thereby setting the fibers free; the semichemical method softens the cementing material partially and then finishes separation of the fibers by mechanical means. In general the mechanical process yields about 90% of pulp, based on the original weight of wood; the chemical processes from 40 to 50%; and the semichemical processes from 50-80%.

Mechanical Pulp—The mechanical or groundwood process is used largely on the long-fibered coniferous woods, especially those with relatively low resin content such as spruce, balsam, hemlock. Jackpine is used in an appreciable quantity and the process is also applicable to young, fast-growth southern pines prior to the time when they develop pitchy heartwood.

The short, barked logs are sent into a grinder where a hydraulic ram presses the logs firmly against a rotating stone in the presence of a stream of water. The grit of this natural or synthetic stone is of a quality selected for the particular kind of groundwood to be produced. The grade of pulp can be modified further by the type of surface which is imparted to the stone by means of special marking burrs. After grinding, the pulp is washed and screened to remove coarse or oversize fibers.

The pulp produced by the mechanical process contains all of the matter present in the original wood, except for the small amount of material which is soluble in water. Since a large portion of the wood is not separated into whole fibers but mostly into small fragments of fibers and fiber bundles, the resultant pulp is relatively low in strength; and it contains so much non-cellulosic material that it has poor resistance to light and aging. Mechanical pulp is used principally for such products as newsprint, wallpaper, wallboard and other paperboard. In these products it may be used alone or mixed with chemical pulp.

Chemical Pulp—Chemical pulp is the material which remains after the treatment of wood by chemicals which remove the cementing materials, such as lignin, and leave the cellulosic fibers. The active chemical ingredient for the removal of the cementing materials is most commonly a sulfite or sulfide, though alkalies such as NaOH or $Ca(OH)_2$ are employed in some processes. For this pulp, the wood is usually cleaned thoroughly of bark and knots. The logs are then conveyed to the chipper where they are forced at an acute angle against a rapidly rotating iron disk on the surface of which are mounted heavy knives. The knives cut off chips of wood which are generally from ½ to 1 inch in length and about $\frac{3}{16}$ inch thick. As a result of their small size, the chips are later penetrated fairly rapidly by the cooking liquors.

The chipping operation always produces some pieces which are too large for easy cooking, and others which are too small for suitable fibers and hence are classified as sawdust. All of these off-size pieces are screened out; the large chips are reworked into smaller size, and the sawdust is burned. The chips are then conducted to storage bins, usually set high above the digesters so that the wood may be fed in by gravity.

SULFITE PROCESS

The sulfite process is employed principally on long-fibered woods of low resin content, largely spruce, hemlock and the true firs. A considerable amount of aspen and small amounts of birch and young southern pine are also used. The digesters are huge steel shells generally from 10 to 20 feet in diameter and from 25 to 70 feet high. They have a capacity of from 2 to 25 tons of pulp per cook. (See Figure 4.) The interior of these cookers is lined with special acid-resisting

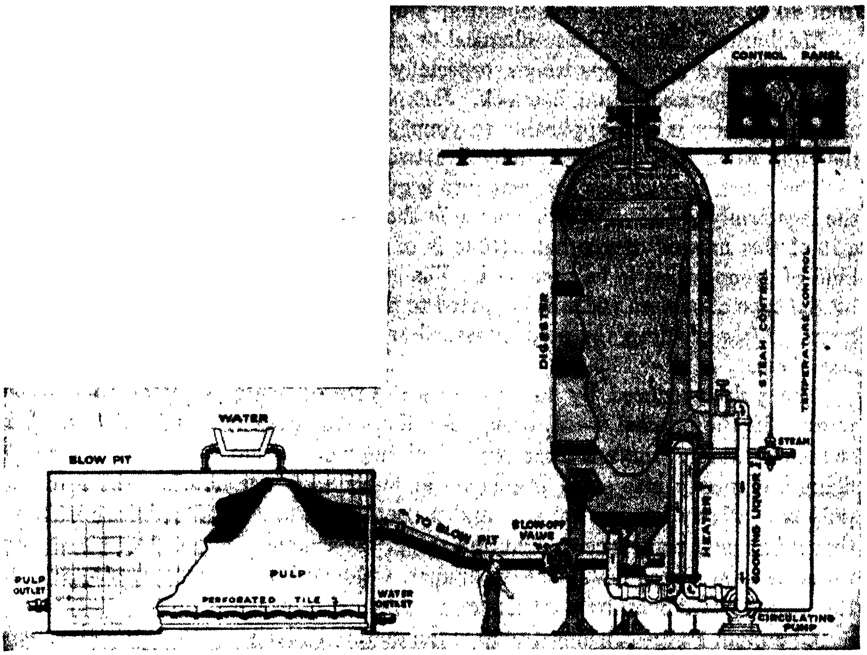

FIG. 4. Digester and Blow Pit.

Immense digesters, over fifty feet high and lined with acid-proof brick, are filled with chips uniformly distributed by a chip distributor. Preheated acid cooking liquor, under automatically controlled temperature and pressure, circulates through the chips. After twelve to thirteen hours these chips are reduced to pulpy cellulose fibers which are "blown" into the blow pit, where they are washed and made ready for purifying operations that follow. (Courtesy Hammermill Paper Co.)

brick. Some modern digesters are equipped with circulating systems which maintain uniform temperature and concentration of liquor during the cook.

The cooking liquor is prepared as follows: Sulfur is melted and then burned to sulfur dioxide in special rotary burners where the supply of air is regulated to prevent the formation of objectionable sulfur trioxide. The gas is cooled in water-immersed pipes, after which it is absorbed either by passing (1) into large absorbers containing milk of lime, or (2) up through tall concrete towers packed with limestone over which water is trickling. The first reaction which occurs is as follows:

$$H_2O + SO_2 = H_2SO_3$$

This sulfurous acid reacts with calcium base, in each case, to form insoluble calcium sulfite. However the reaction is allowed to proceed further until soluble calcium bisulfite has been formed. The final reactions are then, respectively, as follows:

$$Ca(OH)_2 + 2H_2SO_3 = Ca(HSO_3)_2 + 2H_2O$$
$$CaCO_3 + 2H_2SO_3 = Ca(HSO_3)_2 + H_2O + CO_2$$

A certain portion of free sulfurous acid is allowed to remain in the finished cooking liquor.

In the parlance of the pulp manufacturer, the "combined" sulfur dioxide is that portion which is bound to the base as a neutral salt; the "free" sulfur dioxide is that which exists as free sulfurous acid plus that portion which requires alkali to convert from a bisulfite to a neutral sulfite. "Total" sulfur dioxide is the sum of the "combined" and the "free" sulfur dioxide. While, in most mills, the combined sulfur dioxide is generally maintained at 0.9 to 1.2% concentration, the free sulfur dioxide may range from 2.5 to 5.0%.

Cooking the Chips—The requisite quantity of chips is charged through the top of the digester; the cooking liquor is pumped in from the bottom; the cover of the digester is bolted on and the cooking is started. In the ordinary quick-cook Ritter-Kellner process, steam is introduced directly into the mass of chips and liquor; the temperature is gradually brought to about 130-145° C. and from 70 to 100 pounds gauge pressure. The digester is maintained under steam for a period of 7 to 12 hours. In the Mitscherlich process the cooking is carried out with indirect steam by means of closed coils set in the digester; the cooking temperature is lower; there is less dilution of cooking liquor, but the operation is slower and the period of cooking is extended up to as long as 30 hours. However, a stronger, better grade of pulp is obtained by this process than by the Ritter-Kellner method. In the quick-cook process the blowoff valve in the bottom of the digester is opened at the end of the cook and the softened chips are blown against a "target" where they readily fall apart into pulp, thence onto the perforated bottom of the blowpit. The steam and residual sulfur dioxide gas are wasted through the "vomit spout," although a few mills have installed equipment to recover the gas and heat from the steam. In the Mitscherlich process the pressure is blown down at the end of the cook and the pulp is washed out of the digester.

Washing the Pulp—After the waste liquor has drained from the pulp in the blowpit, the washing begins. Although warm water is preferable, many mills employ cold water for this operation. The washing may be carried out by filling the blowpit with water, permitting the water to drain off and repeating the operation several times. In another method, the washing is carried on by means of high pressure hose streams directed onto the pulp from openings in the sides and top of the blowpit, and the water runs out continuously through the perforations in the bottom of the blowpit. Ordinarily these types of washing take several hours since they are carried on until the wash water shows no color from the waste liquor.

Very efficient washing may be obtained with a vacuum type of washer. This equipment consists of a wire-covered cylinder which rotates in a vat of pulp suspension so that, for about one-half of a revolution, suction draws a layer of pulp onto the wire and the waste liquor passes through the wire. Showers of water, either cold or hot, are then forced against the mat of pulp and the wash water is drawn through the wire.

Uses of Sulfite Pulp—Unbleached sulfite pulp finds wide application in newsprint, boards, wrapping papers and certain grades of printing papers, where reasonably light color and good strength are required but where cleanliness is not so important. Bleached sulfite pulp is used in writing and typing papers, tissues, greaseproof paper, printing papers and in the higher grades of wrapping paper.

Waste Recovery—The waste liquor from the sulfite process has received extensive study, not only because of its undesirability in bodies of water but also because of its possible economic importance. The solids in this liquor may be recovered by evaporation, although the most promising process today is that employing two stage precipitation: [28] (1) treatment of the undiluted waste sulfite liquor with caustic lime reagent to bring down a precipitate consisting essentially of calcium sulfite. This material is returned to the acid plant and is used in making fresh cooking acid. (2) The effluent from the first stage is again treated with lime to a higher pH, whereby the principal part of the organic constituent of the waste liquor is precipitated. This material, consisting principally of lignin compounds, is used as a raw material for preparation of such products as vanillin, dispersing agents, tanning agents and plastics.[29]

SULFATE PROCESS

The sulfate process derives its name from the fact that loss of alkali and sulfur is made up by adding sodium sulfate (salt cake), or its equivalent. The term kraft, meaning strong, is often applied to the pulp prepared by the sulfate process, purposely undercooked to produce a strong pulp. However, the terms kraft and sulfate are now used interchangeably for all grades of pulp produced by the sulfate process. The sulfate process is employed with long-fibered woods, regardless of the resin content. Principal among these woods are southern pine, spruce, hemlock, balsam, jackpine and tamarack. In this process the steel digesters may be stationary or rotating, ranging in capacity from 2 to 8 tons of pulp. The cooking liquor is alkaline because of the presence of NaOH produced in the recovery operation—as will be explained later. Hence, no lining is required in the digester.

Cooking the Chips—The cooking liquor charged to the digesters contains sodium hydroxide and sodium sulfide as the active ingredients, and smaller amounts of sodium sulfate. This liquor consists of chemicals reclaimed from the spent liquor of previous cooks, suitably reinforced with fresh chemicals added to make up for any losses, as explained later.

The pulp digester is filled with the requisite quantity of chips; cooking liquor is added and the digester is closed. The cooking conditions for a typical grade of pulp consist of heating with direct steam for 2 to 3 hours at approximately 110 pounds pressure. The pulp is then washed by one of two procedures.

Washing—In one method the pulp is blown into a diffuser, which is a closed vertical metal tank capable of withstanding pressure, so that heat from the steam

[28] Howard, G. C., Chem. & Met. Eng., *46*, No. 10:618-619 (October, 1939).
[29] See Chapter 31.

may be recovered with heat exchangers and used for processing. Each cook is blown into one of a battery of diffusers, so that it may be washed countercurrently with previous cooks in their respective diffusers. Hot water is used for washing, and the liquor is taken off until the specific gravity reaches a point below which recovery is unprofitable. This more concentrated liquor is taken to evaporators for recovery while the weak wash liquor is discharged to the drain.

In recent years the washing of kraft pulp has been carried out by blowing the pulp into a tank, together with the liquor; then pumping the whole mass to a vacuum type of filter, as described under the sulfite process on page 1417. The entire countercurrent washing operation may be completed in a single pass over one filter of the proper diameter, operating at slow speed. A layer of pulp is formed on the filter in the first part of the operation, and the strong liquor is taken away for evaporation and burning. The pulp is then washed with weak liquor, pressed to remove the liquor, and finally washed with clean, hot water. Where especially good washing is required, two, or even three, filters in series may be employed.

Recovery of Sulfate Liquor—In the sulfate process the liquor is regularly recovered for re-use. The older method of recovery still employed in some mills is as follows: The black liquor is concentrated in multiple effect vacuum evaporators and then in direct evaporators, of the disk and cascade types, using hot waste gases to complete the concentration to about 50 to 60% solids. The liquor then goes to a rotary furnace or kiln, consisting of a cylindrical sheet iron shell, 20 to 30 feet in length and 9 to 10 feet in diameter. This kiln is lined with firebrick to protect the shell from hot gases and chemicals. At this point sodium sulfate (salt cake) is mixed with the liquor to make up for the alkali and sulfur which have been lost in washing and which are subsequently lost in combustion of the black ash. As the concentrated liquor passes through the rotating cylinder, it becomes thicker and dryer and the organic matter partially burns, leaving a mass called "black ash," which is discharged from the kiln to the smelting furnaces at about 85 to 90% dry.

The smelting furnace is a chamber lined with soapstone or other basic refractory material, which is not readily attacked by the molten alkali. Combustion in the chamber is brought about by a primary air blast introduced through water-cooled tubes below the fuel bed, thus burning the organic material in the liquor. The principal problem is to burn off the carbon from the black ash and, at the same time, to reduce the sodium sulfate to sodium sulfide according to the equation

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

The hot gases from the smelting furnace go back through the rotary kiln, thus drying the black ash as it passes through the kiln.

The most recent method of recovery of chemicals and waste heat from black liquor involves the use of the spray furnace. One type of recovery unit [30] (see Figure 5) comprises a cascade evaporator, a boiler with superheater, and a smelter furnace, with the necessary auxiliary equipment. Strong wash liquor from the pulp is first sent through a multiple effect evaporator, issuing at about 45 to 55% concentration of solids. The thickened liquor then goes to the cascade

[30] Rosencrants, F. H., Paper Trade J., *112*, No. 8:120-126 (Feb. 20, 1941).

evaporator, which employs waste gases from the furnace and boiler for further concentration of the liquor. The evaporator contains a wheel, to the periphery of which are attached long baffles of sheet metal slightly tilted and spaced some distance apart. Within the periphery are set, more or less concentrically, several more baffle surfaces. As the wheel turns, the baffles pick up black liquor and

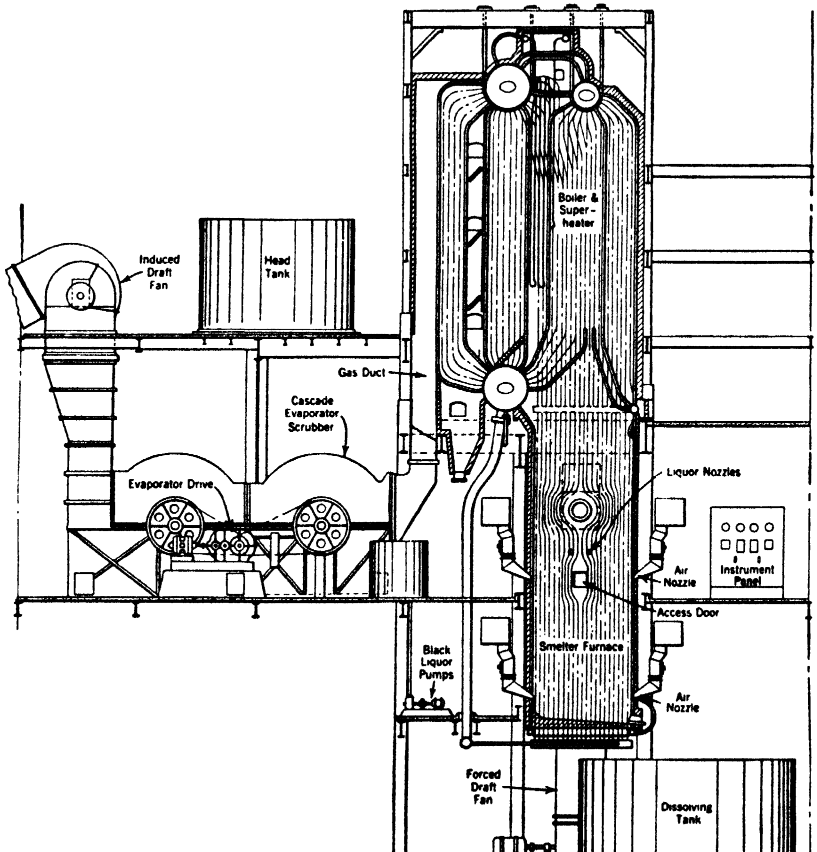

FIG. 5. Recovery System for Waste Liquor from the Sulfate Process. (Courtesy Combustion Engineering Co.)

allow it to cascade from one baffle to another. Hot spent gases from the furnace and boiler, passing through the evaporator, concentrate the liquor to about 65% solids. Then the liquor is pumped to the spray furnace where it is to be further dried and burned.

The spray furnace is a unit similar to a modern water-walled steam generating furnace, having a refractory bottom for molten material. Before feeding to the furnace, the liquor is reinforced with sodium sulfate for makeup, and it is then fed under pressure through nozzles, so directed that the liquor is sprayed evenly over the cross section of the furnace. As the sprayed liquor comes into contact with hot gases from the furnace, the solids dry and fall to the bottom of the furnace, where combustion takes place. Nozzles introduce air at suitable points in the lower part of the furnace. The hot gases pass up through the boiler and superheater, producing as much as 10,000 pounds of steam per ton of pulp. Then the gases are circulated through the cascade evaporator to extract as much residual heat as possible. The hot smelt flows continuously from the bottom of the furnace into the dissolving tank beneath.

In another type of recovery unit [31] the black liquor is concentrated in multiple effect evaporators and is then sent through a spray tower (or cascade evaporator) for further concentration with hot waste gases. Then it is pumped into the furnace through a single oscillating nozzle which sprays the liquor against the water-cooled walls. The partially dried solids cling to the walls and continue to dry until the mass of material becomes so large that it falls to the floor of the furnace, where it burns. In this unit, also, heat is extracted countercurrently from the burned gases by passing through a boiler and thence to the spray tower for concentrating the incoming black liquor. As in the unit previously described, sodium sulfate for makeup is added to the liquor as it is fed to the spray furnace; air for combustion is introduced through nozzles suitably located; the hot smelt issues from the bottom of the furnace into the dissolving tank beneath.

When the hot smelt from the furnace drops into the dissolving tank, the chemicals are taken up in water to form "green liquor." Upon adding slaked lime to the green liquor, double decomposition occurs with sodium carbonate in the liquor whereby caustic soda is formed [32] and calcium carbonate is precipitated. When the calcium carbonate has been removed by sedimentation and filtration, the resultant "white liquor" is suitable for return to the cooking process. The calcium carbonate sludge is used as a neutralizing agent for acid soil, as a filler in paper, or it may be burned to produce quicklime for re-use in the process.

Typical analyses of the solids in various stages of the recovery process are shown in Table 1.

TABLE 1—ANALYSES OF SOLIDS IN SULFATE PROCESS

	Original Melt	*Green Liquor*	*White Liquor*
Sodium carbonate	61%	64%	11%
Sodium sulfate	4	5	6
Sodium sulfide	27	31	22
Sodium hydroxide	..	..	61
Silica	2	..	..
Insoluble	6	..	..

Uses of Sulfate Pulp—Unbleached kraft pulp has a brown color. It has high strength and flexibility, hence it is especially suited for wrapping papers and shipping containers. Bleached kraft pulp may have a good white color and yet maintain most of the original strength and flexibility of the unbleached pulp, dependent on the extent of bleaching. It is an important contender with sulfite pulp for high grade wrapping and printing papers.

[31] Wilcoxson, L. S. and Ely, F. G., Tech. Assoc. Papers, *23*:410-416 (1940).
[32] See Chapter 10.

MISCELLANEOUS PROCESSES

Soda Process—In general, the soda process is employed in cooking short-fibered deciduous woods, of which the most commonly used are poplar, birch, gum, maple and cottonwood. Sometimes coniferous species are employed, such as fir, spruce and jackpine.

The cooking liquor is a solution of caustic soda made by evaporating the spent liquor from previous cooks; then drying and burning the solids in one operation, using a rotary furnace, as described on page 1419. The resultant ash is then extracted countercurrently in a battery of leaching tanks [33] to remove the remaining carbon and to leave the sodium carbonate in solution as "green liquor." Sodium carbonate is added to the green liquor to make up for losses. When this liquor is treated with slaked lime, calcium carbonate is precipitated. After filtering off the precipitate, the "white liquor" remains, the principal component of which is caustic soda. As in the sulfate process, the precipitated calcium carbonate may be re-used.

Semichemical Pulp—The method of producing this pulp is the result of efforts to obtain a higher yield than with the chemical processes and yet to have a better quality of pulp than with the mechanical process.[34] It is relatively new, having been introduced since 1920.

The first stage of the process consists of a short, mild cook employing any of the suitable cooking liquors to produce partial digestion. The spent liquor from the cook is wasted and the softened chips are subjected to mechanical attrition, as in a rod mill or a disk refiner.

As may be expected, the pulp from this process is generally dark-colored, coarse, relatively weak and hard to bleach. It is suitable for lower grades of paper products, such as corrugating board, liners and coarse papers.

Rag Pulp—Rags are employed for the manufacture of many fine papers, such as bond, ledger and writing grades, and for some book and other printing papers, particularly where exceptional resistance to aging is desired. Even in these fields certain grades of highly refined wood pulps are now offering competition to rag pulp. New rags, especially shirt cuttings, and old rags of high quality are employed for the better grades of rag paper; low-quality old rags find use in cheap products such as roofing felt.

The rags are first cleaned, sorted and graded. They are then cooked from 10 to 15 hours with lime or a mixture of soda ash and lime. This process, carried out at steam pressures of 10 to 40 pounds, removes greases and waxes. The cooked rags are washed in a beater or Hollander, a type of processing equipment described under "Processing of Pulp," on page 1427.

Other Pulps—Straw pulp is made principally from the straw of wheat, rye or oats. It is used for making the corrugated ply in shipping container board and, to some extent, as solid paperboard for mailing-tubes and setup boxes. The straw is cooked with milk of lime in large rotary digesters of about 6 to 7 tons capacity. After 10 to 12 hours of cooking, the pulp is dumped, beaten and washed.

[33] For a discussion of countercurrent leaching see Chapter 2.
[34] Curran, C. E., Paper Trade J., *88*, No. 5:66-68 (Jan. 31, 1929).

Jute fiber is obtained from beneath the bark of the jute plant, an annual plant growing in India. The raw material employed for pulp making is obtained from old sacking, burlap and string. The cooking and bleaching processes are similar to those used for rag pulp. The pulp made from this treatment is durable; hence it is especially adapted to the manufacture of tough wrapping paper, covers and tags.

Hemp fiber, of which the Manila type is the most important, is employed extensively for the manufacture of rope. This rope fiber is cooked into pulp in about the same manner as for rags. The pulp is so strong that it is generally employed for making bags to handle heavy materials, such as cement.

Cornstalk pulp has been made commercially at different times in attempts to bring it into economic importance. Because of the wide difference in properties of the pith and bast fibers of the cornstalk, the resultant pulp does not adapt itself readily to ordinary paper making. Moreover, the cost of acceptable pulp is considerably higher than that of wood pulp.[35] However, wallboard is being produced successfully from cornstalks.

Cotton linters are short fibers attached to the cotton seed as it comes from the gin. These linters are removed mechanically from the seed, cooked in a solution of caustic soda, and the pulp is subsequently washed and bleached. At the present time this pulp is of little economic importance for paper making although appreciable quantities are used for the manufacture of cellulose derivatives.[36]

Nearly 30% of the paper made in this country is produced from waste paper. This paper must be sorted into the various grades and then baled. On receipt at the mill, the baled sheets are sorted again, dusted and then shredded to suitable size. The shredded paper is cooked with a solution of caustic soda or soda ash, washed to remove the ink and fillers, then bleached. This pulp is employed in the manufacture of container board, wallboard, tissue, towels and printing papers. In general, other types of chemical pulp are mixed with the pulp made from waste paper.

PROCESSING OF PULP

Before suitable paper can be made from any given pulp, there are a number of intervening operations, one or all of which must be applied to the pulp.

Screening—Wood pulp will have associated with it such impurities as slivers, knots, bark, cinders and other foreign material. In general these are removed by (1) gravity alone, as in rifflers, (2) screening with gravity and suction, as in vibrating screens, (3) screening with centrifugal force as in rotating screens and high-speed centrifugal equipment.

Removing Coarse Material—The first step is to remove coarse dirt by passing the pulp, at ½ to 1½% consistency (i.e., ½ to 1½% solids in suspension), over a "sliver" screen. This type of equipment employs a screening element which is a perforated steel plate mounted on a stationary, rotating, or oscillating frame. An inclined, stationary screen is generally used with groundwood. The

[35] Weber, C. G., Shaw, M. B. and O'Leary, M. J., "Papermaking Quality of Cornstalks." U. S. Department of Commerce (1935).
[36] See Chapter 38.

pulp suspension flows against the screen plate so that oversize pieces of material are taken out and subsequently removed from the plate by a chain scraper.

A rotating sliver screen, called a knotter, is used almost entirely for the coarse screening of pulp. (See Figure 6.) The machine has a horizontal, rotatable cylinder which is divided into several sections. Each section has perforated screen plates attached to its periphery, with divider plates placed inside the section in order to form a number of individual compartments. The pulp suspension enters the first section through one end of the cylinder, flowing successively into each compartment as it rotates into place. Accepted stock passes through the plates; the coarser particles are carried upward until they fall by gravity

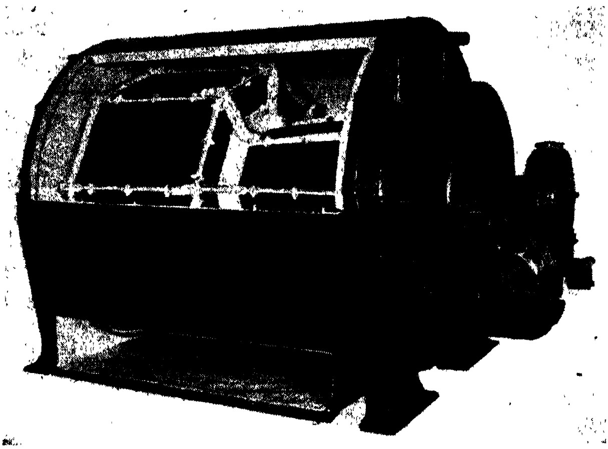

FIG. 6. Knotter Screen for Wood Pulp. (Courtesy Improved Paper Machinery Co.)

into a spout which carries them to the next section. Here they are washed further with shower water so that the accepted stock passes through the plates. The rejections are discharged from the machine.

Coarse screening is also performed on chemical and groundwood pulps with worm knotters. These machines have perforated cylindrical plates which turn slowly. The pulp suspension enters at one end and works toward the other end. Fine stock passes through the plates, while the coarser stock is gradually propelled to the outlet end by a worm or helix. During this travel, spray pipes keep the screen from clogging and wash acceptable fibers through the perforations.

The riffler settling system consists of long troughs, sometimes lined with felt, in the bottom of which are placed baffles to divide the trough into pockets. A thin pulp suspension is allowed to flow slowly through the system so that heavy dirt, such as cinders and metal, will settle out by gravity. The dirt is removed at intervals by flushing, and the accepted stock flows away over the dam at the outlet of the system.

Separation of Large from Small Fibers—After the large particles have been removed by one of the foregoing methods, additional treatment is required to separate the acceptable fiber from dirt and oversize fibers. This consists in passing the dilute pulp suspension over a flat or "diaphragm" screen, comprising a continuous series of slotted plates, set horizontally or on a slight slope. Beneath each plate is a rubber diaphragm which can be given a vertical vibrating motion, by means of an eccentric or cam action. As the dilute pulp suspension flows over the screen plates, vibration of the diaphragm induces slight suction on the plates, thus causing fine fibers to flow through the slots, while the rejects remain on the screen. The oversize fibers on the screen plates are removed by hand or mechanical scrapers, thence usually returned to equipment for refining and rescreening.

An alternate method is to use a centrifugal screen. Such a screen has circular plates provided with perforations. The screen plate drum rotates on a shaft at 300 to 400 r.p.m. The pulp suspension is introduced at one end and is thrown by centrifugal force against the plates. Acceptable pulp passes through the plates into the system; coarse fibers are discharged by a separate outlet.

One centrifuge type of refiner employs a long vertical cylinder so arranged that the pulp suspension is pumped in tangentially at the top of the apparatus. The stock travels downward with a rapid, rotating motion such that the heavier dirt is thrown against the walls of the cylinder, thence settles down to the bottom of the equipment. The clean stock passes up through the center of the cylinder and out again at the top.

Thickening—Since the screening process is performed best at low fiber concentration, the stock generally leaves the screens at 0.2 to 0.6% consistency. This operation dilutes the pulp with so much water that further pumping and conveying would be unduly expensive. Hence much of the water is now removed by a process which is known variously as thickening, dewatering, slushing, deckering, or concentrating. Here, as in certain other operations in making pulp and paper, the use of a fine wire screen is essential. This screen, known in the industry as a "wire," is generally made of a wire cloth of from 60 to 80 mesh. In some cases, as in the covering of cylinders, this cloth is supported by another coarser wire of from 15 to 20 mesh. The fine wire serves as a filter on which the pulp suspension is deposited so that the wet pulp remains on the wire and the water passes through as the cylinder turns. The effluent liquid, called "white water," is of considerable importance because it may contain a fairly large amount of fine fiber. About 60,000 gallons of water are used per ton of pulp; hence proper methods are indicated for reclaiming this fiber, as described later.

The decker is a type of thickener in which the level of water is higher on the outside of a horizontal, rotating wire-covered cylinder than on the inside, thereby causing a flow of water through the wire. As the cylinder turns in the pulp suspension, stock is caught on the wire and is carried up until it reaches the felt-covered couch roll at the top. This roll presses firmly against the cylinder mold, squeezing water from the pulp. The stock adheres to the surface of the couch roll until, as the roll advances, the stock is scraped off by a blade, called a "doctor," set against the roll.

Another type of thickener is known as the wet press or wet machine. The sheet-forming part is like that of the decker. However the couched pulp is picked up by an endless felt and carried through additional press rolls to remove more water. The pulp adheres to the top press roll where it is allowed to build up to suitable thickness, and it is then cut off deftly with a pointed stick and folded to constitute a "wet lap."

In general the decker will deliver stock at about 4 to 6% dry consistency, whereas the wet machine will produce stock of 30 to 35% consistency. If additional press rolls are used, even up to 45% consistency may be attained; and if hydraulic presses are employed, 45 to 55% is possible.

The white water obtained from these and other stockhandling machines may be filtered through wire or woven cloth to remove fiber. Another sedimentation system (Dorr type thickener) employs superimposed settling compartments which have a common center opening. When stock is fed into the compartments, it settles, whereupon it is swept slowly by moving arms into the center opening and thence to a stock tank.

Bleaching—Bleaching is the chemical process used to alter the color of a substance so that it will reflect more white light and appear brighter. The operation is usually carried out with oxidizing agents such as potassium permanganate, hydrogen peroxide, chlorine, and hypochlorites—of which the last two are by far the most important economically. Reducing agents are sometimes used. These include sulfur dioxide, sodium or calcium bisulfite, and zinc hydrosulfite.

The bleaching operation may be performed in high concentration of stock (10 to 30%) or in low concentration (4 to 7%). Of the many types of equipment employed for bleaching, the Bellmer is one of the most common. This bleaching engine comprises a divided rectangular concrete tank with a screw propeller at one end to induce circulation by driving stock down one side of the partition and back on the other.

The older method of bleaching was to bring the pulp into the bleaching engine together with the necessary amount of hypochlorite bleach liquor. As circulation proceeded, steam was injected, bringing the temperature gradually to about 100° F. In bleaching sulfite pulp the time of treatment varies from 5 to 10 hours; with soda pulp from 3 to 6 hours. However, modern procedures utilize the fact that coloring matter, once solubilized, can be removed from the system before it is fully oxidized, thereby reducing chemical cost and producing better color in the pulp.

In bleaching sulfite pulp, the most common present method is to add chlorine and water direct in the first stage; then to wash the pulp either in an acid condition or after neutralization with lime. The second stage of bleaching is accomplished by the use of calcium hypochlorite liquor. Three or four stages of treatment are generally used for sulfite bleaching, and almost invariably for kraft bleaching. These stages, which may be arranged in a number of different ways, include chlorination, bleaching with calcium hypochlorite liquor, caustic extraction, acid wash—all with suitable intermediate washing with water.

Sulfite pulp of the easy-bleaching type requires only 3% of its weight of chlorine to give a good color; hard-bleaching pulp may need up to 10%. Sulfate or kraft pulp takes from 8 to 15% of chlorine to produce a high-white color. In all cases, a suitably bleached pulp of high color should have about as much strength as that of the unbleached pulp.

Groundwood bleaching is carried out by the use of sodium bisulfite, zinc hydrosulfite, or hydrogen peroxide. However, the resultant color is poor and not permanent, and the stock will gradually assume a gray appearance.

Refining—Before pulp can be made into suitable paper, it must undergo further physical treatment. Beating is the process of separating the fibers, brushing them out into fine fibrils and causing them to absorb and hold more water—an operation often referred to as "hydration." A pulp which is unbeaten will usually allow water to drain away relatively quickly, and it is therefore termed "free"; while a well-beaten pulp will lose water slowly and is thus called "slow." Strictly speaking, refining is another mechanical treatment, generally applied after beating, which further separates and usually shortens the fibers. However it is not possible to distinguish sharply between beating and refining; moreover, the various types of equipment may produce both effects in varying degrees.

FIG. 7. Pulp Beater. (Courtesy S. D. Jones & Sons Co.)

All of these refiners operate on the general principle of passing the pulp between two contacting surfaces, one or both of which are in motion. As the fibers advance, they are rubbed against each other and against the refining surfaces. The pressure, time of contact and type of refining are dependent on the particular equipment employed and on the setting of the refining surfaces.

The beating engine, or beater, is used commonly for separating, brushing and hydrating the fibers. This equipment consists of a large oblong tub having rounded ends and with a partition or midfeather running through the center but cut off at each end so as to permit circulation up one side of the vessel and down the other. (See Figure 7.) The beater is equipped with circulating and refining mechanism, of which the beater roll is an important part. At regular intervals around the circumference of the roll are mounted steel bars parallel to the shaft and extending out several inches from the roll surface. In the bottom of the beater, directly under the roll, is the bedplate. This consists of parallel bars set on edge and separated by wooden filling. The bedplate is in a fixed position, with bars parallel to those of the roll. The setting is adjustable so that the distance between the roll and the bedplate may be controlled.

When the beater is operated, the proper amount of water is introduced, the roll is set in motion and pulp is added. The average beater will hold from 1000 to 3000 pounds of stock, dry weight, at 5 to 6% consistency. During operation the fibers circulate in the tub, passing periodically between the bars of the roll and the bedplate, thus causing the fiber bundles to be separated and the fibers to be brushed out or "fibrillated." As the beating progresses, the roll is brought closer to the bedplate so that the fibers are brushed out still further and continue to take up more water of hydration. Some mills beat for only a short time, but glassine paper mills may beat for a period of 6 hours, and rag mills often for a period of 20 hours.

Several other types of refining equipment are used in the processing of pulp. In the rod mill, refining is produced by the rolling action of iron rods within a rotating hollow cylinder.[37] Wet pulp is introduced at one end of the cylinder, traveling toward the other end with constant rubbing motion between the rods.

Operating on a different principle is the disk refiner, in which the stock is fed between parallel plates with special surfaces. One plate only may be driven or both plates may be rotated in opposite directions. Pulp stock is fed in at the center between the plates, working out to the periphery and undergoing abrading action.

Most mills employ a Jordan refiner to separate and shorten the fibers further after beating. This machine has a conical plug which turns within a conical shell. Both plug and shell are fitted with bars running lengthwise, and the assembly is so arranged that the plug may be moved as close to the shell as is desired. Stock enters the small end of the engine, passes between the opposing bars at continually increasing speed and leaves at the large end in a separated and refined condition.

Furnishing and Filling—The beater is used as a convenient place to mix filling materials, coloring matter and "sizing," or waterproofing agents, with the pulp—an operation which is known as "furnishing." While these materials may be introduced in the solid form, it is sometimes preferable to add them in solution or as a suspension in water. "Furnish" includes all material placed in the beater, whereas "fillers" are inorganic substances used in the furnish for one or all of the following reasons: (1) to improve the appearance, (2) to increase the opacity, (3) to make a better printing surface, or (4) to reduce the cost of the finished product. Since different fillers will vary in the degree of retention in the finished sheet, it is necessary to add to the beater a quantity of filler which will yield the proper amount in the finished sheet. Of the fillers most commonly used, typical additions (based on total dry weight of beater furnish) are 10 to 40% for clay, calcium carbonate or calcium sulfate, 5 to 20% for talc and from 1 to 10% for high opacity fillers, such as titanium dioxide and zinc sulfide.

Coloring—Coloring materials are of importance in the paper industry since practically all paper is colored to some extent. Nearly all coloring is done with synthetic dyes, including the acid, basic, direct, sulfur and vat types.[38] Careful selection must be made to get coloring matter which will meet, at an acceptable cost, such requirements of the paper as shade, brightness, resistance to light, acid and alkali.

When pulp is dyed in the beater, it is necessary to know how the coloring matter will attach itself to the particular type of pulp; how the color will be affected by alum and the heat of the paper machine dryers. Usually it is best to

[37] See Chapter 2.
[38] See Chapter 28.

make preliminary laboratory matchings, then adjust the shade in the beater as may be required. Surface coloring may also be employed, either in a special tub on the paper machine or in the water boxes on the calender. Since the principal objective of this method is to obtain lower color cost, basic dyes are usually employed.

Sizing—For most purposes, paper requires some degree of water resistance. The operation of imparting this quality to paper is termed "sizing." There are two methods of sizing: (1) engine sizing, where the waterproofing material is applied before the paper is formed, generally in the beater; (2) tub sizing, where the material is applied after the paper is formed, usually in a special tub set part way along in the paper machine dryers, or even after the dryers.

In beater sizing, the material commonly employed for waterproofing is rosin size. This is a product obtained by cooking rosin with soda ash and water, yielding a mixture of free rosin and a rosin soap. The thick rosin size is mixed with water to obtain an emulsion containing from 2 to 3% solids. The emulsion is then added to the beater in the requisite quantity—in the case of lightly sized papers, such as newsprint, this may be less than 0.5% solids, based on the weight of pulp; in heavily sized sheets, such as container board, up to 5% may be used. After the size emulsion has dispersed completely throughout the pulp, it is set or coagulated on the fiber by adding alum, either as a solid or in solution.

In recent years, wax emulsions, either alone or in combination with rosin size, have been employed for beater sizing.[39, 40] Starch in solid or gelatinized form is likewise used in the beater, not to impart water resistance but to add rattle and strength to the paper. Starch, glue and casein likewise find application in the tub sizing of paper. They are made up with water into gelatinous mixtures of the proper concentration, then placed in the size tub. A roll, running in the size tub, picks up the solution and transfers the desired quantity to the paper. Then the sheet is dried and calendered to impart a smooth, leathery feel. Tub sizing also imparts strength to the paper.

MANUFACTURE OF PAPER AND PAPERBOARD

The pulping processes involve the separation and refining of fibers originally present in the wood; the paper making operation comprises the re-forming and interlacing of these fibers into a continuous sheet material.

There are two principal types of machines for making paper and paperboard—the cylinder and the Fourdrinier. The Yankee and Harper are modifications of the latter. In the Fourdrinier, the web of paper is formed on a traveling wire screen; in the cylinder machine the web is formed on a rotating, wire-covered cylinder. Since there may be a number of forming cylinders, each may carry its own type of stock and later the individual sheets will be pressed together, while wet, to form a single sheet.

Fourdrinier Machine—The Fourdrinier paper machine comprises sections for forming the pulp into a sheet, for pressing water out of the wet sheet, for drying and for calendering, or smoothing, the dried paper. (See Figure 8.) On

[39] Kumler, R. W., Paper Trade J., *104*, No. 10:36-38 (March 11, 1937).
[40] Cobb, R. M., Chamberlin, D. S. and Dombrow, B. A., Paper Trade J., *97*, No. 10:35-38 (Sept. 7, 1935).

the wet end of the machine, stock of from 0.1 to 1.0% consistency emerges from the flow box over an apron and onto the traveling wire screen. This wire is a long, endless belt, up to 300 inches wide. On many machines there is an endless, heavy rubber "deckle strap" on each side of the wire, resting on the wire and traveling with it to prevent the stock from flowing out over the edges of the wire. As the wire moves forward, water is drawn through by gravity, later assisted by vacuum from the suction boxes over which the wire travels. These forces cause a sheet of wet pulp to form on the wire. During this process of water removal, another important action is going on. Since the natural flow of water and stock onto the screen tends to lay down fibers lengthwise in the direction of travel and thereby to produce a sheet of unbalanced strength, a short, jerky cross movement (the "shake") is imparted to the wire, thereby promoting better interlacing of the fibers.

After the preliminary formation, the wet sheet goes over the couch roll, whose function is to remove more water and to pack the fibers firmly so that the unsupported sheet can then leave the wire. Now the web is picked up by an endless woolen blanket or "felt" which carries the sheet through a pair of squeeze rolls called the first press. More water is removed at this point and the fibers are compacted in the sheet. Then comes the second press, similar to the first. On some machines there may be a third press.

Drying the Sheet. Now the sheet containing 60 to 70% water leaves the supporting felt and passes to the dryer section. This consists of a series of cast iron cylinders, usually arranged in two horizontal tiers, the rolls of the upper tier being placed above the openings separating the rolls of the lower tier. The dryer rolls are heated by low pressure or exhaust steam, which is introduced at the dry end of the machine and then passes countercurrently on through the system. As condensation of steam takes place, at the wet end of the machine, the condensate is returned to the boilers for makeup. In order to maintain progressive and constant increase in temperature on the dryers from the wet to the dry end of the machine, the several sections of cylinders are equipped with automatic controls which regulate the steam pressure in their respective sections.

The ventilating system around the dryers is of great importance in supplying fresh air of low humidity which, on subsequent heating, becomes saturated with water as it passes over the wet paper. Most machines are equipped with hoods over the drying section, to induce better circulation of air, to keep down condensation in the machine room and to reduce the cost of drying. Paper enters the dryers with from 60 to 70% moisture and leaves the machine with 5 to 8% moisture. Thus, in the drying operation about 2 pounds of water are removed for each pound of dry paper produced. With a modern newsprint machine 15 feet wide and traveling at 1000 feet per minute, water removal on the dryers would be at the rate of 200 tons per 24 hours. This would require the circulation of about 170,000 cubic feet of air per minute. During the process of drying, the wet sheet of paper shrinks, both crosswise and lengthwise. On a machine yielding a finished sheet of 100 inch width, the cross shrinkage may be as much as 6 inches. Shrinkage in the machine direction must be compensated for by varying the relative speeds of the sections of dryers.

Another method of drying which is finding favor, especially for heavy sheets, involves the use of vacuum. The wet paper enters a vacuum chamber through rolls which act as seals, then passes over dryers maintained at low temperature. Since the vacuum in the chamber is approximately 28 inches, the water boils off at about 100° F. The resultant paper has better quality and the drying cost is less than with drying under atmospheric pressure. This system is also used for drying pulp.

In some paper mills there is a size tub, or press, set at a suitable location part way down in the dryer section, or even after the dryers. The tub, usually made of wood, is provided with rolls so arranged that they dip into the solution of sizing material which is placed in the tub. This solution is then brought onto one or both sides of the paper and the excess material is taken off as the paper passes between the squeeze rolls.

Calendering. When the paper has been dried, the surface is generally rough and irregular. The next operation is that of compacting and smoothing the sheet much as the housewife irons clothes. The equipment for finishing the paper is a calender stack consisting of a vertical assembly of iron rolls (usually 8 or 9) resting one upon the other. As only the bottom roll is driven, the others acquire motion by contact with this roll. In operation, paper is started at the top of the stack, passes downward and comes out from the bottom. Water is often added during the calendering, through the medium of the "water box," which is so located that water contacts the surface as the paper enters the stack. Heat is generated by friction of the rolls on each other, or it may be supplied through steam rolls on the calender.

After this smoothing operation, the sheet goes to the reel where it is wound into a large roll of finished paper. When one roll has been built up to the proper diameter, the machine operator breaks the sheet and starts another roll. Meanwhile the finished roll is being drawn through a slitting machine where the paper is cut into rolls of proper width and diameter.

Cylinder Machine—Paper made on the Fourdrinier machine has the same composition throughout, and it is of relatively light weight, although sheets of up to .016" thickness are sometimes produced. When heavy paper or paperboard is to be made, two or more layers of sheet material are formed simultaneously on wire-covered cylinders and then pressed together while still wet. This process of manufacture is made possible by the cylinder machine, an invention of the early part of the 19th century.

The same principle of sheet formation is used on both the cylinder and the Fourdrinier machines, but the mechanism of the wet ends is quite different. The cylinder machine usually has from 4 to 7 parallel vats into which the dilute stock suspension flows. In each vat there is a wire-covered cylinder, called a mold, which rotates in the stock. Water passes through the wire leaving a layer of stock on the wire; and as the cylinder turns further, this layer comes in contact with the bottom of a traveling felt, to which the wet sheet adheres. The felt and wet paper pass under a couch roll which presses out some of the water. Then as the felt and paper travel on further, another layer of wet paper is picked up from the next mold and pressed firmly onto the first layer. This procedure is repeated for each mold until a composite wet sheet or board has been formed. The board then passes through several pairs of press rolls so operated as to remove the water effectively without injuring the formation of the wet sheet.

When it reaches the dryers, the board usually contains about 65 to 70% moisture. Since the sheet is relatively thick and strong, there is less difficulty in carrying it over the dryer section than with the Fourdrinier machine; but the heavier weight of the sheet requires higher temperature on the dryers and greater pressure on the smoothing calenders.

The cylinder machine is versatile in operation since different kinds of stock may be used on each mold if desired. Consider, for example, a six-cylinder machine making board for cartons. Two cylinders forming the back of the board might be furnished with a light-colored combination of unbleached sulfite and groundwood pulp; the two middle cylinders might have reclaimed paper or board; and the "top liner" cylinders might have a furnish of bleached sulfite to give a good appearance to the sheet. Suitable bonding of the plies to one another requires, however, that the various stocks shall not be too dissimilar in characteristics.

Yankee Machine—The Yankee machine, or Flying Dutchman, for making paper has either a Fourdrinier or cylinder mold on the wet end, followed by the customary presses. The individual feature of this machine lies in the single large dryer, usually from 9 to 15 feet in diameter. When paper is run on this machine, the high polish on the surface of the dryer is imparted to the contacting surface of the sheet, producing what is called a machine-glazed paper.

Harper Machine—The Harper machine resembles the Fourdrinier except that the flow box is placed near the presses; the wire travels away from the presses instead of toward them. The paper which has been formed on the wire is picked up on a long felt and then carried back to the couch rolls. Since the paper is supported all the way until it enters the presses, and sometimes even to the dryers, this machine is particularly suitable for very light weight papers such as cigarette paper and tissues.

Production of Boards—The production of very heavy boards, such as wallboard, ranging from one-eighth to one inch thickness, may be carried out in two ways: (1) by making a sheet of maximum thickness (e.g., 0.060″) on a cylinder machine and then laminating a number of these sheets to produce the desired caliper, (2) by forming a very thick wet sheet in one operation, then pressing and drying it. In many respects the latter method gives a better board because it is more thoroughly bonded together. Dependent on the freeness of the pulp, such a board may be made either on a Fourdrinier wet end or on a cylinder mold of the continuous vacuum filter type. As the wet sheet is usually very thick, it is preferable to have a stock of high freeness so that the water will drain away readily. The forming part of the machine operates at a relatively slow speed. The sheet passes through press rolls to take out the free water, and it is then cut into suitable lengths. The drying is accomplished by holding the board between heated platens in a hydraulic press or by passing the sheets through a long, heated tunnel supplied with carrying rolls.

CONVERSION OF PAPER

There are two types of operation for finishing or converting paper: (1) those which alter the size and form of the sheet without changing the composition, (2) those which alter the composition of the sheet by adding matter. The first type of conversion is that which goes on in the finishing room of an average paper mill—cutting, rewinding, supercalendering, plating and embossing. The second type involves such operations as coating, gumming, waxing, lacquering and printing.

Cutting—Paper or paperboard comes from the paper machine in the form of sheets or rolls. In most cases it is necessary to adapt the size and shape to the purpose for which the products are to be used. Writing paper must be cut to the proper size, inspected and packaged; adding machine rolls must be rewound to the correct width and diameter on small cores.

Rewinding is carried out by taking the large rolls of paper or board and passing them through a machine which slits the sheet to produce rolls of the proper width, diameter and degree of hardness. Cutting paper into sheets is accomplished on a machine equipped with unwinding stands and knives for cutting both lengthwise and crosswise of the sheet travel. Usually from 8 to 12 rolls of paper are mounted on the reel stand, from which they are fed simultaneously through the cutters. The rotating circular-disk slitter knives cut the sheet to proper width; another rotating knife operating against a stationary bed knife cuts the sheet across the direction of travel to the proper length. These sheets may then be squared accurately or reduced to smaller size by the trimmer. In this machine the pile of paper is held firmly in place while a heavy knife cuts entirely through the pile.

Finishing the Surface—Supercalendering is the operation of imparting high density and finish to a sheet of paper or paperboard. The calendered paper, as compared with uncalendered, has a smoother, better printing surface; is less absorbent of ink, wax or lacquer; may have considerably better transparency as, for example, when greaseproof paper is calendered to make glassine. Supercalenders are similar in construction to paper machine calenders in that they consist of a series of from 3 to 14 rolls arranged in a vertical stack. However, every other roll is of chilled iron and the alternate rolls are of either paper or cotton.

For some sheets, such as certain writing and wrapping papers, it is desirable to have a surface which has been roughened rather than smoothed. This is accomplished either by plating or embossing. In the plating operation, sheets of paper are alternated in a pile with linen cloths or other materials whose surface is to be imparted to the paper. Metal sheets are laid on the top and bottom of the pile, after which the assembly is passed back and forth between metal rolls, thus transferring the design to the paper. In the embossing operation the paper is fed in rolls or sheets through a pair of rolls engraved with the desired design.

Coating—While the foregoing finishing operations do not add material to the paper, there are other converting processes which do. The first coating, to obtain a better printing paper, was carried out commercially about 1880. The early coated papers were surfaced with clay, but many other pigments are used today, including chalk, satin white, lithopone and titanium dioxide. The pigment is mixed with water and a binder, such as casein or starch. This slurry is then applied to the paper directly on the paper machine or on a separate coating machine. In the latter method the wet, coated paper passes through a dryer of the festoon type, or one in which the paper is floated through with heated air. The dried sheet is calendered to impart a smooth finish.

Gumming—Gummed tape is used widely for sealing containers and packages, so it must meet certain specifications—quick tack, good strength and permanence of the adhesive, and the ability to lie flat. The base paper may be either unbleached or bleached kraft or bleached sulfite. The adhesive, usually animal glue or dextrin, is made into a solution of proper consistency, applied by a pickup roll to the paper, then the coated sheet is dried by passing through a festoon or tension dryer.

Waxing—Modern packaging methods require paper which has high moistureproofness, gloss and heat-sealing qualities. One of the cheapest and best ways of securing these properties is to coat paper with hot wax, usually of a paraffin base. There are two principal methods of applying the wax: (1) wire waxing, in which each side of the sheet is alternately coated with hot wax and then doctored free of excess wax by means of a rigid wire; (2) roll waxing, in which the whole sheet is plunged into a bath of hot wax, then through a pair of squeeze rolls, where the excess wax is removed. Gloss is imparted to the waxed paper by passing it quickly into cold water or over chilled rolls.

Other hot coating materials and methods of applications are employed for making sheets of interesting characteristics as to moistureproofness and heat-sealing. Usually wax is one component of such hot melt compositions, the other being a thermoplastic material, such as rubber or a resin. The resultant mixtures may have high viscosity, in which case they are applied to the paper by special coating machines employing heavy rolls.

Lacquering—Quick-drying lacquers are employed on papers to produce gloss, moistureproofness and heat-sealing. There is a large variety to choose from, including those with a base of cellulose ether or ester, and the types made from rubber hydrochloride or other synthetic resins. Generally the lacquers are applied to papers of high density and close formation, such as glassine. Thus an excessive absorption of lacquer is avoided; the drying time is reduced and final cost is kept down. The lacquered sheet is passed through a drying tunnel in which the volatile organic solvent is driven off. In certain cases the solvent is wasted but generally some type of solvent recovery is employed.

GRADES OF PAPER

There are a number of methods by which paper may be classified: (1) by the type of furnish used in making the paper, e.g. sulfite or kraft paper; (2) by some particular property, e.g. greaseproof paper, absorbent paper; (3) by the use to which the sheet is put, e.g. bag paper, newsprint. Since these methods are generally used interchangeably, paper nomenclature is not necessarily logical, even though it has become firmly established.[41] The following designations will furnish a relatively simple basis for grading paper.

Tissue—Under this term are grouped the lightest weight papers, generally made on a Yankee machine. Examples are napkins, light weight wrappings, toilet papers.

Wrapping—Because of the strength and pliability usually required of these papers, the furnish often contains kraft pulp or a good grade of sulfite pulp

[41] Clark, F.C., Paper Trade J., *98*, No. 8:71-108 (Feb. 22, 1934).

These papers are employed for manual and machine packaging and for the production of bags and envelopes. Butcher's manila and breadwrappers illustrate this group.

Writing—As used in the paper industry, this term includes a wide range of papers, generally made from rag or sulfite pulps. Among these are the various kinds of stationery, typewriter sheets, ledger and document papers.

Printing—Under this heading are gathered an important group of papers, ranging in furnish from high groundwood content to almost pure rag content. The weight, strength factors and optical properties vary widely, dependent on the use requirements. Characteristic of this class are newsprint, catalog, rotogravure and Bible papers.

Book—A special class of printing papers is employed for making the better books and magazines, since the important characteristics are printability and appearance. Sulfite and soda pulp constitute most of the fiber furnish; usually little sizing is added, but small to large quantities of filler are employed.

Building—These thick, bulky papers, made of reworked stock sometimes mixed with asbestos, are employed in construction work. They include sheathing papers to prevent wind from penetrating buildings; felt papers, unsaturated for heat insulation or saturated with asphalt to make roofing material; deadening felts for acoustic properties in walls and floors.

Boards—By far the largest production of the industry falls in this class. Generally these sheets, of greater than .010″ thickness, are made on a cylinder machine. The subdivisions are numerous, including container, Bristol, binder, bottle cap, chip and wallboard.

ECONOMICS OF THE INDUSTRY

The production, in the United States, of the important grades of paper is shown in Figure 9; and the price range of various papers is shown in Figure 10.

The profitable manufacture and sale of any given pulp and paper product is dependent on the cost of that product laid down at a certain point and on the competitive situation existing both in the industry and with respect to other industries. In the manufacture of pulp and paper these factors will determine the location of mills, because of nearness to raw materials, cheap power or markets. A new source of material or a change in tariff may cause a shift in the industry; the manufacture of a new grade of pulp or paper may bring in additional plants and thus cause further changes in existing plants; a new development in a competitive industry may give an incentive for the reduction in costs of certain products.

When pulp and paper manufacture began in the United States at the start of the 18th century, the chief fibrous raw material was rags, and the operations were conducted by hand. Most of the mills were located in and around Philadelphia. At that time rags sold for about 4 cents per pound. There seemed to be a continuous dearth of this material, yet at the beginning of the Revolutionary War the price was but 6 cents per pound. In 1778 the price had advanced to 16 cents and in 1780 to 72 cents.[42] No wonder that people were searching intensively for cheaper raw material!

[42] "Two Hundred and Fifty Years of Paper Making in the United States," p. 7.

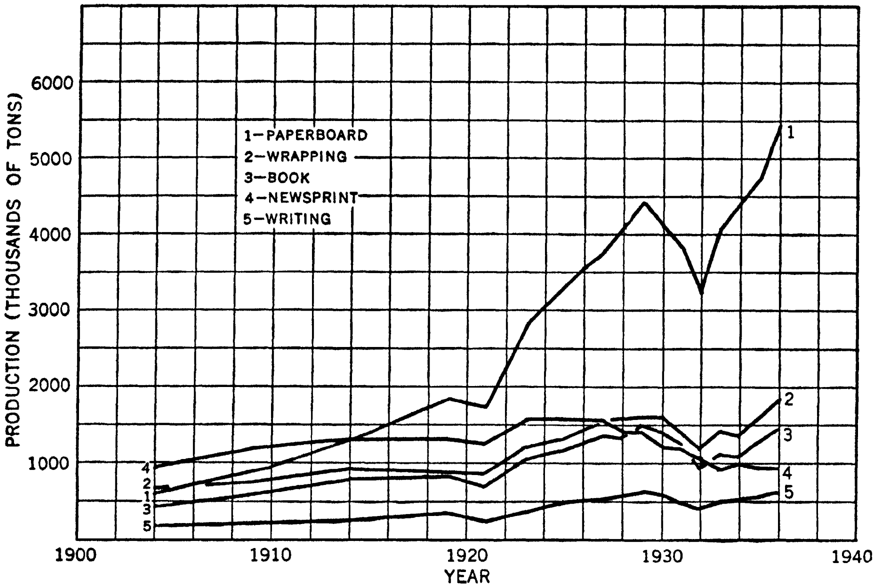

FIG. 9. U. S. Production of Paper and Paperboard by Kinds. ["U. S. Pulp and Paper Industry" (1938), U. S. Dept. of Commerce]

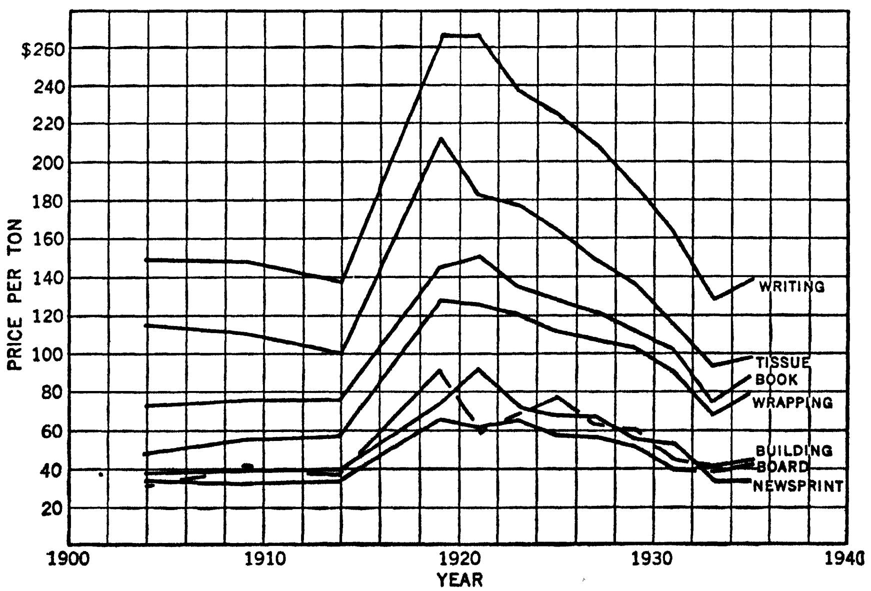

FIG. 10. Price of Various Grades of Paper in the U. S. ["U. S. Pulp and Paper Industry" (1938), U. S. Dept. of Commerce]

Shifts in Production Centers—Shortly after the turn of the 19th century, wood gradually came into use for making pulp, and paper machines were manufactured in Connecticut. These developments caused mills to locate in New England where they would be close to the source of raw materials, machines and markets. As the population of the country increased, there was a demand for additional grades and for increased tonnage of paper products. The westward movement of population caused the establishment of mills in the states bordering on the Great Lakes, close to the developing markets.[43] Because of the available supply of raw material, straw paper was made in Ohio, Indiana, and Illinois; Michigan concentrated on book papers; Wisconsin and Minnesota produced pulp and paper by the mechanical and sulfite processes. About 1910 the manufacture of kraft pulp and paper started in Wisconsin and Michigan.

A year later the tariff was taken off newsprint and there was a rush to build newsprint mills in Canada. Since that time, the shift to Canada has been so extensive that at present only one-third of our own newsprint consumption is made within our borders and many newsprint mills have been forced to make other grades. The recent development in the use of southern woods may cause still another shift in newsprint production.

At the beginning of the first World War we imported from abroad certain materials such as pulp, clay, rags and dyes. When a shortage came about in these materials and as the demand for paper grew, there was a sharp increase in the price of materials and of finished products. Nevertheless it was this situation which brought about such developments as the building of a strong dye industry, the improvement of American clays and the production of new pulps.

As the demand grew for more, better and cheaper wood pulp, there were further shifts. In the Pacific Northwest, lumber companies found it profitable to make sulfite and kraft pulps from sawmill waste or from species of timber more suitable for wood pulp than for lumber. Freight rates through the Panama Canal were so low that pulp could be laid down cheaply on the Eastern seaboard. Then came the realization that the South apparently had advantages in the costs of wood, labor, factory construction and raw materials. The possibility of producing sulfite pulp from southern woods, and the improvements in kraft bleaching, brought about the establishment of many mills in southern states. Yet with all these movements, New York State still has the greatest number of pulp and paper mills in the country and manufactures the greatest value of pulp and paper products, with Wisconsin ranking second. In these states, important factors are cheap power, good water and proximity to markets and to supplies of pulpwood in the United States and Canada. (See Figure 11.)

Growth of the Industry—This growth of the industry has been occasioned by the increased demand for cheaper and better goods. In 1770 the whole industry produced about half a million dollars' worth of paper; today it produces well over a billion dollars per year. In 1880 the usage of paper in the United States was 20 pounds per person; in 1917 about 120 pounds; and in 1935 a little over 220 pounds. (See Figure 9.) No other country in the world even approaches this consumption. Having only 5% of the world's population, the United States still uses 60% of the world's paper production. The capital investment in pulp

[43] Everest, D. C., Paper Mill, *80,* No. 10:2 (March 8, 1930).

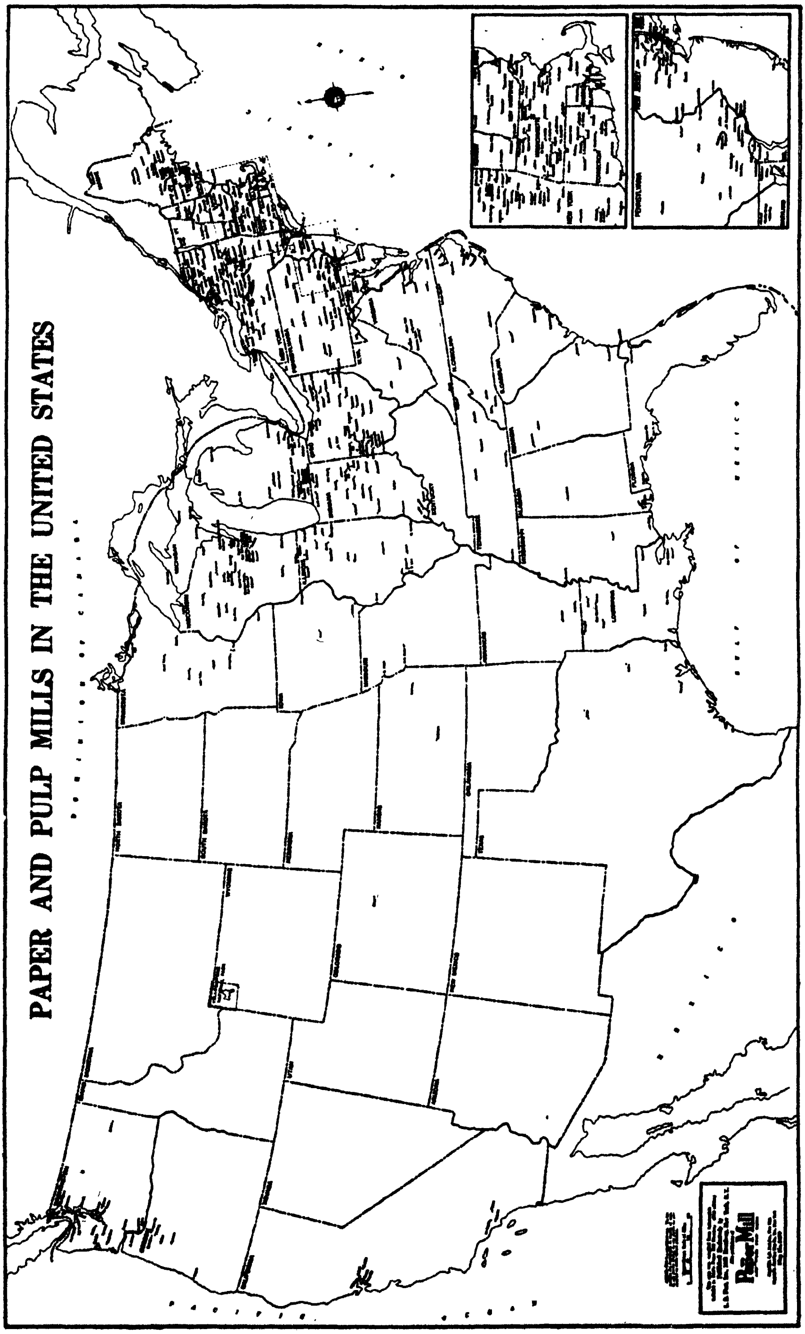

FIG. 11. Paper and Pulp Mills in the United States.

and paper manufacture for 1933 was over $1\frac{1}{2}$ billion dollars, or more than $2 for each $1 of annual output.[44] This high ratio was further indicated by the fact that the industry had an investment of $15,000 for each workman which it employed.

In normal times there is an overcapacity for production of at least 25%. This lends an urge to expand the present uses of paper and to develop new papers with better properties, such as aging, wet strength or printing. Many of these new products will bring direct competition with other industries. For example, in the past twenty years the production of paperboard has tripled, due largely to the fact that the fiber shipping container has supplanted the wooden box. This results in low shipping costs and it serves to utilize about 4 million tons per year of waste paper—over one-fourth of the whole requirement of fibrous raw material for the industry. Paperboard packages for dairy products, such as milk, butter, cheese and ice cream, have replaced wooden, metal and glass containers. Paper towels and napkins have supplanted cloth for many uses.

Competitive Materials—At the same time the paper industry has experienced competition from the products of other industries. The introduction of cellophane[45] created a new philosophy in the merchandising of certain goods, permitting display and protection at the same time. A cellophane sheet of inferior quality sold at the extravagant price of $2.65 per pound in 1924. Ingenuity, imagination and perseverance brought about such improvements in the sheet that the use increased enormously. By 1940 the price of cellophane had dropped to 33 cents per pound.

The large market for cellophane has been an incentive for the development of other transparent sheets. Cellulose acetate solution is spread on a highly polished drum, dried to film form and taken off as clear, transparent, waterproof sheeting. Recently ethyl cellulose has been cast into a transparent film of unusual stability to light and water. Rubber hydrochloride in thin sheets possesses good transparency, flexibility, stretch and moistureproofness. Casein film has been made semicommercially, and even colloidal clay can be formed in thin sheets suitable for electrical insulation.

The Stimulus to Research—Research products of competing industries have stimulated increased activity in the field of pulp and paper manufacture. Prior to the first World War secrecy was the watchword in such operations; but the application of science and engineering during the war brought about a community of interest between the manufacturer and the technical man. The former already had a well-knit trade organization, founded originally in 1878 as the American Paper Manufacturers' Association and later converted to the present American Paper and Pulp Association. In 1915 a group of technicians and operators formed the Technical Association of the Pulp and Paper Industry to promote research and interchange of ideas. These organizations have had an important effect in building up the industry.

The applications of science and engineering in pulp and paper manufacture have brought about improved operation and notable progress in the manufacture of new and better products. Unusual circumstances, such as the first World

[44] Stevenson, L. T., "The Background and Economics of American Papermaking," p. 25, Harper (1940).
[45] See Chapter 38.

War, will cause a temporary increase in prices but, generally speaking, research will cause a reduction in prices. Note in Figure 10 that the trend of paper prices was steadily downward in the 1920's, a period when average commodity prices were either constant or rising. Hence there is an increasing demand for technically trained men, who are now employed in all phases of the industry. Various educational institutions have introduced courses in pulp and paper making, including universities in the states of Maine, Michigan, Idaho, Iowa, New York and Washington. In 1910, at the University of Wisconsin in Madison, the Federal Government founded the Forest Products Laboratory—an institution which has become a center of information on wood and its derived products. In 1930 a group of progressive manufacturers established The Institute of Paper Chemistry in Appleton, Wisconsin. Selected graduates of other colleges and universities are given intensive training in the classroom and the plant whereby they are prepared for positions in pulp and paper organizations. Many research laboratories have also been built in the mills themselves so that steady progress is assured for the industry.

READING LIST

CHEMISTRY

Schorger, A. W., "The Chemistry of Cellulose and Wood," McGraw-Hill Book Co., Inc., 596 pp. (1926).

Sutermeister, Edwin, "Chemistry of Pulp and Papermaking," third edition, John Wiley & Sons, Inc. (1941).

DEFINITIONS

"Dictionary of Paper," published under the auspices of the American Paper and Pulp Association, 365 pp., George Banta Publishing Co., Menasha, Wis. (1940).

ECONOMICS

Stevenson, L. T., "The Background and Economics of American Papermaking," 236 pp., Harper & Brothers Publishers (1940).

GENERAL

"The Manufacture of Pulp and Paper," prepared under the direction of the Joint Executive Committee on Vocational Education representing the Pulp and Paper Industry of the United States and Canada, McGraw-Hill Book Co., Inc.

Vol. I. Mathematics, Reading Drawings, Physics.
Vol. II. Mechanics, Hydraulics, Electricity, Chemistry.
Vol. III. Preparation and Treatment of Wood Pulp.
Vol. IV. Rags, Waste Papers, Loadings, Sizing, Coloring, Mill Equipment.
Vol. V. Paper Machines, Paper Coating, Finishing, Testing.

Studley, J. D., "United States Pulp and Paper Industry," 99 pp., U. S. Department of Commerce (1938).

West, C. J., "Bibliography of Papermaking," 1900-1928, 1928-1935, and annually thereafter, Lockwood Trade Journal, Inc., and The Technical Association of the Pulp and Paper Industry.

HISTORY

Hunter, Dard, "Papermaking Through Eighteen Centuries," William E. Rudge (1930).

Weeks, L. H., "A History of Paper Manufacturing in the United States, 1690-1916," 355 pp., Lockwood Trade Journal, Inc. (1916).

CHAPTER 38

CELLULOSE INDUSTRIES

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The Cellulose Industries—In the broad meaning of the term the cellulose industries constitute one of the oldest and largest groups of industries in the world today. If wood be regarded as an impure cellulose, which is what it really is, its use is found well established at the dawn of history. Cotton, linen, and flax, which are cellulose in a relatively pure form, also date back in their use for thousands of years. Even paper, another quite pure form of cellulose, has been known for over a thousand years. It is obvious that the products of these three industries alone—lumber, textiles, and pulp and paper—comprise a volume of output rivaled by few others.

In addition to these basic cellulose industries there has gradually developed during the past seventy-five years a further group of industries based on the effect of various chemicals on cellulose and many of these have now reached very respectable proportions. Included in this group are such products as vegetable parchment; vulcanized fiber; cellulose ester plastics (including both nitrate and acetate) and articles made from them including toys, toilet articles, and various novelties; photographic films; lacquers and finishes for automobiles, furniture, and interior woodwork; artificial leather; smokeless powder; rayon; safety glass; cellophane; and sausage casings. This chapter is limited to a consideration of this second group of industries, involving chemical treatments of purified cellulose. Smokeless powder, however, is not included since this is discussed in the chapter on explosives.[1]

Definition—Cellulose is the characteristic material of the cell wall of the vegetable kingdom where it serves as the structural frame work. It occurs in nature in the highest proportion in cotton fibers (about 90 per cent), but is to be found to a lesser extent in all plants. Coniferous woods contain about 60 per cent while cereal straws contain 40 per cent of cellulose. It has the empirical composition $(C_6H_{10}O_5)_n$ and thus belongs to the general class of carbohydrates.

Cellulose Raw Materials—For the various chemical treatments discussed in this chapter a relatively pure form of cellulose is required. Formerly paper made from rags or even bleached cotton in the form of roving was considered essential. Later cotton linters became the source of a good deal of the cellulose used for chemical purposes. By linters is meant those fibers which still remain on the cottonseed after the longer fibers suitable for spinning into cotton yarn

[1] See Chapter 32.

have been removed. Usually a first cut of linters is taken from the seed and used for such purposes as upholstery and mattress stuffing. The second cut is composed of still shorter fibers and this is the grade which is purified to serve as a chemical raw material. The purification consists of cooking with dilute caustic soda in large digesters followed by thorough washing and bleaching. In the United States the annual production of linters for 1937, 1938 and 1939 was 1,357,296, 1,754,516 and 1,329,208 bales of 500 pounds each respectively.

During the last twenty years cellulose prepared from wood by the sulfite process[2] has been used extensively in the manufacture of rayon by the viscose process and for the manufacture of other cellulose derivatives. The chemical pulp produced for this purpose is only about 2 per cent of the total production of wood pulp in the United States, but is nearly 9 per cent of the sulfite process pulp production.

The sulfite process which dissolves the non-cellulosic constituents under pressure in an acid calcium sulfite liquor is the principal method for the production of chemical pulp. Recently hardwood sulfite cellulose has been used experimentally for the manufacture of cellulose derivatives, particularly viscose rayon. This development opens for future use an extensive source of chemical pulp. Recently further purification of this pulp has made it suited for nitration and acetylation.

PROPERTIES OF CELLULOSE

Physical Properties—Outwardly cellulose is a white amorphous material, although X-ray studies have shown it to be a colloidal complex characterized by oriented molecular micellæ. It generally occurs in fibrous form but the fibers may vary from 0.5 to 200 mm. in length and from 0.01 to 0.07 mm. in diameter depending upon the source from which the cellulose is obtained. Its specific gravity is between 1.50 and 1.53,[3] dielectric constant 7, specific heat in the dry state about 0.32,[4] and heat of combustion to carbon dioxide and water 4208 calories. It burns quietly with a luminous flame and is a poor conductor of heat and electricity.

Cellulose fibers absorb liquids readily, the air from the cell canals being displaced. This absorptive power is increased by proper preparation of the fiber and is an important factor in several industries.

Heat Effects—In general it may be said that cellulose is resistant to the action of moderate dry heat, although it has been shown by heating cotton in air in a sealed tube at 80 to 100° C. for several weeks that even at these moderate temperatures cellulose combines slowly with oxygen with a resulting deterioration in strength. Everyone is familiar with the scorching of paper or cotton cloth which results if somewhat higher temperatures are used,[5] and if the temperature is raised still further, decomposition sets in and at about 270° C. this becomes an exothermic reaction with the production of considerable quantities of gas.[6] The yields of the various distillation products are given in Table 1.

[2] See Chapter 37.
[3] Marsh and Wood, "An Introduction to the Chemistry of Cellulose," p. 37, D. Van Nostrand Co., Inc. (1939).
[4] Schorger, "Chemistry of Cellulose and Wood," p. 21 (1926).
[5] Matthews, Color Trade Journal, *12*, 255 (1923).
[6] Hurd, "The Pyrolysis of Carbon Compounds," pp. 278-283, Reinhold Publishing Corp., New York (1929).

TABLE 1—PRODUCTS OF DESTRUCTIVE DISTILLATION OF CELLULOSE

	Per Cent
Charcoal	20-40
CO_2	10
C_2H_4	0.2
CO	4
CH_4	0.3
Acetone	0.2-0.3
Acetic acid	3.1
Organic substances in acetate	8-5
Tar	7-4
Water	34

It should be noted that no methanol is produced in the dry distillation of cellulose and only a small amount of tar.

It has been shown [7] by heating cellulose *in vacuo* that the first product in the decomposition of cellulose by heat is probably glucose, which in turn at once loses a molecule of water and becomes levoglucosan. As the heating is continued, secondary and tertiary reactions set in, which account for the formation of the various materials mentioned in the above table and also for the formation of the many substances (particularly phenols) which have been isolated from the tar. Cellulose heated at high temperature under pressure gives a coal-like residue which, when highly compressed, resembles anthracite.[8]

Solubility—Cellulose does not form a true solution in any liquid, but it can be colloidally dispersed in certain salt solutions. However, some change beyond mere dispersion takes place, the exact nature of which is not fully understood because cellulose recovered from such a dispersion appears more highly hydrated than the original material. One of the well-known solvents for cellulose is ammoniacal cupric oxide. The exact mechanism of the solvent action is somewhat in doubt, some [9] considering it to be strictly a chemical process while others [10] believe that it is a case of adsorption. Cellulose is also soluble in a hot 40 per cent aqueous zinc chloride solution and in a cold 33 per cent zinc chloride solution [11] in hydrochloric acid. Other combinations which exert a peptizing action on cellulose are aqueous solutions of the thiocyanates of calcium, magnesium, strontium and lithium; and the double thiocyanates of sodium with zinc, mercury, cadmium or manganese. Various theories have been suggested to account for this peptizing action such as a loose union between the hydrated salt and surface of the cellulose molecule or even actual compound formation. Williams [12] has shown that cellulose is dissolved by neutral or very slightly acid solutions of any salt with the following physical characteristics:

Viscosity greater than 3.3 times the viscosity of water at 20° C.
Boiling point above 133° C.
"Positive heat of dilution value between well-defined limits."

[7] Pictet and Sarasin, Helvetia Chim. Acta., *1,* 87-96 (1918).
[8] Bergius, Chem. Ztg., *37,* 977, 1236 (1913); Z. Electrochem., *19,* 858-860 (1913); Waterman and Perquin, Rec. trav. chim., *45,* 638 (1926).
[9] Hess and Messmer, Koll. Zeit., *36,* 261 (1925); Ber., *55B,* 2432 (1922); Neale J. Tex. Inst., *16,* 363 (1925).
[10] Baur, E., Koll. Zeit., *36,* 257 (1925).
[11] Hanausek, Chem. Zeit., *18,* 441 (1894).
[12] Manchester Memoirs, 65, No. 12 (1921).

It has been found possible to dissolve cellulose in caustic soda[13] (4-10%) at temperatures of −5° to −10° C. Strong organic bases of the type of quaternary ammonium compounds are also solvents for cellulose.[14]

Chemical Properties—As they occur in nature, cellulose fibers are chemically relatively inert. This inertness combined with physical toughness is responsible for the marvelous suitability of cellulose for the part which it plays in nature. Cellulose is resistant to atmospheric conditions, which makes possible the use of wood as a structural material. It resists water, both hot and cold, as well as the action of dilute alkalies, soaps, and mild bleaching agents. This permits the use of cotton and linen as textile materials.

Cellulose absorbs moisture from the atmosphere with which it is in contact and is therefore to be classed as hygroscopic. The amount of moisture absorbed depends not only on the humidity of the surrounding atmosphere but also on the source of the cellulose and the treatment it may have received in purification. For example, the "water of condition" of cotton at 20° C. and 50 per cent relative humidity is 6 to 7 per cent and may rise to 21 per cent in an atmosphere saturated with moisture. On the other hand, cellulose in the form of viscose rayon at 70° F. and 65 per cent relative humidity absorbs about 14.5 per cent moisture.

Properties in Alkaline Solution. Dilute alkaline solutions at normal temperatures have practically no effect on cellulose, but as the temperature and pressure are raised, even a 1 per cent solution of sodium hydroxide exerts a dissolving action on cellulose. The solubility also increases as the strength of the alkali is increased.[15]

When cellulose is treated with cold concentrated caustic soda it swells.[16] If the fibers are kept under tension, when treated and during the subsequent washing and drying processes, varying degrees of luster may be produced together with increased tensile strength.[17] This treatment was discovered by Mercer and for this reason is known as mercerization. In carrying out the process on a large scale there is a pretty balance between the temperature and the concentration of the alkali. At a temperature of 15 to 20° C. an 18 to 25 per cent solution of sodium hydroxide would be used, while at 2 to 9° C., a 12.5 to 16 per cent solution would work equally well. In practice it is usually the custom to keep the caustic solution cool.

Effect of Mineral Acids. When cellulose is placed in contact with dilute mineral acids at normal temperature, it slowly loses its structure, and if the action is continued long enough the cellulose finally breaks down to a powder. This action proceeds much more rapidly if the acid is warmed. The product is known as hydrocellulose, and was long considered to be a chemical individual, but more recently it has been shown to consist of unchanged cellulose and certain decomposition products which are soluble in alkali.

With concentrated acids (for example nitric acid), with acid anhydrides, and with acid chlorides, cellulose behaves like an aliphatic alcohol with three hydroxyl

[13] Lillienfeld, Brit. Pat. 212,864; Hall, J. Soc. Dyers Colourists, *45*, 98 (1929).
[14] Lieser and Leckzyck, Ann., *522*, 56 (1936); Lieser, Ann., *528*, 276 (1937).
[15] Tauss, Dinglers polytech. J., *276*, 411 (1890).
[16] Mercer, Brit. Pat. 13,296 (1850).
[17] Lowe, Brit. Pat. 20,314 (1889), 4,452 (1890).

groups and forms cellulose esters. The nitric acid and acetic acid esters are considered more fully, later on in this chapter.

Effect of Oxidizing Agents. When treated with oxidizing agents, cellulose is converted to a material known as oxycellulose. The exact nature of this material depends upon the kind of oxidizing agents used and the conditions under which the action takes place, but in every case the oxycellulose consists of a mixture of cellulose with various decomposition products. The oxidized part shows marked reducing properties and is soluble in alkali. The extent to which a given sample of cellulose reduces Fehling's solution is sometimes taken as a measure of the extent to which it has been oxidized.

Alcoholic Properties. Cellulose further exhibits its alcoholic properties when treated with caustic soda. In contact with a sodium hydroxide solution of at least 16 per cent concentration, cellulose combines with the sodium hydroxide in the proportion of two $C_6H_{10}O_5$ residues to one NaOH.[18] When this compound is treated with carbon bisulfide it reacts similarly to sodium ethylate to form a product known as cellulose xanthate.[19]

$$C_{12}H_{19}O_9ONa + CS_2 = C\begin{cases} \diagup SNa \\ = S \\ \diagdown O - C_{12}H_{19}O_9 \end{cases}$$

Ether Formation. Cellulose also forms ethers when treated with an alkyl halide or alkyl sulfate, preferably after a preliminary treatment to convert the cellulose into a more reactive form. A number of other cellulose compounds are described in the literature, the formation of which depends upon its alcoholic character, but these will not be considered here because they have not as yet achieved industrial importance.

Chemical Constitution—As has already been indicated, cellulose is found in many manifestations in the vegetable kingdom. It can be obtained from trees on the one hand and from grasses and straws on the other. The question naturally arises whether the cellulose from these various sources has the same chemical constitution even though it may differ somewhat in physical properties. Careful investigation [20] seems to indicate that cellulose derived from any form of vegetation has essentially the same chemical constitution, although a few investigators [21] have questioned this conclusion.

It has long been known that cellulose is a carbohydrate with the empirical composition $C_6H_{10}O_5$. It is essentially alcoholic in character, there being three hydroxyl groups in the molecule, of which one is primary and two are secondary. The molecule appears to be built up of long chains of anhydro-glucose residues combined by primary valence forces. The chains themselves may be held together more loosely by secondary forces. In any case, X-ray studies show that

[18] Vierveg, Ber., *40*, 3876 (1907); *41*, 3269 (1908); Karrer, P., Cellulosechemie, *2*, 125 (1921); Bancroft, W. D., and Calkin, J. B., Colloid Symposium Monograph 11, 1-9 (1935).

[19] Cross, Bevan and Beadle, Ber., *26*, 1090, 2524 (1893); *34*, 1513 (1901); Hess, K., et al., Ann., *435*, 120 (1923); Berl and Bitter, Cellulosechemie, 7, 149 (1926).

[20] Heuser and Boedeker, Z. angew. Chem., *34*, Aufsatzteil, 461 (1921); Heuser and Boedeker, Paper Trade Jour., *74*, No. 5, 47 (1922); Heuser and Broetz, Papierfabrikant, *23*, Festheft, 69 (1925).

[21] Sherrard and Froehlke, J. Am. Chem. Soc., *45*, 1729 (1923).

the molecular groupings in the molecule are oriented in the direction of the molecular axis and show a definite X-ray pattern. The size of the cellulose molecule is not known exactly. Recent experimenters have found molecular weights of cotton linters from 20,000 to 120,000 and higher.[22]

Alpha, Beta, and Gamma Cellulose. It has been found empirically that cotton cellulose does not dissolve to any great extent in sodium hydroxide solutions of mercerizing strength (about 18 per cent). This property is frequently taken as a standard against which celluloses from other sources are measured. That portion of a sample of cellulose which does not dissolve in 17.5 per cent sodium hydroxide solution under definite conditions of time, temperature, and manipulation[23] is termed alpha cellulose. The portion soluble in such alkali is further subdivided into a part which may be reprecipitated by acids, known as beta cellulose; and a part which cannot be reprecipitated by acids called gamma cellulose.

Alpha cellulose is the preferred type for chemical processing, and the recovery of cellulose from natural raw materials must be so conducted as to obtain a maximum yield of the alpha type.

Cellulose Derivatives—The first chemical derivative of cellulose to achieve industrial importance was the nitrate. When this contains from 12.4 to 12.8 per cent of nitrogen it is used for smokeless powders and the so-called gelatine dynamites. Nitrates with about 12 per cent nitrogen form the basis of the modern nitrocellulose lacquers and finishes for automobiles and furniture. For the manufacture of pyroxylin plastics (variously known as celluloid, fiberloid, nixonoid, pyralin, viscoloid, xylonite, etc.), a cellulose nitrate with from 10.8 to 11.6 per cent nitrogen is used, usually about 11 per cent.

Another ester of cellulose which is of commercial importance is the acetate, being used for the manufacture of synthetic fibers as well as for molding powders and for sheet materials resembling celluloid, but non-inflammable.

Other esters and mixed esters have been proposed from time to time and patented, such as the propionate butyrate, benzoate, aceto-nitrate, acetate-butyrate and mixed esters containing nitrate and fatty acid radicals.

Of very considerable industrial importance is the cellulose ester of thiocarbonic acid, sometimes called cellulose xanthate and more commonly referred to as viscose. It is made by treating purified cellulose with caustic soda solution followed by carbon disulfide and serves as the basis for the manufacture of viscose rayon, cellophane, bottle caps, sausage casings, etc.

Various cellulose ethers, made for example by treating cellulose with caustic soda solutions and an alkyl or aryl sulfate, have also been developed. The most important at the present time from a commercial point of view are ethyl cellulose, benzyl cellulose and the water-soluble methyl cellulose.

All of these derivatives are considered in more detail below in connection with their commercial applications.

[22] Stamm, A. J., J. Am. Chem. Soc., *52*, 3047 (1930); Haworth and Machener, loc. cit.; Staudinger, Naturwiss, *22*, 797 and 813 (1934); Staudinger and Feuerstein, Annalen, *526*, 72 (1936).

[23] Ind. Eng. Chem. (Analytical Edition), Vol. 1, p. 52 (1929).

CELLULOSE NITRATE PREPARATION [24]

When cellulose is treated with concentrated nitric acid, a series of cellulose nitrates is produced, the limit of reaction being:

$$C_6H_{10}O_5 + 3HNO_3 = C_6H_7O_2(NO_3)_3 + 3H_2O.$$

This reaction, of great technical importance, is always carried on in practice with a mixture of sulfuric and nitric acids. The sulfuric acid takes up the water produced in the reaction, and also tends to form cellulose sulfuric acids, which react with the nitric acid in the mixture, forming cellulose nitrates and regenerating the sulfuric acid.

The important factors are:

(*a*) Strength of the acid.
(*b*) Temperature of the acid.
(*c*) Time of nitration.
(*d*) Proportion of acid to cellulose.
(*e*) Relative proportions of nitric acid, sulfuric acid, and water.

By varying these conditions, products of widely different properties may be obtained.

(*a*) The proportion of sulfuric to nitric acid is of minor importance, the essential thing being that there is an excess of the latter. Proportions of 1 : 1 to 3 : 1 are used. Too much sulfuric acid makes it harder to stabilize, though there is indication that it may improve solubility. The effect of the acid mixture depends mainly upon the total acidity, or conversely upon the percentage of water, which varies from 10 to 20 per cent. A low percentage of water causes a nitration approaching more closely to the limit of reaction. A higher water content gives a lower percentage of nitrogen in the product.

(*b*) Increasing the temperature increases the rate of reaction. Thus a nitration in cold acid may require twenty-four hours to be complete, while with the same acid mixture at a temperature of perhaps 40° C., the reaction would be complete inside of an hour. As the temperature of the acid bath increases, secondary reactions occur, so that the properties of the product are modified.

(*c*) As indicated above, the time of nitration depends very largely upon the temperature. In practice cellulose is usually nitrated for about thirty minutes.

(*d*) Thirty to fifty parts of acid to one of cellulose are ordinarily used. It is important to use an excess of acid.

The cellulose most commonly used today is purified cotton linters or an absorbent pulp made from a specially prepared sulfite pulp.

Three different forms of apparatus have been used:

1. Iron or earthenware pots, into which the acid is run and the cellulose then immersed. At the completion of the nitration the material is dumped into centrifugal machines, and the excess of acid removed.

2. Centrifugal machines, the machines being started in motion after nitration is complete.

[24] For a discussion of the principles of nitration, see Chapter 3.

3. In the Thomson process stoneware pans, the acid being removed by displacement with water.

Most of the cellulose nitrate produced today is made by the first of these methods.

After nitrating by any of these processes the product is thoroughly washed in water and boiled in slightly acid water to remove unstable by-products. Bleaching with hypochlorite is sometimes necessary.

The washed product is centrifuged to remove excess water and the balance of the water usually removed by mixing with ethyl alcohol and squeezing out the excess in hydraulic presses. The yield varies with the percentage of nitrogen. Theoretical yields vary from 160 to 210 parts. In practice these yields are reduced by solution in the acid, secondary reactions, and mechanical losses, and vary between 130 and 175 parts.

Properties—As ordinarily prepared, cellulose nitrates, also called pyroxylins, have the unaltered appearance of the original fiber, but are harsher to the touch. The specific gravity is only slightly higher than that of cellulose, the volume rather than the density being increased in nitrating. They ordinarily float in water, on account of the presence of air in the fibers. They are less hydroscopic than cellulose; thus a pyroxylin with 13 per cent of nitrogen has about 1.5 per cent water of condition, and a pyroxylin with 11 per cent of nitrogen, about 3.5 per cent.

These derivatives burn very rapidly, the rate of combustion increasing with the percentage of nitrogen. It is to be noted that nitration is a progressive phenomenon, and that we cannot recognize any definite steps in the reactions, so that any names such as tri-nitrate, hexa-nitrate, penta-nitrate, etc., are not well founded.

The maximum theoretical percentage of nitrogen is 14.14 per cent, but this has never been reached in practice. The most highly nitrated products contain 13.3 to 13.7 per cent of nitrogen, and are known as guncottons. They are soluble in acetone and ethyl acetate, but insoluble in ether-alcohol, nitroglycerine, and other solvents of the lower nitrates. Guncotton is ignited by shock, differing in this respect also from other cellulose nitrates.

Pyroxylins, as used for smokeless powders and gelatine dynamites, contain 12.4 to 12.8 per cent nitrogen, and are less soluble in wood-alcohol, amyl acetate, and camphor-alcohol than lower nitrates. Pyrocellulose is the standard pyroxylin of this class, containing 12.6 per cent of nitrogen.

Soluble pyroxylins, called variously collodion cotton, soluble cotton, and lacquer cotton, contain from 11.8 to 12.2 per cent of nitrogen, and dissolve in ether-alcohol, amyl acetate, wood-alcohol, and other solvents to solutions of less viscosity than any other pyroxylins.

Celluloid pyroxylins contain 10.8 to 11.5 per cent of nitrogen, and are soluble in all these solvents, but give solutions of greater viscosity than the varnish cottons. It may be noted here that two pyroxylins with the same percentage of nitrogen may show very different solubilities and viscosities, due to secondary reactions in the nitration.

Pyroxylins containing 10 per cent of nitrogen and soluble in grain alcohol alone may also be made, but have not found any applications. Cellulose nitrates containing less than 10 per cent of nitrogen are not soluble in organic solvents.

Industrial Applications—For a discussion of the various industrial applications of the cellulose nitrates, see Chapter 25, Surface Coatings, Chapter 32, Explosives, and Chapter 31, Synthetic Plastics.

CELLULOSE ACETATE

Preparation and Properties—When purified cellulose (usually linters) is subjected to the action of a mixture of acetic anhydride and glacial acetic acid in the presence of a peptizing agent such as sulfuric acid or zinc chloride, acetylation[25] takes place. The glacial acetic acid serves chiefly as the vehicle for the anhydride. Considerable heat is evolved in the reaction and cooling is usually resorted to in order to prevent an undue rise in temperature. Since cellulose acetate is soluble in acetic acid the cellulose appears to dissolve as the reaction proceeds and a thick liquid or paste results. If the cellulose acetate is precipitated at this point it is obtained as the tri-acetate containing about 62 per cent combined acetic acid (44.7% acetyl). It is soluble in chloroform[26] and in mixtures of alcohol with chloroform or with tetrachlorethane[27] but is not soluble in acetone. The acetone-soluble material is produced by allowing a period of so-called "ripening" between the completion of the acetylation and the precipitation of the product with water. Usually a little water is added to the reaction product and sometimes a little acid to facilitate the action which is essentially that of hydrolysis. When the desired solubility in acetone has been attained, the product is precipitated with water and it is then found to have a composition intermediate between the tri-acetate and the di-acetate, which latter contains about 43 per cent of combined acetic acid (35% acetyl). It is thoroughly washed with water to remove all traces of acid and then dried.

For a discussion of the uses of cellulose acetate, see the section on Rayon in this chapter and see Chapter 31: Synthetic Plastics.

OTHER CELLULOSE ESTERS AND ETHERS

Acetate-Butyrate-Propionate Esters—Recently two new mixed esters of cellulose have been manufactured on a commercial scale. These are the acetate-butyrate, which is partially esterified with acetic and partially with butyric acid (up to 40%), and the acetate-propionate, which is partially esterified with acetic and partially with propionic acid. Both of these mixed esters are recommended primarily for use in lacquers and other protective coatings, and they have recently received much attention as molding materials. Cellulose acetate butyrate[28] has superior weathering qualities and is free from warping. It has been reported together with cellulose acetate-propionate as best suited for airplane dopes. Cellulose acetate butyrate is more suited for molding than is cellulose acetate but it has the disagreeable odor of butyric acid.

Benzyl Cellulose—Benzyl cellulose is an ether of cellulose which is formed by a typical etherification reaction: namely, the treatment of cellulose in an

[25] In this case, the acetylation is an example of esterification. For a discussion of this unit process, see Chapter 3.

[26] See compound 136, Chapter 27.

[27] See compound 131, Chapter 27.

[28] Clark and Malm, U. S. Patent 1,880,808 (1932).

alkaline medium with benzyl chloride. It was developed commercially in England several years ago, but has not been manufactured on a large scale in this country. For molding purposes benzyl cellulose does not exhibit sufficient advantage over cellulose acetate to compensate for its higher cost. However, it has achieved limited application in the form of thin transparent sheets for wrapping purposes because of its superior resistance to moisture penetration.

Ethyl Cellulose—Another ether of cellulose has been developed commercially in this country for use in molded plastics, in lacquers and other protective coatings, and in thin transparent sheets for wrapping material. Ethyl cellulose plastics are capable of being molded either in compression or injection molds. They do not require a high molding temperature, are compatible with a wide range of plasticizers, resins and lubricants, have low moisture absorption, good electrical properties and high shock resistance, with the further advantage of retaining their toughness and flexibility at lower temperatures than other cellulose derivatives.

Methyl Cellulose—This ether of cellulose which, in a certain range of methoxy content, possesses the distinction of being soluble in water is, in another range, soluble in strongly alkaline aqueous solutions and precipitated by acids. This second form is being successfully used in the production of linen-like finishes on cotton fabrics.

The lower methylated celluloses are soluble in cold water, but insoluble in hot water. The water solubility diminishes with increases in the methylation until complete water-insolubility is reached. The solubility of methyl cellulose in water may be greatly diminished by treatment with an aldehyde, such as formaldehyde. Methyl cellulose is chiefly used as a thickener for textile printing pastes and cosmetics and as a sizing or finish for textile fabrics.

For a more detailed discussion of the uses of these cellulose esters and ethers, see Chapter 31.

RAYON

One of the most important of the cellulose industries is the production of rayon. Rayon is a generic term applied to synthetic fibers composed of regenerated cellulose. The first practical fibers were made about 1890 by Chardonnet. However the industry grew slowly at first and was not introduced into the United States until 1910. At the present time there are four commercial processes for producing these synthetic fibers. Of these the viscose method accounted for about 81 per cent of the 1,190,000 tons of world production in 1940; the acetate method for about 15 per cent; the cuprammonium method for about 4 per cent; and the nitrocellulose process for less than half of one per cent.

The Viscose Process—For the manufacture of rayon by the viscose process both purified sulfite pulp and purified cotton linters may be used as a raw material. It is not uncommon to use a mixture of these materials, the relative amounts depending to a large degree upon the current price [29] of the purified cotton linters. While cotton linters pulp imparts strength and whiteness to rayon produced from it, its use in the viscose process is uneconomical except when it is priced low. These materials are supplied to the rayon manufacturer

[29] See Chapter 1.

in the form of sheets and these sheets are first immersed in a sodium hydroxide solution of about 18 per cent strength until thoroughly saturated. This solution is maintained at a closely regulated temperature, usually somewhere between 16 and 22° C. The next operation is to remove the excess of the caustic soda, which is carried out in large hydraulic presses, following which the sheets of pulp are transferred to machines known as "shredders," where they are shredded into a very fine and fluffy form known as "crumbs." These shredders are essentially machines of the kneading machine type in which the saddle and the blades have been given a saw-tooth edge. They are water-jacketed to prevent an undue rise in temperature. The crumbs are then placed in cans and stored for two or three days in specially designed rooms which are maintained at a uniformly cool temperature. The exact time and temperature has to be very carefully worked out in connection with the other steps in the process.

After the proper aging period, the crumbs are treated with carbon bisulfide in revolving drums or other suitable form of churn. This converts them into a deep orange-colored product which is then dissolved in dilute sodium hydroxide solution. The resulting sirupy liquid is also stored for two or three days under very carefully regulated temperature conditions during which it is filtered several times to remove every last particle of dirt or dust, and after removal of air bubbles, it is ready to be "spun."

Spinning. In rayon manufacture, the "spinning" operation consists in forcing the solution through very fine orifices. In the viscose process, the spinnerettes are usually made of alloys of platinum and gold or of tantalum and may contain any number of orifices, depending upon the number of filaments which are desired in the rayon thread. As the solution is forced through the spinnerettes, it comes in contact with a coagulating bath which consists essentially of a solution of sodium acid sulfate, although there are numerous patents which describe the advantage of adding various other materials as well. The properties of the coagulating bath are so adjusted that while each individual jet of liquid is hardened into a filament, these filaments do not stick together but are removed from the bath and collected either on the outside of a perforated metal bobbin or more usually on the inside of a perforated centrifugal pot about 6 ins. in diameter. The fibers are then thoroughly washed to remove the coagulating bath, following which they are treated with a dilute solution of sodium sulfide to remove any sulfur compounds, and then bleached.

Recently one viscose rayon plant has been constructed in which the spinning, washing, desulfurizing and bleaching processes are combined in one continuous machine to produce dry twisted yarn ready for conversion into fabrics.

The unit of size of rayon filaments is the denier which is the weight in grams of 9000 meters. The most common size is 150 denier and this may be obtained in viscose rayon with anywhere from 24 to 150 filaments. It is also available as fine as 50 denier and as coarse as 600 or 900 denier. The large sizes, however, are usually made by combining several threads of smaller sizes.

In the last ten years a considerable portion of the filaments produced by the viscose process have been cut into predetermined lengths of from 1 to 6 inches and sold as staple fiber for combination with cotton, wool and linen fibers in the production of spun yarns.

The Cuprammonium Process—In the manufacture of rayon by the cuprammonium process, the raw material is usually purified cotton. In outline, the process consists of dissolving the cellulose in a copper ammonia solution, followed by the extrusion of this solution through fine orifices into a coagulating bath. The resulting filaments are collected and treated to remove the copper and then bleached. In the early days of this method, the cuprammonia solution was prepared by blowing cooled air through ammonia solution in contact with copper shavings or turnings. More recently, however, a method has been developed by which a thick paste of copper hydroxide is made by running a cold concentrated solution of sodium hydroxide into a similar solution of copper sulfate, and this "sludge" is mixed directly with the cellulose which has previously been beaten to a pulp with water. This mixture is then washed in a filter press to remove the sodium sulfate formed by the reaction, following which it is mixed with ammonia to form a solution containing 7 or 8 per cent of cellulose. A certain amount of glucose is usually added to this solution to increase its stability.

The same very careful filtering operations have to be conducted in this method as in all the others, and after freeing from air bubbles, the cellulose solution is extruded under pressure into a coagulating bath which may be either acid or alkaline. When alkaline precipitating baths are used, it is necessary in a subsequent step to remove the copper from the finished fibers.

One of the well-known modifications of the cuprammonium method involves the use of a succession of precipitating baths of gradually increasing strength which permits of a stretching of the fibers as they are being gradually hardened. In this way, individual filaments almost as fine as natural silk are produced.

The Nitrocellulose Process—For the manufacture of artificial fibers by the nitrocellulose process, the raw material is also a purified form of cotton. This is nitrated with a mixture of sulfuric and nitric acids to give a nitrate with about 11.5 per cent nitrogen, and after suitable purification and dehydration, it is dissolved in a mixture of alcohol and ether to form a rather thick viscous mass. This is very carefully filtered to remove all traces of dirt and is then extruded under a fairly high pressure into a stream of warm air through a nozzle with a single fine orifice. The solvents evaporate and are recovered from the air stream for re-use. A suitable number of these filaments are gathered together to form a thread which is then denitrated by treatment with a dilute solution of an alkaline sulfide, and bleached. At the present time there are only two plants in the world operating by this process, one in Brazil and one in Hungary.

Cellulose Acetate Process—The fourth commercial method for the manufacture of artificial fibers from cellulose involves the use of cellulose acetate. The manufacture of this material has already been described. When used for making synthetic fibers, it is dissolved in acetone to form a thick sirupy solution which is extruded through a fine orifice into a stream of warm air somewhat after the manner of the nitrocellulose process. The acetone is to a large extent recovered from the air. There is, however, a marked difference between the cellulose acetate process and the other three which have been described, since the product of the cellulose acetate method is an ester of cellulose, whereas the product of the other three is essentially cellulose itself in a slightly modified form. The practical result of this is that, particularly in their chemical properties and reactions towards dyes, the rayons made by the viscose, cuprammonium, and nitrocellulose methods are all similar and differ quite markedly in these respects from synthetic fibers made by the cellulose acetate process.

Since the products of various manufacturers making rayon by the same process vary somewhat, it is not possible to give exact figures for the strength of rayon. In general, however, it may be said that the commercial synthetic fibers are from 50 to 80 per cent as strong as natural silk when in equilibrium with normal room conditions of temperature and humidity. When wet, the rayons made by the viscose, cuprammonium, and nitrocellulose methods lose from 50 to 60 per cent of their strength, while fibers made by the cellulose acetate process lose only from 20 to 40 per cent of their strength in the dry condition. Recently, a new variety of viscose rayon has appeared on the market which is nearly as strong as natural silk when dry, and when wet is at least as strong as natural silk in the same condition. It is being used to replace cotton thread in rubber tires where its use is claimed to result in superior strength and wearing qualities.

In the early days of cellulose acetate fibers, considerable difficulty was experienced in dyeing them, and advantage was often taken of the fact that they resisted ordinary dyes for the production of interesting dye-resist effects. Later, however, several new classes of dyes were developed,[30] particularly for use in connection with cellulose acetate fibers so that now there is little difficulty in this regard.

MISCELLANEOUS CELLULOSE APPLICATIONS

Cellophane and Sausage Casings—Cellophane is essentially a thin transparent film of regenerated cellulose. The usual method of manufacture[31] is to use a viscose solution similar to that used for producing rayon by the viscose process, which has been considered earlier in this chapter. However, substantial amounts of transparent film are now being prepared from cellulose acetate, and in Germany a certain amount of this material has been manufactured by regenerating cellulose from cuprammonium solutions.[32]

In preparing the viscose solution for this use, it is necessary to make several very careful filtrations to remove all traces of dirt. The clarified solution is then forced through a suitable nozzle into a coagulating or hardening bath, which may consist of a solution of sodium and ammonium sulfates. The nozzle is so designed that it delivers a thin sheet of viscose solution about 40 ins. wide which is almost immediately coagulated into a continuous ribbon. This is conveyed continuously through suitable hardening, washing, desulfurizing, and bleaching solutions in successive baths. The last bath usually consists of a 25 per cent solution of glycerine in water, the glycerine being absorbed by the regenerated cellulose film and rendering it soft and pliable. The product is finally passed through a drier where the excess moisture is removed by means of warm air. It is used for wrapping a wide variety of products, particularly food products. It is also used in the manufacture of artificial flowers and millinery trimmings.

A similar process[33] is used for the manufacture of sausage casings except that

[30] See Chapters 28 and 29.
[31] Ind. and Eng. Chem., *21*, 405 (1929).
[32] U. S. Patents 1,590,601 and 1,590,602 (June 29, 1926) to Zeigh and Ziegler.
[33] Henderson and Dietrich, Ind. and Eng. Chem., *18*, 1190 (1926).

the viscose solution is forced through a die which produces a continuous tube rather than a flat sheet. These synthetic casings offer the very distinct advantage of uniformity in size, and it has further been found possible to strip them from the finished sausage before it is sold and still have a sausage which has sufficient strength and firmness to retain its shape while being prepared for eating.

Cellophane is readily affected by moisture and becomes soft and flabby when exposed to humid air. A moisture-resistant form of cellophane is prepared by applying to the surface of the cellophane an extremely thin layer of nitrocellulose with which has been incorporated a small amount of wax. This produces an attractive, moisture-resistant, transparent sheet which finds wide use as a wrapping material.

Vegetable Parchment—This product, sometimes also referred to as vulcanized fiber, is obtained by a short immersion of unsized paper in 66 to 70 per cent sulfuric acid, followed by immediate washing in water and drying. A layer of semi-transparent gelatinous amyloid or cellulose hydrate is thus deposited on the surface, and the paper becomes tough and resembles in appearance natural parchment. In the process, the sulfuric acid is contained in lead-lined tanks, and the paper is unrolled and drawn through the bath and then between rolls of acid-resisting material into a bath of wash-water. Thick sheets are made by pressing together layers of paper which have just been parchmentized.

The important factors are the condition of the paper, the strength of the acid, the temperature of the acid, the time of immersion, and the completeness of washing. Under- or over-treatment by the acid must be avoided and no trace of acid should remain in the parchment.

In thin sheets it is used for packing greasy materials and in heavier weights as electric insulation.

Vulcanized Fiber—A second variety of vulcanized fiber is prepared by treating unsized rag paper in a warm solution of zinc chloride in water. The solution contains 65 to 70 per cent $ZnCl_2$ and is maintained at a temperature close to 40° C. A roll of paper is unwound, passed over heated cylinders and then through the bath, and is then rolled up on large cylinders until the desired thickness is obtained. The surface is gelatinized so that the paper welds together on the receiving drum where it is squeezed by the pressure of a heavy roll above it. The sheet is then cut off the drum and is washed in zinc chloride solutions of diminishing concentration, and finally in pure water until no test, or a very faint test for chlorides is obtained. This washing treatment is slow, depending on the size of the sheet; ¼-in. material takes three or four weeks, and 2 ins. six to eight months. Zinc chloride is recovered from the stronger wash waters by using them on the counter-current principle. This matter of washing is of the greatest importance because of the danger of blistering, which is thought to be caused by osmotio pressure. If the washing is not complete, inferior fiber is the result.

The product shrinks on drying and is remarkably homogeneous. It comes on the market in reddish brown, gray, or black colors, which are obtained by using differently colored papers containing iron oxide, lamp black, or other coloring matter. The product is very hard, of a horny consistency and is worked by sawing, turning, etc., may be threaded and embossed, but is not properly plastic to heat.

The fiber, particularly that made by the sulfuric acid process, has a dielectric strength of 400 to 600 volts per mil. It is oilproof but not waterproof, absorbing 20 to 50 per cent of its weight of water upon prolonged immersion, but dries again to its original size; it is not soluble in any organic solvents and is very resistant to chemical action except the hydrolytic action of mineral acids on long exposure.

The specific gravity varies from 1.25 to 1.5; the tensile strength from 8000 to 20,000 lbs. per square inch, depending somewhat on whether the measurement is made in the machine direction or the cross direction of the sheet of paper; and the crushing strength from 30,000 to 45,000 lbs. per square inch.

These two kinds of fiber find a wide variety of uses, such as for trunks, bags, handles of cheap cutlery, receptacles, such as waste baskets, and for a considerable number of engineering purposes, notably gears, washers, valves, etc.

Decomposition Products of Cellulose—The action of heat in decomposing cellulose has already been referred to. Dilute acids convert cellulose to glucose. When this process was first carried out on a commercial scale, it was not possible to recover much more than 50 per cent of the theoretical amount of fermentable sugar. Recent developments, however, have provided a process which claims to accomplish an almost theoretical conversion of the cellulose into glucose so that as high as 60 to 70 per cent of fermentable sugar may be obtained from dry wood. The primary product as it is obtained from this process, is a sugar intermediate in composition between starch and glucose and has been used directly as a cattle food, the claim being made that it actually produces a little more weight than an equal quantity of corn.

If it is to be fermented, this intermediate sugar is inverted to glucose by treatment with very dilute acid. In the laboratory it has even been found possible to obtain the sugar in a white crystalline form.

These processes have had their chief development in Germany and have operated there on a small commercial scale.

Recent experiments have also shown that when cellulosic material is inoculated with sewage sludge and allowed to react under anaerobic conditions, the cellulose is decomposed into carbon dioxide and methane yielding a gas with about 500 B.t.u. per cubic foot. The decomposition of the cellulose, however, is not complete, it being apparent that the so-called hemicelluloses are attacked first.

READING LIST

CELLULOSE

Bonwitt, Gustav, "Das Celluloid und seine Ersatzstoffe," 813 pp., Union Deutsche Verlagsgesellschaft, Berlin (1933).

Brown, Bruce K. and Crawford, F. M., "A Survey of Nitrocellulose Lacquer," 368 pp., The Chemical Catalog Co., New York (1928).

Doree, Charles, "The Methods of Cellulose Chemistry," 499 pp., D. Van Nostrand Co., New York (1933).

Hall, A. J., "Cotton Cellulose, Its Chemistry and Technology," 228 pp., Ernest Benn, Ltd., London; 228 pp., D. Van Nostrand Co., New York (1924).

Hawley, Lee F. and Wise, Louis E., "The Chemistry of Wood," 334 pp., bibl., footnotes, Chemical Catalog Co., New York (1926).

Heuser, Emil, "Textbook of Cellulose Chemistry," translated from the second German edition by C. J. West and G. J. Esselen, Jr., 212 pp., McGraw-Hill Book Co., New York (1924).

Krüger, D., "Zelluloseazetate und die Anderen Organischen Ester der Zellulose," 391 pp., Verlag von Theodor Steinkopff, Dresden and Leipzig (1933).

Marsh, J. T. and Wood, F. C., "An Introduction to the Chemistry of Cellulose," 431 pp., D. Van Nostrand Co., Inc., New York (1939).

Schorger, Arlie W., "The Chemistry of Cellulose and Wood," 596 pp., references pp. 467-9, bibl., footnotes, McGraw-Hill Book Co., New York (1926).

Stamm, A. J., "Colloid Chemistry of Cellulosic Materials," 90 pp., U. S. Government Printing Office, Washington, D. C. (1936).

Worden, E. C., "Technology of Cellulose Ethers," 5 vols., 3396 pp., Worden Laboratory and Library, Millburn, N. J. (1933).

RAYON

Avram, Mois H., "Rayon Industry," 603 pp., D. Van Nostrand Co., New York (1927).

Eggert, Johann, "Die Herstellung und Verarbeitung der Viskose," second edition, 243 pp., Julius Springer, Berlin (1931).

Schwarz, E. W. K., and Mauersberger, H. R., "Rayon and Staple Fiber Handbook," third edition, 832 pp., Rayon Publishing Corp., New York (1939).

Mortgat, Raymond, "La Fabrication de la Soie Artificielle par le Procede viscose," 597 pp., L'Edition Textile, Paris (1930).

Mullin, C. E., "Acetate Silk and Its Dyes," 454 pp., D. Van Nostrand Co., Inc., New York (1927).

Woodhouse, Thomas, "Artificial Silk or Rayon," 231 pp., Isaac Pitman and Sons, Ltd., London (1929).

CELLOPHANE

Halama, Marta, "Transparantfolien," 289 pp., Chemischer-Technischer Verlag Dr. Bodenbender, Berlin (1932).

CHAPTER 39

RUBBER AND RUBBER-LIKE PRODUCTS

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Natural rubber is a hydrocarbon polymer of great molecular size and distinctive physical characteristics occurring in many varieties of trees, shrubs and vines. Commercially, however, separation of rubber from plants has been confined to those growing in a zone extending about 10° of latitude each side of the equator. Until about the end of the 19th century rubber was extracted only from wild growth. More than half the world's supply came from South American trees growing along the Amazon River and its tributaries. The rest came from Central America, Africa, various tropical islands and Mexico. About 1900 there first appeared on the market rubber prepared on plantations in the Far East from trees grown from seeds obtained in South America. The tonnage from this eastern area increased slowly until 1912, when the total production of rubber from wild growth, 62,300 tons, was still almost 90% of the total. By 1927 the production of "wild" rubber had diminished to 37,690 tons, then representing only about 6% of the world supply. In 1937 Far Eastern sources supplied 97½ of all rubber produced, 1,133,324 of the total of 1,160,282 long tons.

PLANTATION INDUSTRY

Early in the 1870's Henry Wickham, an Englishman, visited[1] South America to study the botany of trees of the species *hevea brasiliensis*, from which the best commercial grade of rubber was then obtained. He believed that these trees could be planted and cultivated in British possessions and the cost of collecting and preparing rubber greatly reduced. Although he feared that the Brazilian Government would bar the exportation of rubber, Wickham succeeded in carrying a large supply to England. About 70,000 were planted at Kew Botanical Gardens, of which 2,700 germinated. Approximately 1,900 of the seedlings from Kew Gardens were selected and sent to Ceylon for replanting in 1876. These throve in their new environment and became the source of the hundreds of millions of trees now growing in the Federated Malay States, Java, Sumatra and Ceylon. Plantations were first financed and managed by the English and the Dutch. As the industry grew, natives in the various countries made small plantings and the amount of "native" rubber increased until it totalled almost half of

[1] Wickham, H. A., India Rubber World, *38*, 358 (1908).

the Far Eastern supply. The total plantation acreage devoted to rubber growing under the Regulations Agreement [2] of 1939-1943 is approximately as shown in Table 1.

TABLE 1—PLANTATION ACREAGES

	Acres
British Malaya	3,273,100
Ceylon	605,200
Sarawak	228,000
British North Borneo	126,600
British India and Burma	232,400
Netherlands East Indies	3,214,900
French Indo-China	314,200
Siam	312,000
Liberia *	55,000
Brazil *	10,000

* Not included in the Agreement. Figures approximate.

The plantations in Liberia and Brazil are of more recent origin, as well as minor areas in Africa and the Philippines. Today about 99½% of all rubber on the market is obtained from *hevea brasiliensis*. A typical rubber tree planting is shown in Figure 1.

Preparation of Crude Rubber—Hevea trees are tapped for rubber at about their sixth year, although they have not then attained maximum growth. Rubber exists in the tree in the form of a milky latex consisting of globules of rubber hydrocarbon about 0.09 to 1.85 μ in diameter [2a] suspended in a watery serum. Latex in the tree is contained in a network of tubular cells located in the cortex or inner bark. It is entirely separate and different from the sap, which flows through the woody structure and the cambium layer immediately outside it. For producing rubber, the latex is obtained by cutting a groove spirally part way around the tree through the cortex layer but not into the cambium. Latex exudes from the severed latex tubes and flows along the groove, dropping into a small cup attached to the tree at the bottom of the cut. Each tapping yields about one ounce of latex containing roughly ⅓ ounce of rubber. (See Figure 2.) There are approximately 100 trees to the acre and the average annual yield per acre is from 400 to 500 pounds of dry rubber. New methods of grafting from high yielding trees upon those of hardy root growth indicate that, in time, the yield per acre may be more than doubled.

The latex is collected from the cups by native or Chinese laborers and carried to central stations where, after dilution with water to 15% to 20% dry rubber content, it is strained to remove any rubber which has already coagulated as well as bark or other foreign material. The strained liquid is then placed in coagulation tanks of 50 to 100 gallons capacity and acetic or formic acid stirred in to coagulate the rubber. The rubber clots and forms a flabby slab of coagulum which is then squeezed between mill rolls to separate the serum. Certain grades are also washed by water running over the mill during the squeezing operation.

Commercial Grades—On European estates where the processing is carefully controlled mainly two grades of rubber are prepared. *Pale Crepe* is made by

[2] Revised Text, International Agreement to Regulate Production and Export of Rubber.

[2a] Lucas, F. F., Ind. Eng. Chem. *30*, 146 (1938).

FIG. 1. Rubber Trees on a Plantation. Tapped areas of the trunks of the trees are clearly visible.

FIG. 2. Tapping a Rubber Tree.

Latex slowly exudes from the inner bark, flows along the freshly cut groove and drops through the spout into the cup.

squeezing and washing slabs of approximately 25 pounds of coagulum on roll mills until they form thin, rough surfaced sheets. These are cut to convenient lengths for handling and hung in lofts to dry naturally in unheated air, an operation requiring about two weeks. In order to obtain crepe of light color, calculated amounts of bleaching agents such as sodium bisulfite are added to the diluted latex before coagulation. The resulting product is a thin, pale yellow, crinkled sheet. This grade finds use mainly in the manufacture of light colored goods. It is more costly to prepare than *Smoked Sheets*, which represent the largest output of the plantations. In the preparation of smoked sheets the rubber is rolled out somewhat thicker than for crepe and passed between embossing

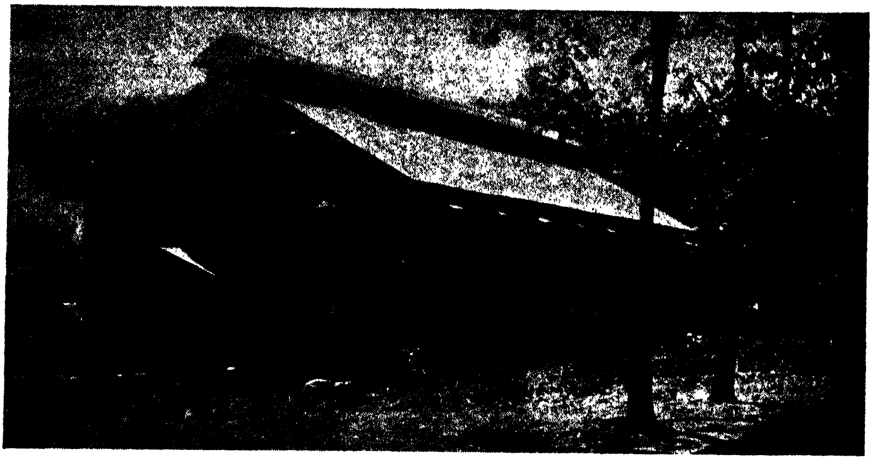

FIG. 3. A House for Smoking Rubber.

Sheets of wet rubber are hung in the upper part of the structure and dried by warm gases and smoke from fires burning in the lower portion.

rolls which mark the sheets with a design, consisting usually of raised ribs (whence the name "ribbed" smoked sheets) and with the name of the producing estate. These sheets are soaked for a few hours in a tank of water to remove more of the serum and then hung in the upper part of smoke houses. (See Figure 3.) They are dried by hot smoke (110° to 120° F.) from fires of cocoanut husks or hard wood in the lower part of the buildings. The drying period is from 7 to 11 days. Antiseptic substances absorbed by the rubber from the smoke preserve it from moldiness and prevent fermentation of any serum remaining in the rubber. About 60% of all rubber from the Far East is smoked in this way.

Crepe rubber which becomes discolored or dirty during its preparation is sold as *Faulty Latex Crepe*. Other grades are obtained from (a) the rubber which coagulates naturally before the latex is put into the coagulation tanks, *Thin Brown Crepe*; (b) the rubber adhering to the shavings of bark cut off in tapping, *Tree Scrap*; (c) the rubber coagulating from latex spilled on the ground, *Earth Scrap*. Many of the natives sell undried coagulum to be washed and dried by refiners in factories in the large export cities. Some of the lower grades from plantations are also washed in these factories. These refiners turn out thick, rough surfaced sheets known as *Blankets.*

Composition of Latex and Crude Rubber—As obtained from hevea trees, latex varies somewhat in composition according to the age of the tree, the season of the year and the character of the soil. Table 2 gives approximate amounts of the various constituents.[3]

TABLE 2—COMPOSITION OF LATEX

	%
Water	60
Proteins	2
Fatty acids and esters	1
Quebrachitol	1
Inorganic salts	0.4
Rubber hydrocarbon	35

(See p. 1482 for structure)

The composition of rubber obtained by coagulation also varies with differences in the latex and according to the method of preparation. Table 3 shows the amounts of various constituents of the two high grade varieties.

TABLE 3—COMPOSITION OF RUBBER

	First Grade Smoked Sheet	*First Latex[4] Crepe*
Moisture	0.6%	0.4%
Acetone soluble material	2.9	2.9
Esters insoluble in acetone	1.0	1.0
Proteins (Nitrogen $\times$ 6.25)	2.8	2.8
Ash	0.4	0.3
Water soluble material	1.0	1.0
Total non-rubber constituents	8.7	8.4
Rubber hydrocarbon	91.3	91.6

The acetone soluble materials are mainly sterol and sterol compounds, quebrachitol and fatty acids,—oleic, linoleic and stearic. The composition of the proteins is not definitely known. Water solubles consist of sugars, inorganic salts and some nitrogeneous compounds. Mineral constituents of residues after burning off the organic matter are, in decreasing order, phosphoric acid (as P_2O_5), potash (as K_2O), lime (as CaO), magnesia (as MgO), soda (as Na_2O), sulfuric acid (as SO_3) and the group: chlorine, carbonic acid (CO_2) and iron.

Supply and Consumption—Shipments[5] of crude rubber, plantation and other varieties, attained their largest volume in 1937 when the amounts produced and net imports into various countries were as shown in Table 4.

[3] Gibbons, W. A. and Brass, P. D., "Chemistry and Technology of Rubber," Davis and Blake, Reinhold, New York, 1937, p. 600.

[4] Van Rossem, A., ibid., p. 31.

[5] Statistical Bulletin, International Rubber Regulation Committee, January 1939, July 1940.

The trend of world export of crude rubber for the years 1923 to 1939,[6] inclusive, is shown in Figure 4.

Prices—Prior to the development of plantations prices of crude rubber fluctuated widely. In 1860 when the United States consumption was only 54,000

TABLE 4—WORLD SHIPMENTS AND IMPORTS OF CRUDE RUBBER

	Shipments 1937 in Long Tons
Malaya	492,754
Ceylon	70,054
Sarawak	25,922
North Borneo	13,213
India and Burma	17,236
Netherlands East Indies	433,903
French Indo-China	43,374
Thailand	35,551
Philippines and Oceania	1,617
Africa	7,678
South America	16,288
Mexico (Guayule Rubber)	2,692
Total	1,160,282

	Net Imports 1937 in Long Tons
United States	582,500
Germany	98,200
United Kingdom (Great Britain)	91,000
Japan	62 200
France	60,000
Canada	36,100
Russia	30,400
Italy	24,000
Australia	19,300
Belgium	15,000
Czecho-Slovakia	13,000
Rest of the World	78,700
Total	1,110,400

tons the average price in New York was 62 cents a pound. In 1910 the peak was reached with an average for the year of $2.07 a pound. The highest price for the best grade, Fine Para, was $3.12 per pound in April of that year. After the supply of plantation rubber became relatively large prices of crude rubber

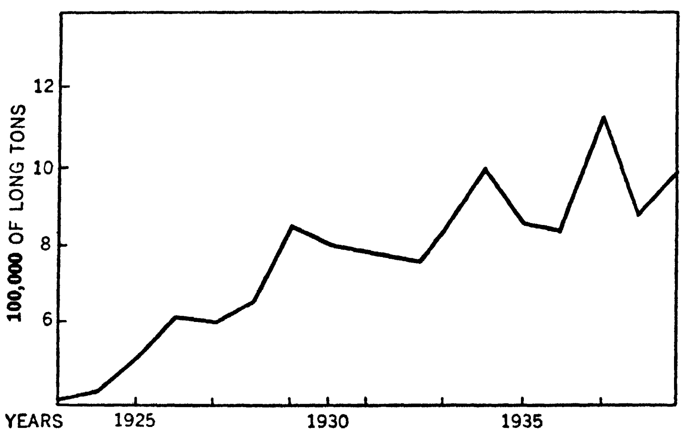

Fig. 4. World Export of Crude Rubber.

dropped but still fluctuated considerably, rising above $1.00 a pound during 1916 and again during 1925 and sinking to the lowest level in 1932 when the average price for the year in New York was 3.5 cents a pound. A production restriction scheme designed to stabilize prices was put into effect by the British and Dutch

[6] Rubber Age, *47*, 284 (1940).

TABLE 5—AVERAGE PRICES OF SMOKED SHEETS

Year	*Cents*
1923	29.45
4	26.20
5	72.46
6	48.50
7	37.72
8	22.48
9	20.59
1930	11.98
1	6.17
2	3.49
3	5.96
4	12.92
5	12.37
6	16.41
7	19.39
8	14.64
9	17.57

Governments in 1934. From that time until June, 1938, prices of prime smoked sheet had fluctuated between 10.25 cents and 27.25 cents per pound in New York.

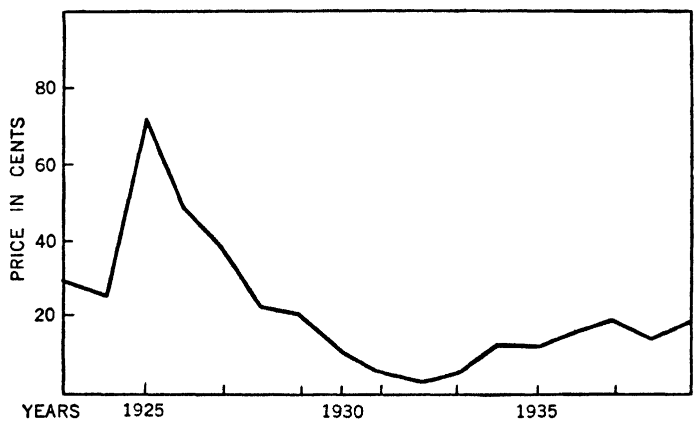

FIG. 5. Average Spot Closing Prices Ribbed Smoked Sheets, New York Markets.

For the period 1923 to 1939, inclusive, the average spot closing prices of ribbed smoked sheets on the New York markets [7] varied as shown in Table 5 and Figure 5.

DEVELOPMENT OF MANUFACTURE OF RUBBER GOODS

About the year 1800 American importers began to purchase shoes and bottles from South America where they were made by the natives by coagulating rubber from latex around clay forms. In 1820 Thomas Hancock established a plant in England for manufacturing goods from dry rubber and in 1823 Charles MacIntosh began the production of water-proof rubberized cloth and garments at

[7] Rubber Age, *47*, 280 (1940).

Glasgow. In 1832 the Roxbury (Mass.) India Rubber Company was founded with a capitalization of $400,000, the first notable rubber fabricating establishment in this country.

Discovery of Vulcanization—Until 1839, however, all rubber goods suffered from two serious defects. They softened with heat and stiffened with cold, so that the rubber surface of waterproof cloth, for example, would be inflexible in winter and would become soft and sticky in summer. Frequently, too, bad odors developed in rubber goods. Many attempts were made to overcome these difficulties. No satisfactory method was found until Charles Goodyear[8] discovered early in 1839 that, when a mixture containing rubber, sulfur and white lead was heated to a moderate temperature, a change occurred which not only prevented the defects common to rubber goods of that day but also made the rubber much stronger and more resilient. This epochal discovery made possible the manufacture of durable rubber products. Hancock,[9] by heating rubber in a batch of melted sulfur, obtained similar results and adopted the name *vulcanization* to the process of reacting rubber with sulfur. Later the process became known also as *curing*; the terms uncured and cured rubber corresponding to unvulcanized and vulcanized rubber. The changes produced by vulcanization are readily observable. Unvulcanized rubber swells in hydrocarbon solvents such as benzene to form viscous solutions; but vulcanized masses, though they increase in size, retain their form. When worked between warm rolls, unvulcanized rubber becomes soft and plastic, vulcanized rubber crumbles. Unvulcanized rubber, strongly deformed, will not resume its original dimensions, vulcanized rubber will recover almost completely. If uncombined sulfur in the mix after vulcanization exceeds the maximum amount soluble in the mass it will separate in crystal form. This will eventually appear on the surface of the goods as a fine powder known in the industry as *bloom*. Other materials soluble to some extent in rubber also bloom to the surface, if used in excess,—paraffin wax, certain age resisters, and so on.

Following Goodyear's discovery, the American rubber manufacturing industry grew steadily. In 1858 the annual value of manufactured goods reached $5,000,000. Bicycle tire production began in good volume in 1877; but the greatest impetus to growth came through the introduction of the automobile and the industry has increased enormously since that time. For several years prior to the business collapse of 1930 the value of rubber goods manufactured in the United States exceeded one billion dollars annually.

MATERIALS OF THE INDUSTRY

The properties of rubber are altered not only by heating with sulfur but also by mixing other materials with it before vulcanization. Substances can be added to modify such properties as hardness, strength, toughness and resistance to abrasion, oils, oxygen, light, chemical solutions, or cracking on repeated flexure. Many of these modifying ingredients are finely powdered mineral substances, others are organic. The effects produced depend on the kind and amount added. Some are *reinforcing pigments*. Rubber compositions containing pigments of

[8] Goodyear, C., U. S. 3,633 (1844); "Gum Elastic," New Haven (1855).
[9] Hancock, T., E. P. 9,952 (1843); E. P. 12,007 (1847).

this class require more energy to stretch them to rupture than those containing rubber and sulfur only. Carbon black, made by imperfect combustion of natural gas, is the outstanding example of reinforcing pigments. Others are zinc oxide, certain clays, magnesium carbonate and blanc fixe. Most pigments of this class are of small particle size,—about 1 μ or less in diameter,—and roughly spherical in form.

Other pigments are used as *fillers*. Ground barytes ore and natural whitings fall in this category. Fillers such as ground cotton or asbestos, diatomaceous earth and asbestine are used to harden rubber compositions. The particle size of fillers is much larger than that of reinforcing pigments and the shape of the particles is irregular or elongated.

Colors were imparted to rubber goods originally by mineral compounds such as ferric oxide, vermilion, antimony sulfide, ultramarine blue, green chromium oxide, zinc chromate, cadmium sulfide, zinc oxide or lithopone. Later, new materials were developed: titanium oxide,—as an exceptionally effective white,—and a number of organic colors and lakes producing the delicate shades seen in bathing caps and hot water bottles in recent years.

Softeners of various kinds are mixed with rubber to improve processing of the compounds or the dispersion of fine powders during mixing or to render dry mixtures sticky and plastic prior to vulcanization or, in certain cases, to improve vulcanization. Softeners such as stearic acid, pine tar, rosin, zinc or lead soaps, vegetable or petroleum oils and coal tar are all used in rubber compositions.

Accelerators—It was early discovered that the time required to produce changes in rubber-sulfur mixtures by heating could be shortened by addition of certain oxides or hydroxides, notably white lead, litharge, slaked lime or magnesium oxide, and these were commonly used as the only accelerators until 1906. In that year George Oenslager of The Diamond Rubber Company, in Akron, Ohio, discovered that aniline is an accelerator of vulcanization and further studies disclosed other new ones, such as thiocarbanilide, p-amino dimethylaniline[10] and hexamethylene tetramine.[11] These *organic accelerators* not only shorten the period of vulcanization to about one-third the time previously required but impart to the finished products superior strength, toughness and life. Many types of organic accelerators are now used, some producing mild accelerations while others—ultra accelerators—are extremely rapid in action or active at relatively low temperatures. Chemically, the most important classes are benzothiazole derivatives (such as mercapto-benzo-thiazole),[12] thiuram sulfides (such as tetra methyl thiuram sulfide or disulfide),[13] salts of dithio acids (such as zinc dimethyl dithiocarbamate), guanidine derivatives (such as diphenyl guanidine)[14] and aldehyde amines (such as acetaldehydeaniline). The economic effect of the use of organic accelerators is tremendous. Millions of dollars have been saved to manufacturers in cost of buildings and equipment, and millions are saved yearly by consumers in lower costs of service of rubber goods.

Vulcanizing Agents—For hot vulcanization, sulfur, the ingredient originally used, has ever since remained the one most commonly applied. It was later discovered that other materials,—selenium, tellurium and organic nitro and

[10] See compound 161, Chapter 27.
[11] See compound 91, Chapter 27.
[12] See compound 469, Chapter 27.
[13] See compound 133, Chapter 27.
[14] See compound 241, Chapter 27.

peroxide compounds,—also vulcanize rubber at elevated temperatures. Their use, however, is not extensive. Some sulfur-bearing accelerators,—thiuram disulfides, for example,—will also vulcanize rubber without addition of any free sulfur to the mix.

In 1846 Alexander Parkes[15] discovered that 2% to 4% solutions of sulfur monochloride (S_2Cl_2) vulcanize rubber at ordinary temperatures. This method is called *cold vulcanization* to distinguish it from Goodyear's, which required heat. Thin articles such as gloves may be vulcanized by immersion in solutions of the reagent in one to three minutes. An alternative method of utilizing sulfur chloride for vulcanizing thin articles is to expose them to vapors of the reagent at 140° F. for half an hour (*vapor cure*). Vulcanization by means of sulfur chloride is also sometimes called the *acid cure*. About 1850 Nelson Goodyear,[16] younger brother of Charles, discovered that by adding larger proportions of sulfur and vulcanizing at higher temperatures for longer periods *hard rubber* (ebonite) could be produced as distinguished from the flexible *soft rubber* compositions which had previously been manufactured. Soft rubber vulcanizates require sulfur only to the extent of 2% to 5% of the rubber; ebonite compositions usually carry 40% to 50% sulfur on the rubber.

Age Resisters—Vulcanized rubber deteriorates with age. Until the discovery of organic accelerators the only methods of controlling the rate of deterioration of vulcanized rubber were by avoiding admixture of substances known to hasten it and by controlling the degree of vulcanization. Soon after organic accelerators came into use, however, it was noted that certain ones retarded the rate of decadence far beyond anything formerly discovered, and a search was made for materials which would not affect the rate of vulcanization but would improve the aging properties of rubber. Certain organic compounds were discovered which, added to rubber to the extent of from ½% to 2%, greatly improve aging characteristics. These have been called age resisters, antioxidants or antiagers. The first of these appeared on the market about 1924.[17] Continued research has increased their number and effectiveness. It was later discovered that certain kinds not only decreased the rate of deterioration but also greatly retarded the cracking of rubber on repeated flexure, and that others were unusually effective in slowing deterioration at high temperatures. Most age resisters are amino compounds, although a few excellent materials have been developed containing no nitrogen. The earliest age resisters were aldehyde amine reaction products (such as aldol alphanaphthylamine).[18] Among later developments appeared secondary aromatic amines (such as phenylbetanaphthylamine), primary aromatic amines (such as 2, 4 diaminodiphenylamine),[19] secondary alkarylamines (such as N, N′ diphenyl ethylene diamine) and acetone-aniline reaction products (such as 2, 2, 4 trimethyl-1, 2 dihydroquinoline). Age resisters have great economic importance, prolonging the serviceability of rubber goods far beyond that commonly encountered in the days before their discovery.

[15] Parkes, A., E. P. 11,147 (1846).
[16] Goodyear, N., U. S. 8,075 (1851).
[17] Winkelmann, H. A. and Gray, H., U. S. 1,515,642 (1924); Weber, L. E., Ind. Eng Chem. *18*, 963 (1926).
[18] See compound 341, Chapter 27.
[19] See compound 211, Chapter 27.

Ground Scrap—Utilization of vulcanized rubber trimmings obtained during production of goods and of discarded articles such as footwear or hose early presented a problem to the manufacturer. The simplest method is to grind them with or without oil, tar or other binding agents and incorporate the ground material with fresh stock. For certain purposes scrap thus prepared may be used effectively in place of mineral pigments. This method was patented by Charles Goodyear in England in 1853.

Reclaimed Rubber—It was obvious, however, that if the vulcanized rubber could be replasticized to its condition before vulcanization, greater value could be obtained than from merely ground material. Many efforts were made to accomplish this but the first commercially satisfactory method was not introduced until 1881, when Chapman Mitchell developed a process of reclaiming by which ground scrap rubber articles were heated in dilute sulfuric or hydrochloric acid by steam at 3 to 5 atmospheres pressure for 18 to 24 hours. This became known as the acid process to distinguish it from another invented in 1899 by Arthur H. Marks.[20] Marks' process was called the alkali process inasmuch as it involved heating the rubber scrap with a dilute solution of sodium hydroxide (about 5%) in closed vessels heated by steam at 350° to 375° F. for 15 to 24 hours. Softening of the rubber is often promoted in both processes by addition of oils to the scrap before heating. The acid process was the first to destroy the cotton contained in scrap footwear or hose. In the alkali process, the cotton is hydrolyzed and washed out of the rubber. In both processes the material, after heating and washing, is refined between tightly set rolls. Neither process produces a reclaimed rubber as plastic as the original compositions used for manufacture of the goods from which it is recovered; nor, when again vulcanized, will the reclaimed rubber yield a product of as good quality as the original. Reclaimed rubber is, however, a valuable economic material of great assistance in improving processing characteristics and in permitting the design of certain rubber articles of a suitable quality at a lower cost than can be obtained from crude rubber compositions. Scrap rubber articles are sorted by kinds and these reclaimed separately. Discarded tires, inner tubes, footwear and hose are obtainable in substantial quantities. The amount of reclaimed rubber used varies in its relation to crude rubber consumption. For the decade ending with 1937 the ratios of reclaimed rubber to crude used in the United States varied from 0.22 to 0.51. The average for the period was 0.32, or 140,000 long tons of reclaimed rubber a year.

Blowing Agents—To produce rubber containing cells, blowing agents are incorporated in the mix. These are substances which when heated decompose to form gas. Sodium and ammonium bicarbonates are common blowing agents. If it is desired to produce pressure during molding on the inside of hollow articles, like syringe bulbs, water is sometimes used, or for toy balls "pills" consisting of a mixture of dry sodium nitrite and ammonium chloride which, when heated, releases nitrogen. The finished article contains this gas under pressure, increasing its resiliency. Blown rubber, unless the cells are connected, will not absorb water as natural sponges do. Stock for rubber bath sponges is therefore run repeatedly between rolls to rupture the cell walls and form connecting series of cells.

[20] Marks, A. H., U. S. 635,141 (1899); E. P. 11,159 (1899); J. Soc. Chem. Ind. *18* 773 (1899).

Auxiliary Materials—Many articles are made of rubber compositions alone. Washers and packing of certain kinds, rubber bands, erasers, dental dam, dress shields, and shoe soling are of this character. Usually, however, as in hose, belting, tires and tubes, heels, waterproof clothing and many other articles, there are included with the rubber composition other structural parts consisting of textile, metallic or other material. By their use the valuable characteristics of rubber are combined with strength and rigidity imparted by other structural members. Thus, in pneumatic tires are cotton cords, strips of woven cotton fabric, and, in the beads, steel wire. Heels contain metal washers or ply-wood strips against which the nail-heads seat when the heels are attached to shoes; hot water bottles have brass inserts into which stopples may be screwed. Packing for high temperature steam lines is produced by binding asbestos fibers together by means of a small proportion of rubber and compressing into dense sheets. The use of cotton in rubber goods in the United States amounts to about 7.2% of the total cotton crop. Tires alone require about 5.4% of all cotton produced in this country; i.e., about 317,000,000 pounds for the year 1939.

Design of Rubber Compounds and Articles—Skill in design both of rubber compositions and of the way they are combined with auxiliary materials determines the suitability of rubber articles for any type of service. Over the years an art of compounding has been developed; so that, through selection of the kinds and proportions of pigments, softeners and other ingredients, rubber compounds may be specially designed to possess unusual resistance to flexing, abrasion, water or chemical solutions. Moreover, technologists in the industry have devised special constructions of textile materials to improve the serviceability of belting, hose, tires and other products. If satisfactory service is to be obtained from rubber articles, the skill of the rubber technologist is required both in selection of rubber compositions and in planning the structure of the article.

PROCESSING METHODS

Washing—Before the advent of plantation rubber all commercial grades contained water or foreign solid material and required washing and drying before use. Most grades now available may be used without washing; but the poorer varieties and rubber for thin walled articles are still washed. The washing operation consists in passing the rubber repeatedly between corrugated rolls, 14″ to 16″ in diameter by 32″ to 42″ long, while water plays over it from a perforated pipe above the mill and parallel to the rolls. (See Figure 6.) Foreign material is loosened by the stretching and kneading action of the rolls. Particles once loosened do not again adhere to the wet surface of the rubber but float off in the water above the roll or fall through into a perforated pan below and are carried by the water into a sewer. Each pass between the rolls exposes new surface to the water. Usually two or three washers are used in series. The rolls of the second and third have finer corrugations than the first and are set closer together. After washing is completed the rubber is squeezed between smooth rolls to form rough surfaced sheets preparatory to drying.

Drying—Rubber is dried in a variety of ways dependent on the use for which it is intended. Rubber selected for thread, for example, is usually subjected to the process of *force drying*. The drier consists of a large room in which the sheets of wet rubber are hung on wooden rods about six inches apart. (See Figure 7.) Filtered air at 90° to 100° F. is blown through the room from one side to the other. Drying requires from 2½ to 6 days. A quicker process is *vacuum drying.* This method is used for soft rubbers too tender to hang in the form of sheets and frequently, also, for tough rubbers for certain purposes. The rubber is sheeted in thick slabs which are cut to size to fit into metal trays. The trays are laid on steam heated, hollow iron shelves in a pressure chamber. Air is exhausted from the chamber to 26 inches to 27 inches vacuum. Time and temperature of drying vary for different kinds of rubber from 260° to 290° F. and from 2 to 6

FIG. 6. Wash Mill for Rubber.

The corrugated rolls, water feed pipe and rough surface of the sheeted rubber are plainly seen. The operator is cutting the rubber from the mill.

hours. If it becomes necessary to dry reclaimed rubber, vacuum drying is applied. Damp pigments may be dried by storage in a room heated to 160° F. Sulfur, however, should be heated only slightly,—to not much above 100° F. Water may be removed from oils and tars by heating them in steam jacketed kettles at about 250° to 275° F. until frothing ceases.

Cotton fabrics in storage usually contain from 5% to 6% moisture and must be dried shortly before rubber is applied to them. Drying is performed by passing the cloth over a series of steam heated rolls or steam heated shelves. Two passes through such driers reduce the moisture to between 2½% and 3½%.

Grinding—In grinding, vulcanized rubber scrap is first passed through a heavy roll mill about 32″ wide known as a *cracker*. The front roll of a cracker is smooth, the rear roll corrugated. Coarse material from the cracker is then passed through a *grinder* consisting of two smooth, hollow rolls of different diameters,—for example a 16″ front roll revolving at 16 r.p.m. and a 24″ rear roll at 20 r.p.m. Before grinding is started the rolls are set tight together by means of adjusting screws at each end of the rolls. The operation develops considerable heat and cold water is passed through the rolls to prevent overheating. The small clearance between the rolls and the difference in their surface speeds causes crushing and shearing action which disintegrates the rubber. A grinder delivers friable sheets of vulcanized rubber as thin as 0.003". Hard rubber may be ground to dust on ordinary grinders but an enclosed type (originally designed for grinding rock or coal) through which a stream of washed flue gas is passed is more economical to operate and avoids all hazard of fire or explosion. The dust passes from the internal grinder through a cyclone separator and is collected in a series of cloth bags which permit the gases to pass through

FIG. 7. Rubber in a Force Drier.

This is one of a number of methods of drying washed rubber.

but retain the dust. Hard rubber dust is a common ingredient of hard rubber compositions.

Sifting—When it is necessary to remove coarse particles from mineral pigments usual forms of screens or rotary sifters are used.

Plasticizing of Rubber—Working rubber between mill rolls causes it to soften and become more plastic. This effect is permanent and rubber is often plasticized before it goes to the mixing machines to be blended with other materials. For many years it was believed that softening was the result of mechanical breakdown of the rubber structure, but a few years ago W. F. Busse[21] in America and F. H. Cotton[22] in England proved that the effect is produced by oxidation. Oxygen of the air is activated by static charges generated by working rubber on cool mill rolls. Oxidation may also be hastened by heating rubber in air to temperatures of 350° F. or higher. Commercially, rubber is plasticized

[21] Busse, W. F., Ind. Eng. Chem. *24*, 140 (1932).
[22] Cotton, F. H., Rev. gen. caoutchouc, No. 75, 179 (1931).

by milling it on moderately cool mills for 15 minutes or more. This is known as *mastication.* Another type of plasticizing machine is known after its inventor as the *Gordon plasticator.* In this machine the rubber is forced by a screw through a steam heated cylinder. The action of the machine mixes air into the rubber and it leaves the plasticator in a porous condition at a high temperature conducive to rapid oxidation. Recently, it was discovered that the addition of certain chemicals, notably hydrazine salts and thio naphthols, to the extent of a few tenths per cent greatly increases the rate of softening and some of these are now on the market.

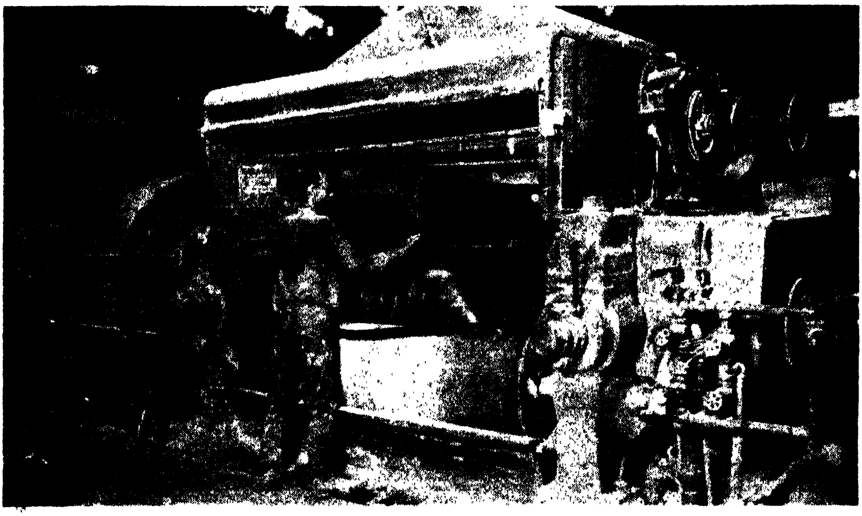

FIG. 8. A Mixing Mill.

Showing adjusting screws for regulating the opening between the rolls, the water lines feeding cold water to the rolls, and the operator cutting and rolling a partially mixed batch to increase uniformity of the mix.

Mixing—Until a relatively few years ago all rubber compositions were mixed on two-roll mills. The first machines were small but, as the volume of manufacture increased, larger mills were developed until rolls 84″ long came into common use. A mixing mill consists of two smooth surfaced, horizontal, hollow rolls set side by side. (See Figure 8.) The front roll is fitted at the ends with adjusting screws for controlling its distance from the back roll, which is fixed in position. The 84″ rolls are 24″ or 26″ in diameter with walls 4½″ thick. To resist wear the surface of the rolls is hardened to a depth of ¾″ by chilling. The speed of front and back rolls may be the same or the back roll may be run faster. Ratio of surface speeds of back to front rolls is usually from 1.1 to 1.25, although still higher ratios have been used. Considerable heat is developed during mixing; and, in order to prevent the rubber mix from becoming overheated, cold water (preferably not over 50° F.) is run through the hollow rolls. The mixing capacity of an 84″ mill varies, with the specific gravity of the rubber stock produced, from 150 pounds for stocks with gravities of about 1.2, to 250 pounds for heavy compositions of 1.85 gravity. Mixing time also varies according to the type of composition from 20 to 50 minutes. In mill mixing the rubber portion of the batch is run around the front roll until it is soft and forms a smooth, plastic sheet. Then the other ingredients are fed between the rolls on top. These are forced into the rubber by the rotating rolls. After the rubber has absorbed all of the other materials the batch is cut from one side toward the other and the loosened portion thrown across to the other end of the rolls. By repeating this operation alternately from each end uniformity of the mix is secured. Finally the stock is cut off in slabs and dusted with soapstone or other powder to prevent their sticking together when placed in a pile.

For compounds produced in large volume, internal mixers have been found more economical than mills. The one most commonly used, the *Banbury mixer*, consists of an enclosed chamber with a lid raised and lowered by hydraulic pressure. In the chamber are two rotors turning in opposite directions and at different speeds. These rotors are of a shape designed to force the rubber between the rotors themselves and between the rotors and the walls of the chamber. The wall jackets and rotors are water cooled. The order of mixing of the ingredients is much the same as in mill mixing. The batch, however, remains in chunks and must be sheeted on mills. The largest type Banbury mixer will mix about 750 pounds of stock of 1.15 specific gravity in 10 minutes. The lumps of mixed stock are discharged at the bottom of the mixer and sheeted on mills while the next batch is mixing.

Calendering—Calenders are machines designed for sheeting rubber or applying it to fabric. An ordinary calender consists of three horizontal, hollow rolls set one above another. (See Figure 9.) Roll sizes vary up to 100″ length by 30″ diameter. The outer surfaces of calender rolls are chilled and the inside cavities are bored to produce uniform wall thickness. A 66″ roll 24″ in diameter will have a wall thickness of 6″. The relative speeds of calender rolls are controlled by two sets of gears, one set at each end, and they may be run even speed or odd. Calender rolls are fitted not only for cooling but also for heating with steam to permit accurate control of roll temperatures. Adjustments are provided, also, for accurately controlling the spacings between rolls.

Sheeting—Rubber is sheeted by feeding stock, previously softened on warm-up mills, between the upper pair of rolls. The sheet thus formed passes half way around the middle roll and then between the lower pair. It is common practice to build sheets up in plies by rolling together a sheet already prepared on the calender with a fresh sheet as it leaves the machine. This may be repeated so that 3-ply or 4-ply sheets are built up. Sheeting calenders have speed controls and run from 10 to 20 yards a minute. For special purposes calenders with one removable roll are used. These removable rolls are engraved to produce pebbled, ribbed or other irregular surfaces on the rubber sheet. Such rolls are used in preparing stock for soles of footwear and for embossing designs of various kinds.

Frictioning consists essentially of forcing warm, sticky rubber into fabric on a calender. The spaces between the threads of the fabric are filled with rubber but very little is forced into the threads or between the cotton fibers. It is important that the fabric be hot when brought into contact with the rubber. Therefore, it is run through a drier (see above) immediately before it is rubberized or it passes over heating rolls or pipes directly to the calender. The rubber is fed between the upper two rolls and passes around the middle one. The fabric is fed between the lower two and the rubber is squeezed into it as it passes between them. The middle roll of a friction calender is run faster than the bottom roll and produces a wiping as well as a squeezing action on the fabric surface. Fabrics may be frictioned on one side only or, by a second pass through the calender, the opposite side may be frictioned, also. The speed of friction calenders is regulated by the kind of material used and varies from 7 yards to 40 yards per minute.

FIG. 9. A Calender.

The picture shows the sheeting operation—the feed between the upper two rolls, the sheet passing around the lowest roll. At the side are seen the steam and water connections for regulating roll temperatures.

Coating—Thin coatings of rubber may be applied directly to cloth or placed over a previously frictioned surface. The latter operation produces a much firmer bond of rubber to cloth. Linings for overshoes are usually coated without previous frictioning. The fabric, heated to prevent chilling of the rubber, passes between the lower two rolls running at the same surface speed, where the rubber sheet formed between the upper pair is squeezed against it. If the cloth is first frictioned, heating of the fabric is not so essential. Many tires are now built of unwoven cords. These are fed parallel through a comb-like device to maintain proper spacing and coated both sides at the same time on a four-roll calender. One sheet of rubber is formed between the top roll and another set horizontally beside it, the other sheet is formed between the lower two rolls. The cords run between the two sheets, meeting between the middle and upper rolls of the three vertically arranged.

Tubing—A tubing machine or, as it is better termed, an extruding machine is a device for making continuous lengths of rubber of a great variety of sectional shapes. In some instances the form to which it is extruded is that of the finished article, as for tubing or channel strips for automobile windows. In other cases the extruded material is later molded into a modified shape. The machine consists of a cylindrical barrel surrounded by a jacket heated with steam. A screw forces rubber previously softened on a mill through the barrel to a head into which is inserted a removable die that determines the shape of the extruded strip. (See Figures 10 and 11.) These machines are used not only for forming tubes and strips of irregular section but also for covering wire and hose with rubber. The material to be covered may be fed straight through the screw from the rear

FIG. 10. Tubing (Extruding) Machine.

The operator is feeding softened rubber compound to the screw. The rubber is formed by a die at the near end of the machine and carried away on a conveyor. This rubber strip is to be used for treads of automobile tires. Steam connections for heating the jackets around the screw are seen above the machine.

of the machine or at right angles to the axis of the screw through a special head with openings at the sides. In some machines special arrangements in the head are available for extruding stripes of one color on strips of a contrasting color.

Refining and Straining—When special uniformity of mixture is required pigment agglomerates which may remain undispersed during mixing can be separated into individual particles and larger masses removed by passing the mixed stock through a *refiner*. This machine is similar to the grinder already described. Coarse particles are forced back from the nip of the rolls and concentrate at the edges and at the end of the sheet last through the refiner. These portions are cut off. Sometimes coarse particles are removed from rubber by passing the mixed stock through a *strainer*, which consists of an extruding machine with a perforated metal disc or a wire screen at the delivery end. The fine screen needed to remove coarse particles is reinforced by heavy screen of coarser mesh. The rubber is forced through the screen, leaving the undesirable particles behind. Reclaimed rubber is frequently cleaned by straining because of metal and other foreign materials which invariably are found in worn out goods.

Cements—For adhering different parts of rubber articles together and for miscellaneous adhesive purposes with other materials, solutions of rubber in volatile organic solvents such as gasoline or benzene are commonly used. These cements are made in churns fitted with rotatable vertical shafts bearing horizontal arms to stir the contents, or in closed mixers with horizontal shafts bearing agitating blades. The viscosity of cements decreases with the degree of milling of the rubber prior to solution. Thus, a cement may be made highly viscous with unmilled rubber, whereas a similar solution of thoroughly masticated rubber will

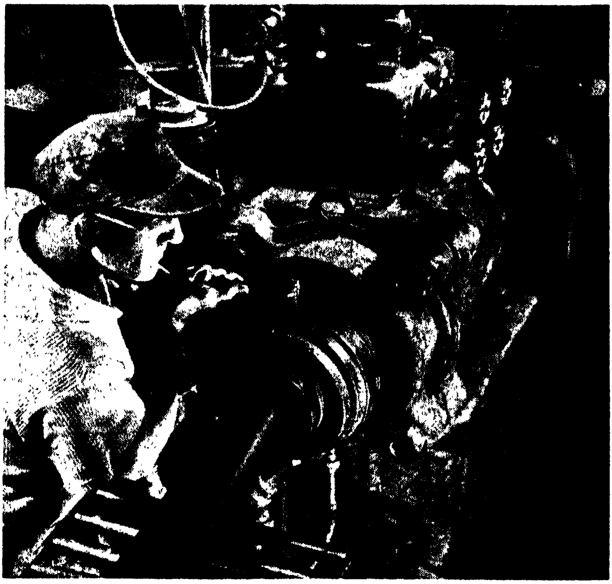

FIG. 11. Extruding a Tube.
This is to be used for forming inner tubes for automobile tires.

be almost as limpid as water. For spreading on cloth, cements of masticated rubber are made in high concentrations to reduce the amount of solvent required. Cements are used also for making thin walled goods such as surgeons' gloves. These are known as *dipped goods* and are formed by immersing a porcelain form in rubber cements and permitting the solvent to evaporate before the rubber is vulcanized.

Spreading—Waterproofed cloth for raincoats, nursery sheeting and offset blankets for the printing trade are prepared by spreading coats of rubber cement on the surface of fabric. The material to be coated passes over a roll situated below an adjustable spreader-knife parallel to the roll. The cement in the form of a thin dough is placed over the fabric behind the spreader-knife. The distance of this knife above the cloth determines the amount of cement applied. The coated fabric then passes over a series of steam heated pipes to drive off the solvent. Thick coatings can not be applied by one pass through a spreader, and it is the practice to pass the fabric repeatedly under the knife to obtain coatings of appreciable thickness. In order to avoid sparks resulting from electric charges developed by friction in the operation, special precautions are taken to remove the charges and to ground the machines.

Water Dispersions of Rubber—Rubber occurs as a natural dispersion in latex tapped from the trees. This may be preserved against coagulation by addition of about ¾% ammonia. Dispersions of sulfur, accelerators and pigments may be made separately in colloid mills and blended with the rubber in calculated amounts to form vulcanizable compounds. On the other hand, water dispersions of rubber compounds mixed by the usual methods from dry materials may be produced in internal mixers by the addition of peptizing agents and protective colloids with the water. The particles of all these dispersions, both natural and artificial, are negatively charged and may be caused to cohere when this charge is neutralized. This may be done by addition of positive ions,—solutions of salts of di- or tri-valent metals,—or by passing a direct current through the suspension to discharge the particles at the anode. This behavior is the basis of the[23] *Anode process* for forming articles such as gloves, overshoes, fountain pen sacs, and for covering metal articles such as wire screen or dish drainers. Water dispersions may be used, also, in place of cements for spreading fabrics. Similarly, water dispersions have taken the place of cements in the manufacture of many kinds of dipped goods. When dispersions are vulcanized without removal of water, microporous structures are formed. Hard rubber sheets of this character are used as separators between the plates in storage batteries. By frothing dispersions mechanically, or by means of blowing agents which release gas when heated, sponge rubber of light texture may be produced. The use of latex for direct manufacture of goods has increased greatly during the past ten years. In 1927 latex containing 1,500 long tons of rubber was imported into this country, in 1937 importations were 23,000 long tons. These figures represent roughly 0.4% and 4.0%, respectively, of the crude rubber imports of the same years.

The rubber content of latex may be increased by centrifuging, by creaming and skimming, or by evaporation of some of the water; and concentrated latices with a rubber content of over 60% are available on the market.

Vulcanizing Processes—The method selected for vulcanizing rubber articles is determined by the character of the goods. Varnished footwear is vulcanized in warm air. The shoes formed on wooden or metal lasts are placed on cars which are wheeled into vulcanizers heated by steam pipes or steam jackets. Originally air at atmospheric pressure was heated by steam pipes at the bottom and sides of large rooms. Later horizontal, cylindrical steel chambers came into use and preheated air was circulated through them by means of pumps or fans. *Dry curing*, as this process is called, is usually carried out by raising the temperature in the oven to 265° to 270° F. The process is used also for other types of goods such as rubber strips laid on a metal tray during vulcanization.

Steam curing is carried out in horizontal or vertical (pot heaters) pressure vessels. Footwear (unvarnished), stationers' bands and certain kinds of hose are thus vulcanized. After the vulcanizers are filled and the covers fastened steam is admitted. Steam cures range in temperature from 250° to 300° F. and the time varies according to the thickness of rubber treated. Hose is often constructed on metal poles or mandrels and wrapped tightly with wet cloth before

[23] Klein, P., U. S. 1,548,689 and 1,825,736; Beal, C., Ind. Eng. Chem. 25, 609 (1933).

introduction into the vulcanizer. Some articles such as tubing are sometimes imbedded in powdered soapstone laid on metal trays which are then placed in vulcanizers and heated by steam coming directly in contact with the soapstone.

Press cures are carried out between steam heated platens. The articles are formed in metal molds placed between the platens. (See Figure 12.) The distance between platens is controlled by hydraulic lifting of one plate. When pressure is thus applied, the rubber inside the molds is forced into all its contours and

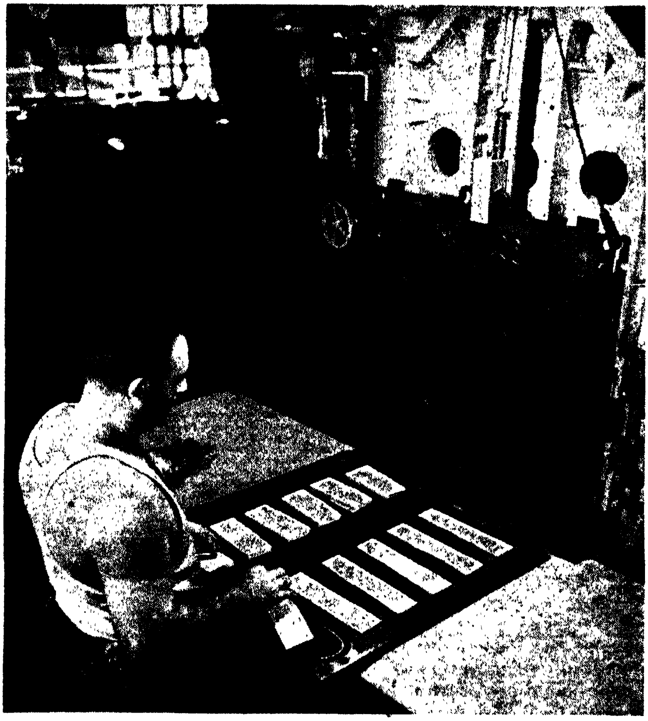

FIG. 12. Placing Unvulcanized Stock in Mold.

When heated and squeezed in the press the rubber flows, filling the cavities being set by vulcanization, in this instance, into the form of shoe soles.

cavities, and is vulcanized by heat conducted from the steam through the platens and mold walls. Belting for transmission of power or conveying of materials is vulcanized directly between the platens of a press. (See Figure 13.) By moving the belting after one section is vulcanized to bring the next adjacent section to the end of the press, any length may be vulcanized in a relatively short press.

The platens of curing presses may be cast hollow or bored with a series of connecting cylindrical cavities. A great variety of articles are molded, such as heels and soles, erasers, and motor supports for automobiles. Other molded articles such as tires are heated by steam coming directly into contact with the molds. For this operation a series of molds is stacked one above another in a vertical pressure vessel and, after the cover of the vulcanizer is closed, forced together by an hydraulic ram. Steam is then admitted around the molds, heating them and vulcanizing the tires, which are expanded to fill the molds by steam, air or hot water under pressure inside flexible rubber bags inside the tires. Tires and auto tubes are vulcanized also in individual heaters. In these one wall of each steam chamber is the mold which determines the shape of the article. The heaters are split in two parts hinged together. (See Figures 14 and 15.) Un-

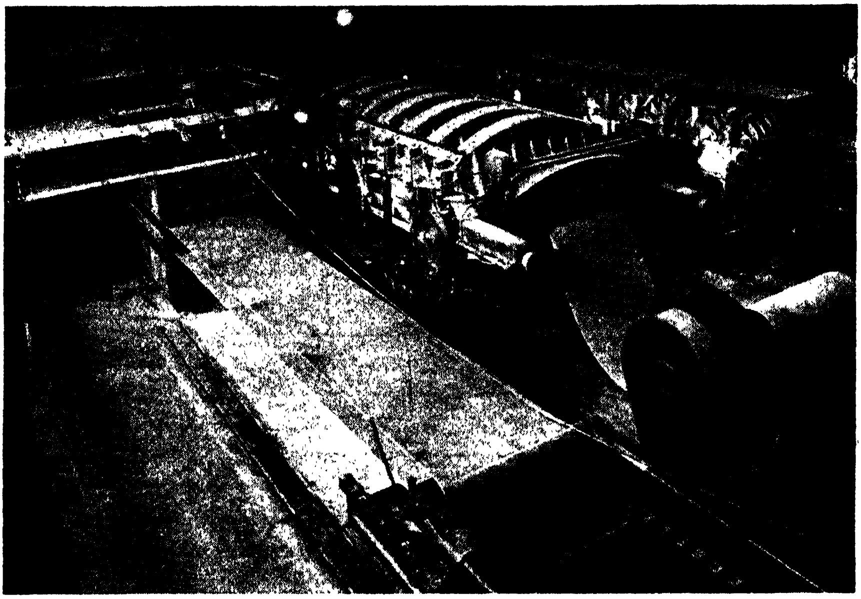

FIG. 13. Belt Presses.

The section of the belt at the right has been vulcanized, the section in the press is in the process of vulcanization. When this is completed, the lower platens will be dropped, the belt drawn forward one press length and another section vulcanized. In this way, any desired length may be cured in a relatively short press.

vulcanized articles are placed inside the molds, the two halves are brought together and the article heated by steam in the surrounding chambers.

A special process is used for molding garden hose. After the hose is formed, a lead sheath is extruded over it. The lead-covered hose is then wound on large drums, wheeled into a steam vulcanizer and heated by steam outside the lead sheath. The lead is then stripped off and melted for further use.

Water Cures. Sheet rubber to be cut into threads and hard rubber sheets are vulcanized under water. The sheets, wound between layers of cloth on metal drums or piled flat between sheets of tin, are immersed in a pressure tank partly filled with water. Steam is admitted under the water, rapidly heating it to vulcanizing temperature.

Combination cures of different kinds are used in special cases. For example, heating goods in air to a specified temperature so that steam later admitted to the vulcanizer will not condense on the articles is a method which has been used for footwear.

Adhering Rubber to Metal—Many uses are made of rubber in combination with iron. Motor supports and vibration dampeners for machinery and rubber-lined pipe and tanks for the chemical industry are examples of these. The best methods of adhesion are brass plating of the iron or adhesion by a special

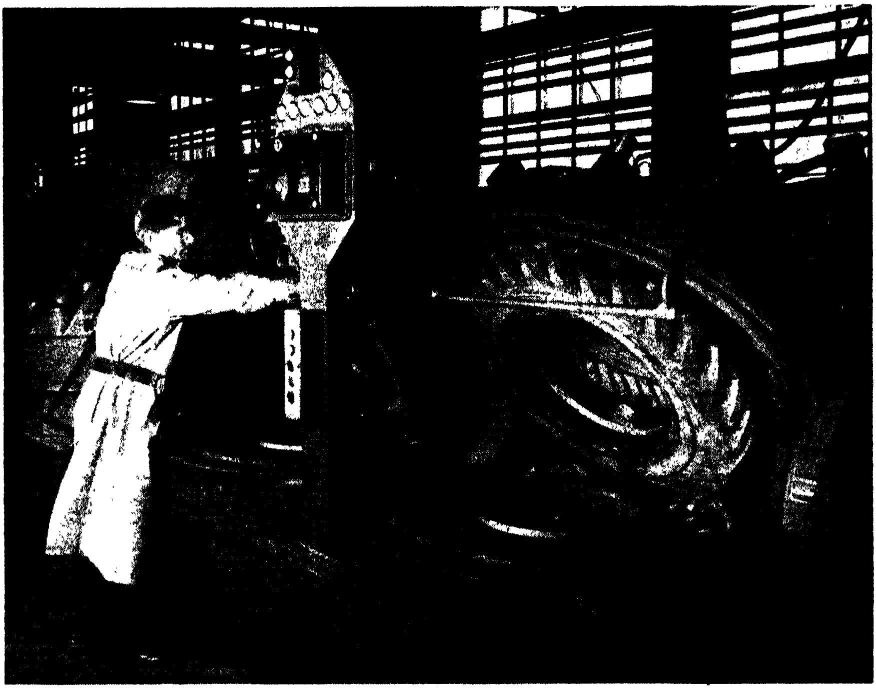

FIG. 14. Individual Tire Vulcanizers.

Presses containing individual steam jacketed tire molds such as those shown here represent the latest type of vulcanizing equipment for pneumatic tires. The presses are electrically driven and are equipped with automatic control for all time- and temperature-curing operations. At the end of the prescribed vulcanizing period, the presses automatically open and remove the tire from the mold halves without the operator's attention.

cementing material. Brass containing about two-thirds copper and one-third zinc is plated on clean iron in a cyanide bath. When the composition of the brass is carefully controlled and certain ingredients avoided in the rubber composition, the rubber will adhere firmly to the brass if held tightly against it during vulcanization. This is the method usually adopted for small molded articles. About 1923 it was discovered that if rubber is mixed and heated with certain agents such as aromatic sulfonic acids it will be changed to a thermoplastic material which will bond rubber firmly to clean iron and other materials. The thermoprene formed by this reaction [24] is dissolved in organic solvents and applied

[24] See p. 1483.

between the metal and the rubber before the latter is vulcanized. This method is known as the *Vulcalock process* [25] and is used for sticking rubber linings in metal pipe and tanks and for adhering ply-wood in heels.

FIG. 15. Curing of Inner Tubes.

To insert the unvulcanized tube the operator is inflating with air. The outer jackets of the heater, hinged at the bottom, are then separated. The tube is placed around the central ring-shaped chamber, and the mold is closed and heated by steam contained in the center ring and the two side chambers.

RUBBER PRODUCTS

The varieties of rubber articles are legion. Rubber serves us not only directly in such familiar articles as tires and running board covers on automobiles, footwear and raincoats, erasers and rubber bands, garden and fire hose, hot water bottles and ice bags, tennis and golf balls, but also indirectly through many industries using in their manufacturing operations valves, gaskets or packing; transmission or conveyor belting; hose for gasoline, pneumatic tools, oil or paint; hard rubber rods or trays; rolls in printing or paper-making or a great variety of rubber-lined sheets, tubes and pipe. The United States Department of Commerce lists rubber manufactures for 1933, 1935 and 1937 as shown in Table 6.

Manufacturing Operations—To describe the mechanical methods of manufacture of even a few kinds of rubber goods would require too lengthy a description for the purpose of this discussion. In general, however, all rubber articles are constructed of rubber compounds formed into blocks, sheets, strips or tubes. When textile materials are combined with rubber, layers of rubberized fabric and rubber parts are assembled on forms. Many articles are constructed by

[25] Geer, W. C., U. S. 1,617,588 (1927).

TABLE 6—RUBBER PRODUCTS—PRODUCTION, BY KIND, 1933, 1935, 1937 [26]

	Unit	Quantity (Thousands of Unit Specified)			Value (Thousands of Dollars)		
		1933	*1935*	*1937*	*1933*	*1935*	*1937*
Total value	....	....	....	....	468,615	671,722	878,626
Tires and inner tubes:							
Pneumatic tires and casings:							
Motor vehicle	Number	45,376	48,765	54,113	221,051	322,193	412,766
Motorcycle and bicycle	"		4,006	5,056		3,852	4,583
Inner tubes:							
Passenger car, truck and bus	"	46,812	47,761	52,373	31,715	44,386	55,739
All other, including motorcycle and bicycle	"		1,550	3,590		728	1,759
Solid and cushion tires:							
Truck and bus for highway transportation	"	....	37	23		1,534	876
Industrial truck, tractor and trailer	"	....	117	232	3,746*	854	1,548
All other, including carriage and other tiring	Pound	....	6,994	13,567		718	1,501
Boots, rubber	Pair	2,622	3,029	3,884	4,659	5,534	7,625
Shoes and overshoes, rubber	"	32,984	37,810	41,599	23,042	30,384	32,602
Shoes, canvas, with rubber soles	"	29,689	23,955	31,519	13,813	12,343	18,042
Heels, for sale as such	"	272,504	278,369	295,081	11,119	11,594	16,285
Soles, including composition or fiber	"	91,995	69,656	72,476	8,316	7,259	10,750
Rubberized fabrics, sold as such or on hand:							
Automobile and carriage	Sq. Yd.	8,620	5,227	6,006	3,362	1,874	2,123
All other	"	62,631	66,119	63,608	14,836	18,186	19,509
Belting	Pound	30,628	48,363	58,706	12,928	20,498	32,060
Hose and tubing	"	....	....	....	18,074	26,626	40,410
Packing	"	9,328	11,409	14,047	1,872	2,737	3,551
Druggist and stationers' sundries	....	....	....	....	8,242	12,387	15,963
Hard rubber goods	....	....	....	....	9,928	14,032	16,711
All other manufacturers of rubber	....	....	....	....	81,912	122,232	164,486
Reclaimed rubber produced (†)	Pound	‡	266,785	399,629	§	11,774	19,738

* Includes data for a small quantity of casings and tubes other than for motor vehicles, motorcycles and bicycles.
† Including reclaimed rubber transferred to other plants of same company. ‡ No comparable data. § Included with "all other manufacturers of rubber."

[26] Statistical Abstract of the United States (1939).

hand but special machines have been developed for forming tires, hose and others manufactured in large numbers. Final shapes are obtained by extruding, molding or building on forms which pass through the vulcanizing operation with the articles. Vulcanizing is usually performed only after the goods are assembled. Occasionally, however, parts are partially vulcanized before they are assembled, the heels on rubber boots, for example. Trimming off mold rinds, washing, lacquering, buffing and other operations are used to improve the appearance of goods.

CHEMISTRY OF NATURAL RUBBER

Structure—The proof of structure of chemical compounds commonly requires that identical substances be synthesized from materials of known constitution by means of well-understood reactions. Although attempts to accomplish this proof in the case of rubber have failed, the study of rubber and certain related materials more amenable to proof of structure has led to the belief that rubber is essentially a large polymer of the hydrocarbon, isoprene. The presence of small amounts of other materials in natural rubber is not generally believed to contribute to its fundamental properties although they do contribute to the retention of these properties on aging. The apparent molecular weight of rubber is reduced by oxidation and varies considerably with the treatment the rubber receives. Published data concerning the molecular weight of rubber vary, therefore, over a wide range—from 10,000 to 435,000,[27] or from 150 to 6,400 C_5H_8 units.

The structure of the hydrocarbon of natural rubber may be interpreted as though large numbers of isoprene molecules had polymerized to produce long chains, the carbon-to-carbon unsaturation of which is half that of isoprene. Thus:

$$n(CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2) \rightarrow (-CH_2-\overset{CH_3}{\overset{|}{C}}{=}CH-CH_2-)_n \rightarrow$$

$$-CH_2-\overset{CH_3}{\overset{|}{C}}{=}CH-CH_2-(-CH_2-\overset{CH_3}{\overset{|}{C}}{=}CH{=}CH_2-)_{n-2}-CH_2-\overset{CH_3}{\overset{|}{C}}{=}CH-CH_2-$$

The question of the disposition of the terminal valences has probably not been answered but in chains of 600 to 25,000 carbon atoms it is quite unimportant. Vulcanization is generally believed to produce occasional cross-linkages between chains at the double bonds, thus forming more rigid structures. In soft rubber only 1% to 5% of the double bonds are cross-linked. In hard rubber practically all double bonds are saturated. The vulcanized rubber molecule may thus be considered of greater size than the unvulcanized molecule.

Gutta Percha and Balata—Although these materials are seldom used in the manufacture of rubber goods, they are often classified with rubber. Both these materials contain a hydrocarbon having the same percentage composition as rubber, C_5H_8, but differing in the arrangement of the atoms. Its structure makes it much tougher than the hydrocarbon from rubber. With this hydrocarbon in gutta and balata are resins which differ in the different varieties. Gutta percha is obtained from trees of the *dichopsis* and *palaquium genera*. It is produced in a limited area in the Federated Malay States, Borneo and Sumatra. That pre-

[27] Staudinger, H., "Hoch-Molekulare organische Verbindungen," Springer, Berlin (1932).

pared by natives from wild growth is obtained by felling the trees and stripping off the bark to expose the gutta. There are, however, at least two plantations where the gutta is extracted from leaves of trees of the palaquium species without injury to the trees. This gutta is, of course, much cleaner and more uniform than most commercial grades. The hydrocarbon content of commercial gutta percha varies from 55% to 70%. For manufacturing articles crude gutta is cut into pieces, softened in hot water and masticated under hot water to remove bark and earthy impurities. Further cleansing may be secured by straining through fine screen in a special type strainer. It is then dried by mastication in a vacuum chamber to a water content of about 1%. The main use of gutta percha in years past was for insulation of submarine cables, a use for which rubber compounds are not suited. Minor quantities are used in dentistry or in the form of thin sheets as a heat-sealing adhesive, or for rollers on flax spinning machinery.

Balata is obtained from a tree of the *Sapotaceae* family, *Mimusops Globosa.* It is produced mainly in the northern part of South America. Sheet balata, about 3/16" thick, is made by drying thin layers of the latex in air. Block balata is made by coagulating the latex by heat and compressing the wet coagulum into blocks. Sheets contain little moisture; the blocks, varying amounts up to 50%. By extraction of the resins from balata or gutta with a special, low-boiling petroleum solvent, the tough hydrocarbon is obtained. This is used for covers of golf balls. A mixture of the hydrocarbon with white pigment is sheeted and formed into hemispherical cups. These are placed in molds around the centers of the balls, which consist of vulcanized rubber thread wound under tension over a small spherical core. Heating under pressure softens the cover stock, forces it a short distance between the strands of rubber in the center and produces on the surface of the ball the familiar dimple or mesh design. Before the balls are removed from the molds they must be cooled. This is accomplished by running cold water through the press cavities.

Commercial Derivatives of Rubber—By the action of certain acidic reagents, the degree of unsaturation of rubber may be decreased through linkage of double bonds to form ring compounds. This change is known as cyclization and the products are known as cyclo-rubbers or thermoprenes. H. L. Fisher,[28] working in The B. F. Goodrich Company laboratories, found that by the selection of kind and amount of reagent a series of thermoprenes could be produced varying from a soft material resembling gutta percha to hard, brittle resins similar to shellac. Thermoprenes are used not only as adhesives but as molding plastics, as bases for chemically-resistant paints,[29] and, mixed with rubber, as stiffening ingredients for such purposes as shoe soling. Thermoprenes have the same percentage composition as rubber, C_5H_8, but contain fewer double bonds. Cyclorubber formed by the action of chloro-stannic or chloro-stannous acids produces a molding resin, Plioform, soluble in hydrocarbon solvents but insoluble in alkalies and most acids and in ketone solvents.[30] Chlorine reacts readily with rubber in solution in organic solvents and chlorinated rubbers containing around 65%

[28] Fisher, H. L., U. S. 1,605,180 (1926); Ind. Eng. Chem. *19,* 1325 (1927).
[29] Geer, W. C., U. S. 1,744,881 (1930).
[30] See also Chapter 31.

of chlorine have been placed on the market for use in chemically resistant paints and lacquers.[31] Another derivative is made by the action of hydrogen chloride on solutions of rubber. The resulting rubber hydrochloride has been manufactured into thin sheets (Pliofilm) and used as package wrappings, rain capes, card table covers, etc

CHEMISTRY OF SYNTHETIC RUBBERS

The valuable physical properties of natural rubber are not dependent on the kind of chemical elements of which it is composed but rather on their arrangement and the size of the molecule. Therefore the term "synthetic rubber" is now commonly used to designate those polymeric substances which resemble natural rubber in physical characteristics even though they are not identical in chemical structure. In fact a number of the commercial synthetic rubbers contain elements other than carbon and hydrogen.

Among synthetic rubbers, however, are not included such long-used materials as *mineral rubber* or the rubber substitutes known as *factice.* Mineral rubber is a blown asphaltic material which does not dissolve in rubber but acts somewhat as a resilient filler. Rubber substitutes, made either by the reaction of sulfur on vegetable oils, such as rapeseed or corn oil—brown substitute—or by reacting sulfur chloride with such oils—white substitute—have found more extensive use in Europe than in America. Except in a very few instances, such as in the manufacture of "Art Gum," factice is not used alone but is added to rubber as a modifying agent.

Varieties of Synthetic Rubbers—The commercially important synthetic rubbers now on the American market may be grouped as follows: [32] butadiene polymers or copolymers, chloroprene polymers, isobutene polymers, organic polysulfides and plasticized vinyl chloride polymers. Although the properties of some polyvinyl chloride compositions resemble those of plastics more closely than they do those of rubber, there is justification from many standpoints for considering these materials as synthetic rubbers.

All of the synthetics mentioned above are processed on standard rubber equipment—mills, calenders and extrusion and spreading machines. All but the simple isobutene polymers and the plasticized vinyl chloride polymers are subjected to vulcanization processes. Like rubber, all are compounded to produce modifications of their properties. They are sometimes blended with natural rubber or with one another to gain advantages not possessed by either ingredient alone. Although all are at present more expensive than natural rubber, some possess economic advantages for specialized types of services even at higher prices because of superior properties. It is probable that when they are produced in larger volume their cost will be materially decreased, in some cases to a level competitive with natural rubber.

Butadiene Polymers and Copolymers—During the war of 1914-1918 the production of synthetic rubber in Germany assumed some importance but the "methyl rubber" of that day was not comparable in quality to present day products. It was made by the polymerization of dimethyl butadiene, i.e., methyl

[31] See also Chapter 31.
[32] Wood, L. A., "Synthetic Rubbers," Circular C427, United States Bureau of Standards.

isoprene, hence its name "methyl rubber." The process was little understood and was not subject to careful control nor reproducibility. However, its operation afforded valuable experience when the efforts of the German people were directed some years later toward national economic self-sufficiency. The use of the simple conjugated diene, butadiene, $CH_2 : CH \cdot CH : CH_2$, was found to be much more promising than dimethyl butadiene so that either alone or in copolymerization with other materials, such as acrylonitrile or styrene, butadiene has become the principal raw material for all foreign-made synthetic rubbers imported into the United States.[33]

The first important butadiene rubbers were produced through the use of metallic sodium as the polymerization catalyst. Hence the name "Buna"—Bu [34] for butadiene and Na, the chemical symbol for sodium. The best of these rubbers were "Buna 85" and "Buna 115," the numbers indicating the approximate molecular weights 85,000 and 115,000 respectively. These rubbers were greatly inferior to natural rubber in many respects, especially aging. They presented extreme processing difficulties and, had butadiene alone been used without complementary materials, its polymers likely would have gained as little commercial importance as dimethyl butadiene before it. But through the use of approximately 25% of acrylonitrile or styrene along with butadiene, greatly improved synthetic rubbers were produced by the I. G. Farbenindustrie A-G. These copolymeric materials received the names "Buna N" and "Buna S," although the nitrile copolymer is now known commercially as "Perbunan." Because of the resistance of compounds of Perbunan to petroleum hydrocarbons, it became fairly widely used during the short time that it was available in the United States. Other synthetic rubbers of this general class manufactured in the United States have recently been announced under the names "Ameripol" (sold uncompounded as "Hycar") and "Chemigum."

Although the principal reaction involved in the synthesis of butadiene rubbers is the formation of long chains through polymerization, the residual unsaturation of the chains is sufficient to afford occasional cross-linking, or cyclization. This imparts to certain of the butadiene rubbers a resistance to processing which may be overcome through the use of a greater amount of softeners than is considered good practice with natural rubber compounds. Continued cross-linking and oxidation during storage are retarded by the addition of stabilizers, such as phenyl beta naphthylamine, to the material. Buna S usually requires heat softening in an oxidizing atmosphere for 1 to 2 hours at about 130° to 150° C. before it can be easily processed on conventional rubber machinery.

The means required to modify the properties and to effect vulcanization of butadiene polymers and copolymers resemble closely those used for natural rubber. Although some of the same kinds of softeners are used, it is often found that ester-type softeners, such as dibutylphthalate,[35] are more efficacious for these synthetic rubbers. The butadiene copolymers have specific gravities of about 0.98, whereas that of rubber is 0.93.

At the present time butadiene copolymers are priced roughly 3 to 4 times as high as natural rubber, but like other synthetics to be described later, some have

[33] See also Chapter 14, The Petroleum Industry.
[34] Stöcklin, P., Trans. I. R. I. *15*, 51 (1939).
[35] See compound 217, Chapter 27.

certain peculiar advantages which for use under special conditions overcome this price handicap. As mentioned, Perbunan compounds are remarkably resistant to aliphatic hydrocarbons. This superiority is doubtless due to the presence of the acrylonitrile in the polymer, inasmuch as butadiene-styrene copolymers are no more resistant than natural rubber. The vulcanizates of butadiene copolymers equal those of natural rubber in aging characteristics.

Chloroprene Polymers—The most widely used synthetic rubbers now on the American market are the polymers of 2-chlorobutadiene-1,3 known as *Neoprene*. These have resulted from the studies of the late Professor Nieuwland[36] of Notre Dame University and the research staff of E. I. duPont de Nemours & Company. The parent monomer, also called chloroprene, is made by the controlled polymerization of acetylene in contact with aqueous solutions of cuprous and hydrogen chlorides. Two molecules of acetylene combine to form vinylacetylene, $CH \equiv C - CH = CH_2$ and this reacts with one molecule of hydrogen chloride to give 2-chlorobutadiene-1,3, $CH_2{=}CCl - CH{=}CH_2$. This molecule resembles that of isoprene, a chlorine atom replacing the methyl group. The chloroprene is then itself polymerized in the formation of Neoprene. Different conditions of polymerization give rise to somewhat different products.

To the influence of the chlorine atom in the chloroprene molecule may be ascribed some of the desirable features of chloroprene rubbers. Their vulcanizates are somewhat less flammable than those of natural rubber and their resistance to the degrading effects of sunlight, heat, oxygen and ozone aging is much greater. They have considerable resistance to swelling by aliphatic hydrocarbons and vegetable oils, being much less affected than compounds of natural rubber.

The neoprenes can be vulcanized by heat alone; i.e., a permanent loss in plasticity and a permanent gain in elasticity are accomplished simply by heating the synthetic rubber. Cross-linking of the polymer chains occurs directly at the double bonds without addition of sulfur. This change can be more accurately controlled by admixing small quantities of magnesia or zinc oxide or both. These oxides appear to behave, therefore, as accelerators or regulators of vulcanization, whereas many of those materials which are accelerators for rubber vulcanization operate merely as plasticizing agents for Neoprene.

Isobutene Polymers—In the presence of certain catalysts, such as boron trifluoride or aluminum chloride, and at extremely low temperatures, isobutene will polymerize to form rubber-like substances[37] whose molecular weights have been estimated as great as 400,000. No unsaturation remains, with the possible exception of a double bond at one end of the long chain. Consequently, these rubbers are not amenable to oxidative plastication nor to vulcanization by sulfur. They are quite soluble in petroleum hydrocarbons and are sometimes used as substitutes for oils in the compounding of natural rubber where their mechanical properties give them an advantage over oils. As yet these materials have not found as extensive use as some of the other synthetics. They were developed by the I. G. Farbenindustrie A-G as "Oppanol" and by the Standard

[36] Carothers, W. H. and Collins, A. M., U. S. 1,950,432 (1934); Nieuwland, J. A., Calcott, W. S., Downing, F. B. and Carter, A. S., J. Am. Chem. Soc. *53*, 4197 (1931); Carothers, W. H., Williams, I., Collins, A. M. and Kirby, J. E., ibid., *53*, 4203 (1931).

[37] Sparks, W. J., Lightbown, I. E., Turner, L. B., Frolich, P. K. and Klebsattel, C. A., Ind. Eng. Chem. *32*, 731 (1940).

Oil Co. of New Jersey as "Vistanex." A polyisobutene modified by the introduction of sufficient diolefine to make the product readily vulcanizable with sulfur has recently been announced as "Butyl Rubber."

Organic Polysulfides—J. C. Patrick [38] and his associates discovered that by reacting various aliphatic dihalides with sodium tetrasulfide a large number of organic polysulfides may be obtained, which are all fairly high in sulfur content and which have some rubber-like properties. The presence of considerable sulfur in the molecule seems to confer on these synthetics an unusual insolubility and because of this property they have found their principal uses in the manufacture of hose and tubing for handling paint and lacquer solvents and thinners. A serious disadvantage that may eventually be overcome is their rather disagreeable odor. Varieties made from different dihalides are sold in America under the name "Thiokol," in Germany as "Perduren," in England as "Vulcoplas" and in Japan as "Thionite."

The polysulfide rubbers resemble neoprene in being vulcanized by heat in the presence of metallic oxides. Sulfur again behaves as an accelerator. The mechanical properties of these rubbers are not as good as those of other synthetics here discussed but they are used principally under circumstances in which these properties are not of primary importance.

Plasticized Vinyl Chloride Polymers—Through the use of a wide variety of plasticizers, W. L. Semon [39] found that some of the properties of rubber may be imparted to the least-soluble amorphous polymers of vinyl chloride.[40] These plasticized vinyl polymers exhibit many desirable features not shared by rubber or other synthetic rubbers. They are thermoplastic materials which are not ordinarily vulcanized, but which, on the other hand, do not need to be vulcanized for many important purposes. These polymers are on the American market as "Koroseal" and "Flamenol." Certain varieties of "Vinylite" consist largely of polymerized vinyl chloride but this group also includes polymers of vinyl acetate and copolymers of vinyl chloride and vinyl acetate which do not resemble rubber.

Outstanding chemical resistance to such agents as ozone, concentrated nitric and chromic acids and resistance to weathering are some of the cardinal virtues of these rubber-like materials. They are thus used extensively in the electroplating industry as protective coatings on the racks on which the metal parts are supported and carried during cleaning and plating. Metal tanks used in the cleaning of stainless steel by mixtures of nitric and hydrofluoric acids are protected by "Koroseal" linings. Electric insulation of wires and cables is offering expanding uses to these materials because of their resistance to water and oil and because the flame-proof qualities imparted by the chlorine content are advantageous. Impermeability to water, oils and gases has led to the adoption of these materials as sealing members in various mechanical assemblies and as coatings on cloth and paper. These coated fabrics have been adopted for clothing and many domestic uses.

The plasticizers used to impart rubberiness comprise a wide range of types. Two of the materials used in larger volume are the well-known tricresyl phos-

[38] Patrick, J. C., U. S. 1,854,423 (1932); Trans. Far. Soc. *32*, 347 (1936).
[39] Semon, W. L., U. S. 1,929,453 (1933); Brous, S. L. and Semon, W. L., Ind. Eng Chem. *27*, 667 (1935).
[40] See also Chapter 31.

phate[41] and dibutylphthalate. Organic and inorganic dyes and pigments are used to impart an almost unlimited variety of colors.

Future of Synthetic Rubber Development—During the century following the discovery of vulcanization the use of rubber grew largely with the improvement in the skill applied to "compounding" it for different purposes. Rubber has proven an extremely versatile material and in its particular field of usefulness it had, for over ninety years, no serious competitor. However, in many applications it has definite limitations. As previously stated various synthetic rubbers already produced commercially have certain advantages over natural rubber. The growing knowledge of polymerization and copolymerization seems to indicate that the general trend for synthetic rubber development will be toward "custom-built" synthetics for specified uses. There will undoubtedly be a great many approaches to the problem as possibilities of polymerizing other materials become better understood. For the immediate future, at least, butadiene is likely to remain the most important single raw material. How the properties of its copolymers may be varied to suit special purposes will constitute one of the interesting chapters in chemical synthesis.

READING LIST

GENERAL

In 1937 there was published under the auspices of the Rubber Division of the American Chemical Society comprehensive discussions concerning various phases of rubber technology in a book entitled "The Chemistry and Technology of Rubber," Editors: Davis, C. C. and Blake, J. T. (Reinhold Publishing Corp., New York). At the end of each chapter are listed references relating to the subject discussed. Nearly 3,000 are thus listed (including duplicates). In a chapter on the Literature of Rubber are listed 18 periodicals directly concerned with some phase of the rubber industry and seven pages of references to books and periodical articles relating to latex, production of crude rubber, general chemistry and technology, organic chemistry, general reference, analysis, physics, reclaiming, practical handbooks, engineering and economic interest. Those interested in further study will find this an excellent source of information.

One other work of reference merits special mention. In 1935 "Rubber: Physical and Chemical Properties," by T. R. Dawson and B. D. Porritt, was published by the Research Association of British Rubber Manufacturers, Croydon, England. This is a compilation of data on rubber in all its forms, derived from 300,000 references in 1,400 publications. It lists: 989 specifications for rubber goods, associations and institutions throughout the world connected with the rubber industry, literature references and a glossary to terms used in the industry.

These two books will direct attention to published data on all phases of the industry.

Other, less complete, works on rubber are listed below.

HISTORICAL

"Annals of Rubber," India Rubber World, New York (1936).

PRODUCTION OF CRUDE RUBBER

Schidrowitz, P., "Rubber," Methuen & Co., Ltd., London (1920).

Whitby, G. S., "Plantation Rubber and the Testing of Rubber," Longmans, Green & Co., London (1920).

Morgan, S., "The Preparation of Plantation Rubber," Constable & Co., Ltd., London (1929).

[41] See compound 326, Chapter 27.

LATEX

Hauser, E. A., "Latex, Its Occurrence, Collection, Properties and Technical Applications," translated by W. J. Kelly, Chemical Catalog Co. (Reinhold Publishing Corp.) (1930).

Marchionna, F., "Latex and Its Applications," The Rubber Age, New York (1933).

Noble, R. J., "Latex in Industry," The Rubber Age, New York (1936).

Stevens, H. P. and Stevens, W. H., "Rubber Latex," Rubber Growers' Association, London (1936).

GENERAL CHEMISTRY AND TECHNOLOGY

Simmons, H. E., "Rubber Manufacture: The Cultivation, Chemistry, Testing and Manufacture of Rubber," D. Van Nostrand Co., Inc., New York (1921).

Weber, L. E., "The Chemistry of Rubber Manufacture," Charles Griffin & Co., Ltd., London (1926).

Memmler, K., with others, "The Science of Rubber," translated by Dunbrook, R. F. and Morris, V. N., Reinhold Publishing Corp., New York (1934).

ORGANIC CHEMISTRY

Schotz, S. P., "Synthetic Rubber," Ernest Benn, Ltd., London (1926).

Freundlich, H., "The Chemistry of Rubber," Methuen & Co., Ltd., London (1935).

ANALYSIS

Tuttle, J. B., "The Analysis of Rubber," Chemical Catalog Publishing Co. (Reinhold Publishing Corp.), New York (1922).

PHYSICS

DeVisser, W., "The Calender Effect and the Shrinking Effect of Unvulcanized Rubber," Lockwood, London (1926).

HANDBOOKS

Russell, W. F., "The Vanderbilt Rubber Handbook," R. T. Vanderbilt Co. (1936).

ENGINEERING

Pearson, H. C., "Rubber Machinery," India Rubber Publishing Co., New York (1920).

Stevens, H. P. and Donald, M. B., "Rubber in Chemical Engineering," Rubber Growers' Association, London (1933).

ECONOMICS

Geer, W. C., "The Reign of Rubber," Century Co., New York (1922).

CHAPTER 40

THE NATURAL RESINS, GUMS, AND GUM RESINS

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The natural resins, gums, and related materials have played a part in human economy from the very earliest times and the trade and use of them today is world-wide. The superficial observer of the trends of chemical industry might be prone to think that the use of synthetic resins might lead to elimination of the use of the natural materials, but such is by no means the case. The natural resins and gums are widely used and bear every indication of continuing to hold their place. In some cases their properties are unique and no satisfactory substitute has been found. In other cases they are valuable as adjuncts to synthetic or manufactured materials. In others they successfully compete with the newer products of the synthetic chemical industry. This chapter summarizes the available information on the most important natural resins, gums, and gum resins.

NATURAL RESINS

The natural resins are exudations of trees of many different genera and species. The products of different species appear on the market as different resins, often named after their geographical origin. These secretions or exudations may be those of living trees or may be the fossilized products of trees long dead. Visual examination commonly does not allow one to differentiate between the various commercial resins, but such identification must rest upon chemical and physical tests. From the botanical and forest viewpoint, the trees and their resins have been thoroughly studied. Collection, grading, sorting, distribution, preparation for marketing, warehousing, and the commerce of natural resins is a coordinated and systematic business, world-wide in its ramifications, connections, and operation.

From the viewpoint of discussion in this chapter, the term natural resins will not include rosin [1] or shellac,[2] both of which are discussed elsewhere. Rosin, however, is a natural resin, being a tree exudation, and is produced in tremendous quantities in the United States.

The natural resins find application in decorative and protective coatings, paint, varnishes, lacquers, inks, paper surfacing, cements, plastics, polishes, rubber and wax compositions, textile sizing, linoleum and floor coverings, and, to a smaller extent, in incense and other miscellaneous applications.

[1] See Chapter 17.
[2] See Chapter 25.

The varnish trade usually refers to the natural resins as "gums." In strict terminology, however, the gums are related to the sugars and carbohydrates. They are soluble in water, forming viscous solutions, and are insoluble in drying oils and organic solvents. On heating, they decompose completely without melting. In contradistinction, the resins are insoluble in water, more or less soluble in organic substances and vegetable oils, and are chemically related to the terpenes or the essential oils. On heating, the resins melt with the distillation of volatile oils terpenic in nature. The residue, termed "run" gum or resin by the varnish maker, is soluble in hot vegetable oils. Some of the softer resins are directly soluble in solvents or oils, but in all cases are totally insoluble in water.

General Classification—In general, the natural resins are divided from the point of use into those which are spirit soluble—the "spirit" originally meaning alcohol but now embracing a large variety of solvents—and those which are oil soluble. The first class is generally soluble directly, while the second needs to be processed by thermal methods. The spirit soluble resins are commonly of the soft variety, while the oil soluble are usually hard. The resins are known under names which are indicative either of their source of origin, or of a distinguishing characteristic of the resin, or of the port at which they enter commerce.

THE CLASSIFICATION, ORIGIN, AND PROPERTIES OF NATURAL RESINS

Classification—From the viewpoint of their chemical and physical properties as well as their applications and reaction to heat, the natural resins may be divided into a number of classes, as shown in Table 1. In the first is **Accroides**, a dark colored, alcohol-soluble resin known as Yacca, Grass Tree Gum, Black Boy, or Red Gum. It contains appreciable quantities of coumaric, succinic, and related organic acids, and shows the property of being heat reactive, being converted into a hard, completely insoluble and unusually chemically-resistant material. Commercial varieties are the yellow and red.

The second group consists of **Mastic** and **Sandarac**. Mastic is an alcohol-soluble resin which is light in color or water white. It reaches the market in the form of droplets or tears and is employed in lacquers and spirit varnishes. Sandarac is a white or very pale alcohol-soluble resin from North Africa, finding application in lacquers and spirit varnishes.

The third class consists of **Elemi**, a soft, balsam-like, plastic resin which shows a wide range of compatibilities and is a mutual solvent for a large number of organic products. Most of the supply comes from the Philippine Islands.

In the fourth class are the low acid number, light colored **damars** of recent origin. These are soluble in petroleum solvents and by simple heating may be incorporated with oils. In contrast to the copals, the damars show alcohol insolubility, but they may be dissolved in hydrocarbon solvents. They are produced by tapping of living trees and consist of true resins and resenes which the lacquer industry often refers to as "wax." For complete compatibility with cellulose derivatives, the damars are "dewaxed" before they are employed in lacquers. They are light colored resins whose films bleach to a complete transparency by sunlight. The commercial grades are known as **Batavia Damar** from Batavia,

TABLE 1—CLASSIFICATION OF NATURAL RESINS

1. Accroides, Red Gum, or Grass Gum, of recent origin, spirit soluble, "heat reactive"
2. Mastic and Sandarac, of recent origin, spirit soluble, oil insoluble
3. Elemi, soft of recent origin, balsam type, spirit soluble, oil soluble, readily compatible through mutual solvent action
4. Damars, low acid number resins of recent origin, solvent and oil soluble
   - A. Batavia
   - B. Singapore
5. East Indias, semi-fossil or semi-recent resins related to the damars, solvent and oil soluble
   - A. Batu
   - B. Black
   - C. Pale East India Singapore (Rasak)
   - D. Pale East India Macassar (Hiroe)
6. Copals, in general higher acid numbers than damars, solvent soluble, oil soluble after thermal processing
   - A. Manila
     1. Melengket or soft resins of recent origin, spirit soluble
     2. Loba or half-hard of semi-recent origin, spirit soluble
     3. Philippine Manilas (Almaciga) of semi-recent origin, spirit and oil soluble
     4. Pontianak, semi-fossil hard, spirit and oil soluble
     5. Boea, fossil hard, oil soluble
   - B. Kauri, New Zealand fossil, hard, solvent soluble, oil soluble after thermal processing
7. Copals, fossil, insoluble
   - A. Hard African fossil Congo, solvent insoluble, oil soluble only after severe thermal processing
     1. White, Ivory, Straw, Pale, and Amber
   - B. Amber
   - C. Miscellaneous fossil copals from other portions of Africa
     1. Benguela
     2. Benin
     3. Accra
     4. Angola, white and red
     5. Sierra Leone
     6. Loango
     7. Gaboon
     8. Cameroon
     9. Tanganyika
     10. Madagascar
     11. Inhambane
     12. Zanzibar

Java, and **Singapore Damar** from the Malay States. These materials are graded by somewhat different methods.

The fifth group consists of the **East Indias** related to the damars and soluble only in a limited range of materials, necessitating more severe thermal treatment to make them completely oil compatible. The East India resins are semi-recent materials related to the damars and when originating from Macassar in the Netherlands Indies are often called Hiroe. The product shipped from Singapore is often termed Rasak and is redder in color. It contains more "wax." **Batu** is a semi-fossil resin of the East India class related to the damars, but differing from these in several important characteristics. **Black East India** is a dark colored resin related to the damars, whose films bleach upon exposure to sunlight. This material is sometimes called Damar Hitam or Black Damar.

The sixth group are the **copals**, which is a term employed to designate natural resins from trees of the Agathis and closely related species. It thus embraces the Boea, Manila, Loba, Pontianak from Agathis Alba, the Kauris from Agathis Australis, and the Congos from a Copaifera related species. Except in their most highly fossilized state, the copals show alcohol solubility. The term is similar in type to rosin which is employed to designate the exudations of the trees of the order coniferae, of which the largest group are the pines. This sixth group includes the Manilas through all the stages of fossilization, and the related New Zealand Kauris.

The **Manilas** are copals derived from Agathis Alba in the Netherlands East Indies, the Malaya Archipelago, and the Philippine Islands. The soft grades are often termed Melengket, the half-hard Lobas, the related semi-fossil materials Pontianak after the point of origin, and the completely fossilized Boeas. The Manilas primarily are employed in spirit varnishes as far as the Melengkets and Lobas are concerned, and in oil varnishes in reference to the Pontianaks and Boeas. **Pontianak** is a semi-fossil Manila copal from Borneo. The varnish resin should not be confused with the rubber type of material known under the same name but also designated as Jelutong or Gutta Siak. **Boea** is a fossilized copal from the Netherlands East Indies and is related to the Manilas and the Lobas in that it is alcohol soluble. **Kauri** is a fossil copal dug from the ground in New Zealand and reaches the market in the pale and brown grades. **Bush Kauri** is commonly lighter in color and is fossilized in place on branches of the trees and thus has not come in contact with earth or soil. It is primarily a varnish resin.

The seventh group consists of the highly fossilized **Congos** which, unlike the Kauris, do not enter commerce in the bush or less completely fossilized form. Congo is a hard, fossil resin from the Belgian Congo in Africa and in its original form is insoluble in most organic solvents with the exception of mixtures of isopropyl alcohol and higher molecular weight ketones. After "running," it shows a wide range of useful properties.

In this seventh group should be included **amber**, a fossil resin formerly used in varnish making but now displaced by less expensive materials. It contains succinic acid and is sometimes known as succinite. Its present-day application is for jewelry and electrical instruments. This resin is chiefly derived from areas in Prussia, either through mining operations or through alluvial digging.

Among the natural resins of the copal fossil type from Africa, there should be included Benguela, Benin, Accra, Angola of the white and red varieties, Sierra Leone, Loango, Gaboon, Cameroon, Tanganyika, Madagascar, Inhambane, and Zanzibar, named after their localities of origin. These are all similar in type to Congo copal, although they differ from these resins in minor degrees. Economically the Congo copals are by far the most important.

ORIGIN OF RESINS

The natural resins in general originate in the Congo district of Africa, from which that resin is named, New Zealand, the Netherlands East Indies, Malaya, the Philippine Islands, and adjacent territory. They are obtained from definite species of trees in a systematic manner, generally under governmental supervision The botanical source and the countries of origin of the commercially important natural resins are given in Table 2.

TABLE 2—ORIGIN OF THE NATURAL RESINS

Resin	*Class*	*Type*	*Tree*	*Country of Origin*
Accroides	Miscellaneous	Recent	Xanthorrhea	Australia, Tasmania
Batu	Damar	Semi-fossil	Shorea	Malaya, East Indies
Black East India	Damar	Semi-fossil	Burseraceae	Malaya, East Indies
Boea	Copal	Fossil	Agathis Alba	Netherlands East Indies
Congo	Copal	Fossil	Copaifera	Belgian Congo, Africa
Damar	Damar	Recent	Hopea, Shorea	Sumatra, Borneo, Java, East Indies
East India Macassar (Hiroe)	Damar	Semi-fossil	Dipterocarpacae	Celebes, East Indies
East India Singapore (Rasak)	Damar	Semi-fossil	Balanocarpus	Sumatra, Borneo, Malaya, East Indies
Elemi	Miscellaneous	Recent	Canarium Communis	Philippine Islands
Kauri	Copal	Fossil	Agathis Australis	New Zealand
Loba (Manila)	Copal	Semi-recent	Agathis Alba	Netherlands East Indies, Philippine Islands
Manila	Copal	Recent	Agathis Alba	Netherlands East Indies, Philippine Islands
Mastic	Miscellaneous	Recent	Pistacia Lentiscus	Island of Chios, India, North Africa
Pontianak	Copal	Semi-fossil	Agathis Alba	Borneo
Sandarac	Miscellaneous	Recent	Coniferae	North Africa, South Africa, Australia

THE PHYSICAL AND CHEMICAL PROPERTIES OF NATURAL RESINS

The physical and chemical properties of the natural resins are given in Table 3. It is to be understood that the range of properties covers the entire group of commercial gradings for each resin.

Softening point is run by the capillary tube method, and melting point by a modification of the mercury method in which the sample is gently sintered to the bottom of a porcelain crucible and covered with mercury.[3] Direct acid number involves solution or dispersion of the sample in a solvent and titration with a standard alkali. The indirect acid number involves the addition of excess alkali and back titration by means of standard acid. The acid number is calculated in terms of milligrams potassium hydroxide per gram of resin. Iodine number is by the Hübl method, and saponification number by the standard procedure.[4]

SIZING AND CLEANING

Commercially, the resins are graded into sizes where the term Bold refers to those which are large and clean, Nubs which are smaller, of the order of 2 to 4 cm. in largest dimension, and Chips, Seeds, and Dust which are primarily size classifications. Decreasing size usually carries with it increasing amounts of impurities. The market materials are sorted and graded according to softness or hardness, color, size, and impurities, with particular reference to bark and foreign matter. In preparation for the market, the natural resins pass through

[3] J. Oil and Color Chemists Assn., Vol. 13, p. 287 (1930).
[4] Wolff, C. H., "Die Natürliche Harze," p. 33, Berlin.

TABLE 3—PHYSICAL AND CHEMICAL PROPERTIES OF COMMERCIALLY IMPORTANT NATURAL RESINS

Name of Resin	*Refractive Index*	*Softening Point, °F.*	*Melting Point, °F.*	*Specific Gravity*	*Direct Acid Number*	*Indirect Acid Number*	*Saponification Number*	*Iodine Number*	*Solubility Type*	*Insolubility Type*
Accroides	....	167–185	230–273	1.34	....	123–133	65	196–200	Alcohols	Aryl and aliphatic hydrocarbons
Batu	1.538	232–270	320–356	1.00–1.05	18–46	33–50	33–56	64–81	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ethers, ketones, terpenes
Black East India	1.541	237–257	318–327	1.04	20–28	31–37	27–46	81–83	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ethers, ketones, terpenes
Boea	1.539–1.540	174–176	266–270	1.07–1.08	118–141	145–150	143–175	110–137	Alcohols and ketones	Aryl and aliphatic hydrocarbons, esters and ethers
Congo	1.540–1.541	165–214	262–403	1.05–1.07	92–115	111–128	119–150	110–137	None	All solvents
Damar	1.535–1.538	153–176	205–239	1.03–1.06	16–33	24–45	27–50	64–127	Aryl and aliphatic hydrocarbons, terpenes	Alcohols, esters
East India Macassar (Hiroe)	1.540–1.543	214–252	261–313	1.03–1.05	16–35	23–69	40–65	66–115	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ketones
East India Singapore (Rasak)	1.540–1.541	228–262	280–325	1.03–1.06	19–31	28–44	33–40	73–87	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ketones
Elemi	....	Plastic	......	....	20–35	22–35	21–44	118	Aryl hydrocarbons and esters	Aliphatic hydrocarbons, alcohols and ketones
Kauri	1.544–1.546	194–275	250–437	1.03–1.05	57–85	63–127	67–124	56–177	Alcohol and ketones	Aryl and aliphatic hydrocarbons
Loba (Manila)	1.538–1.540	160–196	237–266	1.06–1.08	110–149	134–165	160–190	104–130	Alcohols and ketones	Aryl and aliphatic hydrocarbons
Manila	1.526	171–190	239–262	1.06–1.07	127–137	149–165	158–190	118–126	Alcohols, esters, ketones	Aryl and aliphatic hydrocarbons
Mastic	....	131	168	1.04–1.06	50–70	57	62–90	64–142	Alcohols, aryl hydrocarbons	Aliphatic hydrocarbons
Pontianak	1.540	180–275	259–336	1.07–1.08	112–121	122–139	148–180	106–142	Alcohols and ketones	Aryl and aliphatic hydrocarbons, esters
Sandarac	1.545	212–266	275–302	1.05–1.09	117–155	128–155	145–157	112–141	Alcohols	Aryl and aliphatic hydrocarbons

TABLE 4—SOLUBILITY CLASSIFICATION

Type of Resin	*Name*	*Solubility Type*	*Insolubility Type*	*Soluble in:*	*Largely Soluble in:*	*Insoluble or Swollen in:*
Miscellaneous	Accroides (red gum)	Alcohols	Aryl and aliphatic hydrocarbons	Alcohols, esters, ketones	Cellosolve acetate, Cellosolve, acetic acid, aniline, dioxane, phenol	Chlorinated compounds, coal-tar hydrocarbons, petroleum hydrocarbons, ethers, terpenes, carbon tetrachloride, Hexalin, Tetralin, nitrobenzene, tricresyl phosphate, alkali solutions
	Mastic	Alcohols, aryl hydrocarbons	Aliphatic hydrocarbons	Alcohols, coal-tar hydrocarbons, esters, ethers, alcohol-ethers	Cellosolve acetate, aniline, dioxane, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, glycol ether acetate, nitrobenzene, phenol, propylene oxide, Tetralin, methyl acetone	Acetone, alcohol-esters, acetic acid, carbon disulfide, Hexalin, paraffinic and naphthenic petroleum solvents
	Sandarac	Alcohols	Aryl and aliphatic hydrocarbons	Alcohols, ketones, alcohol-ethers, Cellosolve acetate, aniline, dioxane, ethylene oxide, propylene oxide	....	Chlorinated compounds, coal-tar hydrocarbons, esters, ethers, terpenes, alcohol-esters, acetic acid, carbon disulfide, ethylene glycol diethyl ether, glycol diacetate, glycol ether acetate, Hexalin, nitrobenzene, phenol, Tetralin, petroleum hydrocarbons
	Elemi	Aryl hydrocarbons, esters	Aliphatic hydrocarbons, alcohols, ketones	Coal-tar hydrocarbons, esters	Alcohol ethers, glycol monoacetate, carbon disulfide, dioxane, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, Hexalin, phenol, propylene oxide, Tetralin	Chlorinated compounds, ketones, Cellosolve acetate, acetic acid, aniline, glycol ether acetate, nitrobenzene, tricresyl phosphate, petroleum hydrocarbons
Damar	Batavia, Singapore	Aryl and aliphatic hydrocarbons, terpenes	Alcohols, esters	Chlorinated compounds, coal-tar hydrocarbons, petroleum, terpenes, carbon disulfide, Tetralin, paraffin, hydrogenated and naphthenic petroleum naphthas	....	Alcohols, alcohol-ethers, alcohol-esters, Cellosolve acetate, acetic acid, aniline, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, Hexalin, nitrobenzene, phenol, propylene oxide, tricresyl phosphate, diethylene oxide

East India	Batu, Black East India	Aryl and hydrogenated aliphatic hydrocarbons	Alcohols, esters, ethers, ketones, terpenes	Chlorinated compounds, coal-tar hydrocarbons, Cellosolve acetate, hydrogenated petroleum solvents; Black East India in some paraffinic type	....	Alcohols, esters, ethers, ketones, terpenes, alcohol-ethers, alcohol-esters, acetic acid, aniline, dioxane, glycol diacetate, Hexalin, nitrobenzene, phenol, Tetralin, naphthenic petroleum hydrocarbons
	Pale East India	Aryl and hydrogenated aliphatic hydrocarbons	Alcohols, esters, ketones	Hydrogenated and some paraffinic petroleum hydrocarbons, chlorinated compounds, coal-tar hydrocarbons	Ethers, terpenes, linoleic acid, Tetralin	Alcohols, esters, ketones, alcohol-ethers, acetic acid, aniline, dioxane, Hexalin, nitrobenzene, phenol, tricresyl phosphate
Manila copal	Melengket (soft Manilas, MA, MB)	Alcohols, esters, ketones	Aryl and aliphatic hydrocarbons	Alcohols, ketones, alcohol ethers	....	Petroleum hydrocarbons, coal-tar hydrocarbons, chlorinated compounds, terpenes
	Loba (half-hard)	Alcohols, ketones	Aryl and aliphatic hydrocarbons	Alcohols, ketones, low-molecular-weight esters, Cellosolve, Cellosolve acetate	Aniline, phenol, butyl acetate, butyl lactate	Petroleum hydrocarbons, coal-tar hydrocarbons, chlorinated compounds, high-molecular-weight esters, terpenic compounds
	Pontianak (fossil or hard)	Alcohols, ketones	Aryl and aliphatic hydrocarbons, esters	Alcohols, ketones, low-molecular-weight alcohol-ethers, ethyl ether, acetates (ethyl, butyl, amyl)	Butyl Carbitol, Cellosolve acetate, aniline, phenol	Petroleum hydrocarbons, coal-tar hydrocarbons, chlorinated compounds, terpenic compounds
	Boea (fossil or hard)	Alcohols, ketones	Aryl and aliphatic hydrocarbons, esters, ethers	Phenol	Alcohols, ketones	Chlorinated compounds, coal-tar hydrocarbons, esters, ethers, terpenes, alcohol-ethers, aniline, dioxane, Hexalin, nitrobenzene, Tetralin, petroleum hydrocarbons
Fossil copal	Kauri	Alcohols, ketones	Aryl and aliphatic hydrocarbons	Alcohols (ethyl, butyl, amyl), acetates, ketones, alcohol-ethers, aniline, dioxane, phenol, Tetralin	....	Coal-tar hydrocarbons, terpenes, chlorinated compounds, Hexalin, nitrobenzene, tricresyl phosphate, petroleum hydrocarbons
	Congo	None	All solvents	....	....	....

a number of grading and cleaning operations, some of which are done by machine but others by hand. These may involve water-washing, screening, floating, winnowing, sandblasting, hand picking and sorting, and hand scraping to remove surface coatings. Newer processes involve solvent treatment, bleaching, and refining.

SOLUBILITY

The commercial uses of the natural resins are conditioned by their solubility. Table 4 gives the solubilities in concise form. These were determined on the basis of 100 grams of resin treated with 100 grams of solvent. The designation "soluble" is employed when 90 to 100 per cent of the resin dissolved. The resin is termed "insoluble" if less than 50 per cent went into solution, and "largely soluble" is employed to indicate the intermediate zone.

THERMAL PROCESSING OR RUNNING OF NATURAL RESINS

The different classes of natural resins will be discussed in reference to their behavior when subjected to thermal treatment—often called "running," "melting," or "cracking"—to make them oil soluble for use in varnishes. In the first class **Accroides** may be listed, inasmuch as it is not possible to make this resin compatible with oils by heating.

In the second class there are grouped **Mastic** and **Sandarac** which are seldom used for oil varnishes and find their applications when dissolved in solvents.

Elemi, in the third class, may be incorporated in a drying oil at temperatures low enough so that no destructive decomposition of the resin occurs.

In the fourth class are the **damars.** These may be readily made soluble with an oil by simple heating in the oil itself. They will remain soluble or dispersed when the mixture is allowed to cool, and as a result of the processing operation show only a small percentage of loss in weight.

In the fifth class are the **Pale East India** resins, Black East India, and Batu. These may be dissolved in drying oils in the same manner as the damars, without pretreatment. More stable solutions, however, are obtained by first treating the resin before it is brought in contact with the oil. The resin is heated in a kettle until a homogeneous, thin liquid, free from lumps or gummy masses, is obtained. In the case of the East Indias, a suggested procedure is to heat an average size batch in a normal size varnish [5] kettle so that a temperature of 600° F. is reached in a time period of an hour to an hour and a quarter, the mixture held at this temperature until all foaming has subsided and the resin is liquid. Holding the batch for about a half hour at 600° F. will cause the liquid material to drip from the paddle like hot oil. It is obvious that this procedure will be modified in details by the varnish technician for making varnishes of special types. In the case of the East Indias, particularly when processed for flat varnishes, somewhat less simple methods involving step-like operations or heatings and coolings may be desired for definite types of results. Melting procedures may be such as to retain all of the "wax" constituents in the finished oil-soluble resin.

[5] For a more complete discussion of varnish making see Chapter 25.

In the sixth class are resins which cannot be directly incorporated with oils, but which need to be processed in advance. After processing they may have hot oil added to them and be cooked with the oil, or they may be allowed to cool, dissolved in a solvent, and the solvent mixture of the resin be incorporated with an oil which has already been heat processed or bodied. In American practice the first method is preferred. In this class are Kauri, Pontianak, and Boea, all of which may be run in a similar manner. For Kauri, a suggested procedure involves heating the resin to a temperature of 600° F. over a time period of about an hour and a quarter, and holding at that temperature for about a half hour until all lumps, spongy or gummy masses, and all or nearly all of the foam have disappeared. Another suggested method for Kauri, Pontianak, and Boea would be to heat the resins to 625° F. during about an hour, with occasional stirring. They are then allowed to cool to 500–550° F. and again brought up to 600° F. and held for about half an hour until they drip from the paddle like hot oil.

The soft Melengkets and the half-hard Loba Manilas are more often employed in spirit varnishes than in oil base vehicles. The Lobas, however, may be processed in a manner similar to that described for Pontianak, although they do not "run" quite as easily.

In the seventh class are found those fossil resins which are hard and totally insoluble. These need to be drastically processed before they can be incorporated with oils. Congo is an example of this class. A suggested processing method involves heating a normal size batch in an average varnish kettle to 600° F. over a period of an hour. The resin may be held at 600° F. until all of it is plastic, the hard lumps have been disintegrated, and the foam has begun to subside. This may require about an hour. Occasional stirring avoids local overheating. The temperature is raised to 650° F. and held until the resin is liquid and shows a clean drip from the paddle like hot oil. This operation takes about 15 minutes. In another method, the resin is heated to 650° F. in about an hour and a half, and held at that temperature for about a half hour until it is completely oil soluble.

General Methods of Running—There are two general methods of running in reference to the equipment employed. During the running operation, volatile oils are distilled off in variable quantities, depending upon how the procedure is carried out. If the cover be left on the kettle (termed closed kettle), a larger amount of high boiling portions of the volatile materials is retained and the resin becomes oil soluble with a minimum loss of weight. The upper sections of the kettle, which are cooler than the bottom, serve as a condenser. In the other method, the kettle cover is off and the top of the kettle open, so that all of the distillate, volatile matter, and gaseous material may escape without condensation. This is called the open kettle method.

In general, the varnishes prepared from resins thermally processed in closed kettles are not quite as hard as those prepared in an open kettle with greater loss of volatile material. This, however, holds true only if the difference in running method is the only variable in the varnishes under comparison. The loss in weight of resin upon running is a function of the type of resin, the rate of heating, the duration of the heating, the method of running, and the variety of equipment employed. This loss in weight may vary from about 10 per cent in the case of resins like the East Indias, to as high as 35 per cent under special circumstances. Under average conditions, the loss is 10–20 per cent. To obtain special desired properties such as excellent adhesion to metal imparted by the addition of run Congo to a formulation, specifications may call for running losses as high as 40 per cent.

Thermal processing is a tool for the varnish maker which allows him to impart a wide range of properties to resinous materials so that these may fit his special requirements.

TABLE 5—COMPATIBILITY OF NATURAL RESINS WITH OTHER RESINS AND WITH OILS

Natural Resin	*100 Per Cent Phenol Aldehyde Resin*	*Modified Phenol Aldehyde Resin*	*Heat Reactive Phenol Aldehyde Resin*	*Rosin*	*Ester Gum*	*Maleic-Rosin Resin*	*Paracoumarone Resin*
Accroides	I*	I*	......	I*	I*	C	C
Batu	C	C	C	C	C	C	C
Black East India	C	C	C	C	C	C	C
Boea	C	C	......	C	C	C	I*
Congo	I*	I*	......	I*	I*	I*	I*
Damar	C	C	C	C	C	C	C
East India Macassar (Hiroe)	C	C	C	C	C	C	C
East India Singapore (Rasak)	C	C	C	C	C	C	C
Elemi	C	C	C	C	C	C	C
Kauri	C	C	......	C	C	C	I*
Loba (Manila)	C	C	......	C	C	C	I*
Manila	C	C	......	C	C	C	I*
Mastic	C	C	C	C	C	C	C
Pontianak	C	C	......	C	C	C	I*
Sandarac	C	C	......	C	C	C	I*
Run Batu	C	C	C	C	C	C	C
Run Black East India	C	C	C	C	C	C	C
Run Boea	C	C	C	C	C	C	C
Run Congo	C	C	C	C	C	C	C
Run Damar	C	C	C	C	C	C	C
Run East India Macassar (Hiroe)	C	C	C	C	C	C	C
Run East India Singapore (Rasak)	C	C	C	C	C	C	C
Run Kauri	C	C	C	C	C	C	C
Run Loba (Manila)	C	C	C	C	C	C	C
Run Manila	C	C	C	C	C	C	C
Run Pontianak	C	C	C	C	C	C	C

I* = incompletely compatible; disperses but cloudy
C = compatible
I = incompatible

COMPATIBILITIES OF NATURAL RESINS

From the viewpoint of their industrial application, the compatibilities of the resins with synthetic resins, oils, waxes, cellulose derivatives, rubber materials, pitches and asphalts are important. These compatibilities in many cases are conditioned by the solvents which are employed; but when incompatibility is

TABLE 5—COMPATIBILITY OF NATURAL RESINS WITH OTHER RESINS AND WITH OILS—*Continued*

Blown Castor Oil	*Chinawood Oil*	*Chinawood Oil Substitute*	*Fish Oil*	*Hempseed Oil*	*Linseed Oil*	*Oiticica Oil*	*Rapeseed Oil*	*Soya Bean Oil*	*Sunflower Oil*
I	I	I	I	I	I	I	I	I	I
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
......	......	......	......	......	......	......	......	......	......
......	......	......	......	......	......	......	......	......	......
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
......	......	......	......	......	......	......	......	......	......
......	......	......	......	......	......	......	......	......	......
......	......	......	......	......	......	......	......	......	......
C	C	C	C	C	C	C	C	C	C
......	......	......	......	......	......	......	......	......	......
I	I	I	I	I	I	I	I	I	I
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C
C	C	C	C	C	C	C	C	C	C

Resin : resin ratio = 1 : 1
Resin : oil = all ratios

indicated, no common solvents or procedures allow the formation of homogeneous materials which are designated as indicating compatibility. The information on compatibilities is summarized in Tables 5, 6 and 7.

TABLE 6—COMPATIBILITY OF NATURAL RESINS WITH CELLULOSE DERIVATIVES AND WITH CHLORINATED RUBBER

Resin	*Nitro-cellulose* (*Ratio 1 : 1*)	*Ethyl Cellulose* (*Ratio 1 : 1*)	*Cellulose Acetate* (*Ratio 1 : 1*)	*Chlorinated Rubber* (*Ratio 1 : 1*)
Accroides	C	I	C	I
Batu	VSI	VSI	I	I
Black East India	I	I	I	I
Boea	C	C	I	I
Damar	C	C	I	C
East India Macassar (Hiroe)	VSI	VSI	I	I
East India Singapore (Rasak)	VSI	VSI	I	I
Elemi	C	C	SI	C
Kauri	C	C	I	I
Loba	C	C	I	I
Manila	C	C	I	I
Mastic	C	C	SI	C
Pontianak	C	C	I	I
Sandarac	VSI	C	SI	I
Run Black East India	I	I	I	SI
Run Boea	VSI	VSI	I	SI
Run Congo	C	C	I	C
Run Damar	VSI	C	I	C
Run Kauri	VSI	C	I	C
Run Manila	VSI	C	I	SI

C = compatible
I = incompatible
VSI = very slightly incompatible
SI = slightly incompatible

GUMS AND GUM RESINS

Gums embrace a number of amorphous, tasteless plant and tree exudations, seaweed extracts, or seed extracts. In most cases after exudation they harden upon exposure to air. Their chief constituents are carbohydrates such as arabic acid, bassorin, or materials related to the sugars or their degradation products. The true gums form clear solutions with water, while others which are really vegetable mucilages swell up into a gelatinous mass. They are all insoluble in alcohol, carbonize when heated, and have ash contents. They do not distil without decomposition.

The important gums may be classified as in Table 8, with their origin and characteristics in solution. In general they are employed in adhesives, water colors, textile printing, writing and lithographic inks, confectionery, sweetmeats, hair wave preparations, paper coatings, and related uses. They are known by many names.

TABLE 7—COMPATIBILITY OF NATURAL RESINS WITH WAXES, ASPHALTS AND PITCHES

(Ratio = 1 : 1)

Resin	*Bees-wax*	*Car-nauba*	*Japan*	*Mon-tan*	*Ozoker-ite*	*Paraffin*	*Petro-latum Wax and Paraffin**	*Stearic Acid*	*Petro-leum Asphalt*	*Coal Tar Pitch*	*Stearin Pitch*	*Vege-table Pitch*	*Gilson-ite*
Accroides	.....	PC	.....	.....	.....	.....	.....	.....	I	I	I	I	I
Batu	C–2	C–3	C–3	C–3	C–3	C–3	C–4	C–2	C	C	C	C	SI
Black East India	C–2	C–2	C–2	C–2	C–2	C–2	C–4	C–2	C	C	C	C	SI
Boea	C–5	C–5	PC	C–5	PC	PC	PC	C–2	I	C	I	C	I
Congo	C–5	C–5	PC	C–5	PC	PC	PC	C–3	I	I	I	C	I
Damar	C–1	C–1	C–1	C–1	C–1	C–2	C–4	C–1,2	C	C	C	C	C
East India Macassar (Hiroe)	C–2	C–2	C–2	C–2	C–2	C–3	C–4	C–2	C	C	C	C	SI
East India Singapore (Rasak)	C–2	C–2	C–2	C–2	C–2	C–3	C–4	C–2	C	C	C	C	SI
Elemi	C–1	C–1	C–1	C–1	C–1	C–1	C–1	C–1	C	C	C	C	C
Kauri	C–5	C–5	C–5	C–5	PC	C–5	C–5	C–2	I	C	I	C	I
Loba	C–5	C–5	C–5	C–5	PC	PC	PC	C–2	I	C	I	C	I
Manila	C–5	C–5	PC	C–5	PC	PC	PC	C–2	I	C	I	C	I
Mastic	.....	.....	.....	.....	.....	.....	.....	.....	C	C	C	C	C
Pontianak	C–5	C–5	PC	C–5	PC	PC	PC	C–2	I	C	I	C	I
Sandarac	.....	.....	.....	.....	.....	.....	.....	.....	I	C	I	C	I
Run Congo	.....	C–1	.....	C–1	PC	PC	.....	.....	C	C	C	C	C
Run Kauri	C–1	C–1	C–1	C–1	C–1	C–1	.....	.....	C	C	C	C	C
Run Manila	C–1	C–1	C–1	C–1	PC	PC	PC	.....	C	C	C	C	C

C–1 = compatible at temperatures in the range of 90°–120° C.
C–2 = " " " " " " " 120°–150° C.
C–3 = " " " " " " " 150°–200° C.
C–4 = " " " " " " " 200°–225° C.
C–5 = " " " " " " " 275°–325° C.

* 45% Petrolatum wax, 10% paraffin, balance resin
C = compatible
I = incompatible
SI = slightly incompatible
PC = partially compatible

CLASSIFICATION AND PROPERTIES

Acacia, also known as gum arabic and gum Senegal, appears on the market as irregular tears of various sizes or as a fine white powder. It consists essentially of the calcium salt of arabic acid, with galactose and arabinose.

Ghatti is also known as British Indian gum. It is obtained from India and Ceylon. Its uses are the same as gum arabic.

Karaya is sometimes known as Indian tragacanth. It has a high volatile acidity number of the order of 13 to 22, and on long standing may develop a distinct acetic odor. Like tragacanth, it swells instead of dissolving in water.

Tragacanth on hydrolysis yields arabinose and galactose. It may contain a small amount of starch. Its insoluble constituent is bassorin.

Agar agar often contains diatoms and sulfates. It is sometimes called vegetable gelatin. It appears on the market in thin transparent flakes which are readily soluble in hot water and difficultly soluble in cold. It is widely used as a culture medium for bacteriological work. It is extracted from various marine algae indigenous to the Pacific and Indian Oceans. It has many applications as adhesives, as a thickener for food products, sizing for textiles, a thickener for dyeing and printing pastes, and as a constituent of photographic emulsions.

Irish moss is a seaweed or kelp from Ireland and the New England coast which is dried and bleached by the sun. The gum or algin is obtained by treating the seaweed with boiling water and precipitating the material from solution. Its uses are similar to agar agar.

Locust kernel is a mucilaginous extract of the carob bean. It is sometimes called carob or carob gum. It is a purified locust bean gum which contains starch, but otherwise is similar. Locust kernel gum contains 5 to 6 per cent protein and consists largely of galactan and mannan. The commercial product is not a pure carbohydrate and contains 3 to 4 per cent cellular tissue and less than 1 per cent ash.

Quince seed gum is the mucilaginous mass extracted from quince seed. Its properties are similar to the extract from psyllium and flax seed. It is an impure carbohydrate which is used in hair lotions and mucilages.

Related to the gums are the gum resins which are mixtures of resins and gums. They form emulsions with water and find miscellaneous applications in industry. Included in this group are dragon's blood or gum kino, gamboge, benzoin, guaiac, gambier, and myrrh.

Dragon's blood is a resinous substance obtained from the fruit of several species of small palms growing in Siam, the Molucca Islands, and other parts of the East Indies. An exudation appears on the surface of the ripe fruit, which is separated by rubbing, by shaking in a bag, by exposing to steam, or by decoction. The finest product results from the first two methods. It comes on the market in two forms: either as small oval drops (*tear dragon's blood*) covered with the leaves of the plant and connected in a row like beads; or in cylindrical sticks 18 inches long and about ½ inch in diameter, covered with palm leaves and bound with slender strips of cane. An inferior product, prepared by boiling the fruit in water, is in the form of flat circular cakes (*cake dragon's blood*).

TABLE 8—CLASSIFICATION AND PROPERTIES OF NATURAL GUMS

Gum	*Source*	*Plant*	*Color*	*Form*	*Water Soluble, Filterable*	*Swells in Water and Only Partly Soluble*	*Soluble in Hot Water and Set to Gel*	*Other Names*
Acacia	Plant exudation	Acacia Senegal	Whitish, yellowish white, or light amber	Tears	×	....	....	Arabic; Senegal
Ghatti	Plant exudation	Anogeissus latifolia	Yellowish to amber	Tears	×	....	....	British Indian gum
Karaya	Plant exudation	Sterculia urens	White to reddish	Thick flakes, irregular tears	....	×	....	Indian tragacanth gum; sterculia gum
Tragacanth	Plant exudation	Astragalus gummifer	Yellowish to white	Flakes or curls	....	×	....	Bassorin
Agar agar	Seaweed extract	Gelidium corneum	Grayish white to white	Flakes	....	×	×	Bengal or Japan isinglass; vegetable gelatin
Irish moss	Seaweed extract	Chondrus Crispus	....	....	×			
Locust kernel	Seed extract	Locust bean or carob bean or St. John's bread	....	....	....	×	....	Purified locust bean
Locust bean	Seed extract	....	....	....	....	×	....	Carob bean; St. John's bread
Quince seed	Seed extract	Quince seed	....	....	×			

Dragon's blood is odorless, tasteless, insoluble in water, but soluble in alcohol and ether, also soluble in the volatile and fixed oils, forming red solutions.

Gum benzoin is also known as gum benjamin, styrax benzoin, being a balsamic resinous material from the tree of that name. It is obtained from Java, Sumatra, and the East Indies. Its melting point ranges from 77 to 100° C. and its acid number from 100 to as high as 240. It is alcohol soluble.

Gambier is also known as catechu and terra saponica. It is the extract from the wood of the tree Unicaria gambir from India. It appears on the market as an odorless brown powder and finds employment in leather tanning and textile printing.

Gum gamboge appears as grayish or orange-brown amorphous cylindrical pieces having an acid number of 70 to 90. It is insoluble in water but soluble in organic solvents such as acetone and alcohol.

Gum guaiac is the resinous exudation of the tree Guaiacum sanctum which is found in Florida, in the West Indies, and in South America. The material shows melting points of 80 to 90° C. and is soluble in organic solvents such as alcohol and ether.

Gum kino is another name for dragon's blood.

Gum myrrh is obtained from the plant Commiphora myrrha which grows in Nubia, Somaliland, and Arabia. It reaches the market as irregular brown tears having an acid number of 60 to 70, and finds employment in cosmetics, medicine, and to some extent in dye preparations.

Mention should be made of the oleo resins **peru, tolu,** and **storax,** which are mixtures, balsam-like in type, of tree exudation resinous products with essential oils. They find minor application in pharmacy.

READING LIST

GENERAL

Mantell, Kopf, Curtis and Rogers, "Technology of Natural Resins," John Wiley & Sons (1942).

Barry, T. H., "Natural Varnish Resins," Ernest Benn Limited, London (1932).

PHYSICAL AND CHEMICAL PROPERTIES

Kopf, C. W., "Manila Resins and the Properties of Their Alcohol Solutions," Paint, Oil Chem. Rev. (July 21, 1938).

Mantell, C. L. and Skett, A., "Viscosities of Damar Solutions," Ind. Eng. Chem. *30*, 417 (1938).

Mantell, C. L. and Allan, R. W., "Solubilities of Natural Resins in Solvents and Waxes," Ind. Eng. Chem. *30*, 262 (1938).

Mantell, C. L., Allen, C. H. and Sprinkel, K. M., "Physical and Chemical Changes in Congo Resin During Running," Paint, Oil Chem. Rev. (Aug. 20, 1936).

Mantell, C. L., Allen, C. H. and Sprinkel, K. M., "The Physical and Chemical Properties of Natural Resins," I. Analytical Data, Official Digest of the Federation of Paint and Varnish Production Clubs (February, 1937); "The Physical and Chemical Properties of Natural Resins," II. Solubilities of Natural Resins, Official Digest of the Federation of Paint and Varnish Production Clubs (March, 1937).

TECHNOLOGY

Mantell, C. L., Skett, A., Holzberger, J. H., Allan, R. W. and Kopf, C. W., "Studies in Natural Resin Technology," IX, X, Official Digest of the Federation of Paint and Varnish Production Clubs (Reprinted, 1938; February, 1939).

Mantell, C. L. and Skett, A., "Studies in Natural Resin Technology," VIII, Official Digest of the Federation of Paint and Varnish Production Clubs (April, 1938).

Mantell, C. L. and Rubenkoenig, H. L., "Manila Resins: Origin, Properties, and Applications," Ind. Eng. Chem. *29*, 855-859 (1937).

Skett, A., "Recent Developments in Natural Resin Technology," American Paint J. (Jan. 24, 1938).

Skett, A. and Allan, R. W., "Recent Developments in Natural Resin Technology," Paint, Oil Chem. Rev. (Mar. 3, 1938).

USES

Holzberger, J. H., "Natural Resins for Food Container Inks," American Ink Maker (April, 1938).

Rogers, E. M., "Inexpensive Traffic Marking Paints," American Paint J. (May 16, 1938).

Allan, R. W., "Possible Uses of the Resin-Wax Combinations," Chem. Ind. *42*, 507 (1938).

Mantell, C. L. and Skett, A., "Damar in Overprint Varnishes," Paint, Oil Chem. Rev. (Feb. 16, 1939).

Mantell, C. L., "Natural Resins for Printing Inks," American Ink Maker (May, 1937).

Mantell, C. L., "Natural Gums and Resins as Chemical Raw Material," Chem. Ind. *38*, 577-581 (1936).

Mantell, C. L. and Rubenkoenig, H. L., "The Origin, Application, and Properties of Damar," Paint, Oil Chem. Rev. (June 11, 1936).

Mantell, C. L., Allen, C. H. and Sprinkel, K. M., "Natural Resins for the Varnish Industry," Ind. Eng. Chem. *27*, 1369-1373 (1935).

Allen, C. H., "Recent Developments in Natural Varnishes," Drugs, Oils and Paints (October, 1934).

Allen, C. H. and Sprinkel, K. M., "Recent Developments in Natural Resin Varnish," Official Digest of the Federation of Paint and Varnish Production Clubs (February, 1935; March, 1935).

Mantell, C. L., Allen, C. H. and Sprinkel, K. M., "Research on Natural Resins and Their Varnishes," Official Digest of the Federation of Paint and Varnish Production Clubs (January, 1936).

American Gum Importers Association, Inc., "Natural Resin Research," New York (1936).

ECONOMICS

Mantell, C. L., "Resin Economics—Synthetic and Natural," American Paint J (Nov. 28, 1938).

CHAPTER 41

NATURAL OILS, FATS AND WAXES

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The natural oils, fats and waxes have been identified with industry almost since the latter began. To pick out a single example, the use of natural oils as softening agents for leather is probably as ancient as the tanning trade itself. The preparation of soaps from tallow is similarly an industry of considerable age. With the rise of the printing and paint, and more recently, the synthetic resin industries, the demand for oils has increased so rapidly that many sources of oil previously of little value were cultivated for their oils content. Thus the cultivation of tung trees in Florida was begun; soybean production increased both here and abroad; and extraction processes were introduced for increasing the yields of such widely used oils as linseed and castor. Also, the production of hydrogenated oils for utilization in shortenings, margarine and other edible products has demanded a tremendous and constant supply of oils such as cottonseed, soybean and peanut.[1] Lately the production of high molecular weight alcohols from oils and fats has opened fields of ever broadening industrial application.

THE ECONOMIC PICTURE

The production and consumption of animal and such vegetable oils as cottonseed, linseed and tung have decreased in recent years. The first noticeable falling-off occurred just after the World War of 1914-1918. A revival was evidenced during the years 1927-1929, but a steady decline since then has gripped the industry. Castor oil is one of the few oleaginous substances which has returned in production to that of the peak year of 1929 when over 76 million pounds were produced. The popularity of castor oil may be traced to its usefulness in synthetic resin modifiers, and in sulfonate detergents and textile assistants. Blown castor oil has also been marketed as a lubricant and for use in lacquers and artificial leathers. The production and consumption of hydrogenated oils in the United States increased from 5 to 8 million pounds during the period 1934-1939, indicating that this phase of the oil industry is steadily increasing in importance.

However, from present indications it is the field of fatty acids which promises to lift the oil and fat industry from the declining trend.[2] Fatty acids and their derivatives are today more important than ever before and the industry is growing under the impetus of new uses and products created by chemical engineering

[1] Weber, G. M. and Alsberg, C. L., "The American Vegetable Shortening Industry," Food Research Institute, Stanford University, California (1934).
[2] McBride, G. W., Chem. & Met. 47, 830 (1940).

research and development. Fatty acid technology has seen many recent developments. Both animal and vegetable fats and oils are now easily hydrolyzed to their fatty acid constituents. By miscellaneous processes these fatty acids are converted to esters, nitriles, amides, amines, etc. By partial esterification they are converted to mono- and di-glycerides, and these acids are also neutralized to form metal and alkali soaps. Research into the hydrogenation of oils has produced higher alcohols by reduction of fatty acids and esters while re-esterification of these acids has created a new source of drying oils and resins.

Sulfated and sulfonated fats and oils, through their oil and water solubility properties, have found widespread uses in the soap, leather, pharmaceutical, paper, and textile industries. Fatty acids are used in rubber products as softening agents as well as serving as lubricants. The petroleum industry makes use of fatty acids and derivatives to improve metal-wetting qualities of lubricants. In foods these derivatives find use because of their emulsifying, thickening, texture improving, and homogenizing properties.

Antiseptics, drugs, and dyes are now being prepared containing fatty acid chains for the purpose of changing solubility properties. In particular, the oil and resin solubility in these new dyes is promoted.

Fatty acid amines have definite detergent and emulsifying properties and their effectiveness as bactericides and insecticides has been proven. Other nitrogen derivatives as the amides and nitriles are finding use as emulsifiers, wetting agents, lubricants, and stabilizers. Moreover, many resins used in paints, varnishes, and lacquers have improved properties due to the introduction of an oil or fatty acid.

The fatty acids are obviously becoming important industrial raw materials. Judging from research activity and commercial successes, these acids and the oil and fat industry in general seem destined to play an increasingly important part in chemical process industry of the future.

CHEMISTRY OF NATURAL OILS, FATS, AND WAXES

The chemistry of the natural oils, fats and waxes is a subject of considerable complexity. These materials are classified according to their physical state, rather than to any strict chemical differences. Thus, a natural oil generally is defined as a high molecular weight ester that is obtained from natural sources and that is a viscous fluid at ordinary temperatures (i.e., approximately 20° C.). A fat is the same type of compound, except that it is solid under similar conditions. A wax, whether liquid or solid, is defined as a substance which imparts a gloss to an object. Also, natural oils and fats are differentiated on the basis of molecular weight, the oils having lower values than the fats. Analysis shows that the oils and fats are primarily tri- and di-esters of glycerol. Saponification of these substances provides evidence that oils are constituted of acid radicals high in unsaturation while the fats are considerably more saturated in character. Natural waxes, on the other hand, are usually a mixture of the higher alcohols of the linear saturated series ($C_nH_{2n+1}OH$) with esters of these same alcohols and the fatty acids.

The natural oils and fats may be distinguished as being either animal or vegetable in origin.[3] The former include those oils derived from marine animals, e.g., cod liver oil, as well as those secured from terrestrial types, e.g., neat's-foot

[3] Holde, D., "Kohlenwasserstoffole und Fette," J. Springer, Berlin (1933).

oil, or beef tallow. The vegetable oils usually are classified according to their drying properties.

The drying of an oil[4] consists in the formation of a hard film due to oxidation of unsaturated linkages, e.g., $-CH{=}CH-$, or to polymerization of the constituents. The oils used in the paint, linoleum and printing ink industries generally are of the drying-oil class and include linseed and tung oils. Cottonseed and castor oils, because of the slowness with which their films harden, are called semi-drying oils, while olive oil is representative of the non-drying class.

Constitution of Fats—The fats, as stated, are compounds of fatty acids with glycerol (glycerin). The fatty acids occurring in the more common oils, together with a few of their constants, are listed in Table 1.

TABLE 1—PHYSICAL CONSTANTS OF FATTY ACID CONSTITUENTS OF SOME COMMON OILS

Acid	*Formula*	*Melting Pt., ° C.*	*Sp. Gr.*	*at ° C.*	*Refractive Index*	*at ° C.*
	SATURATED ACIDS, $C_nH_{2n+1}COOH$					
Butyric	C_3H_7COOH	−7.9	0.959	20	1.39906	20.0
Isovaleric	C_4H_9COOH	−37.6	0.937	15	1.40178	22.4
Caproic	$C_5H_{11}COOH$	−1.5	0.929	20	1.41635	20.0
Caprylic	$C_7H_{15}COOH$	16.0	0.910	20	1.4285	20.0
Capric	$C_9H_{19}COOH$	31.5	0.8858	40	1.42855	40.0
Lauric	$C_{11}H_{23}COOH$	44.0	0.8679	50	1.4183	82.1
Myristic	$C_{13}H_{27}COOH$	58.0	0.858	60	1.4308	60.0
Palmitic	$C_{15}H_{31}COOH$	64.0	0.853	62	1.4273	79.8
Stearic	$C_{17}H_{35}COOH$	69.4	0.847	69	1.4299	80.2
Arachidic	$C_{19}H_{39}COOH$	76.3	0.824	100	....	...
Cerotic	$C_{25}H_{51}COOH$	87.7	0.836	79	....	.
	UNSATURATED ACIDS, $C_nH_{2n-1}COOH$					
Tiglic	C_4H_7COOH	64.0	0.872	20	1.4342	81.0
Oleic	$C_{17}H_{33}COOH$	14.0	0.895	18	1.463	17.7
Erucic	$C_{21}H_{41}COOH$	33.5	0.860	55	....	...
	OTHER UNSATURATED ACIDS					
Linoleic	$C_{17}H_{31}COOH$	−11.0	0.9025	20	....	...
Eleomargaric	$C_{17}H_{31}COOH$	48.0	....	..	....	...
Linolenic	$C_{17}H_{29}COOH$	...	0.905	20	....	...
Ricinoleic	$C_{17}H_{32}OHCOOH$	17.0	0.945	15	....	
Clupanodonic	$C_{21}H_{33}COOH$	<−78.0	0.9410	15	1.5057	15.0

The fatty acids are all lighter in weight than water. Those having less than ten carbon atoms may be distilled at atmospheric pressure, and are known as the volatile fatty acids. Those containing more than ten carbons cannot be distilled at atmospheric pressure without decomposition, and are known as non-volatile fatty acids. The oils containing the saturated acids do not undergo any marked change when exposed to air. On the other hand, those which contain the unsaturated acids become gummy, and in certain instances when exposed in thin layers form dry, hard films. This change is most marked in the case of those oils containing glycerides of linoleic, linolenic, clupanodonic and eleomargaric acids.

Glycerol and Glycerides—Glycerol, being a trihydric alcohol, can combine with one, or two, or three monobasic acid radicals, forming monacid glycerides,

[4] Bradley, T. F., Ind. Eng. Chem. *29*, 440 (1937).

diacid glycerides, triacid glycerides: these are commonly, but less accurately, named monoglycerides, diglycerides and triglycerides, respectively. The triglycerides are the most important because the neutral fats are composed of them. The structural formulas of the three glycerides of stearic acid are given below.[5]

Monostearin.

$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ \mathrm{HO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ \mathrm{HO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$

Distearin.

$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ \mathrm{HO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$

Tristearin.

$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$

It will be seen that not only is it possible to have compounds in which one acid enters into the combination, but also others, known as mixed glycerides, in which two or even three different acid radicals may be joined to one glycerol group. Such a mixed ester may be represented by a general formula, putting R^- for a monobasic fatty acid radical:

$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ R_a^-— & \mathrm{C} & —\mathrm{H} \\ & | & \\ R_b^-— & \mathrm{C} & —\mathrm{H} \\ & | & \\ R_c^-— & \mathrm{C} & —\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$

R_a^-, R_b^-, R_c^-, may be all different, e.g., stearic, oleic, palmitic, or two of them may be alike. It is also self-evident that isomers may exist, depending on the arrangement of these radicals.

[5] Langton, H. M., Food 4, 323 (1935).

It is now well ascertained that the majority of natural glycerides are mixed esters. Some, probably most, natural fats and fatty oils are composed almost entirely of mixed esters, i.e., they contain little or no glyceride with only one kind of acid. There are fats and oils, however, which must contain large quantities of unmixed triglycerides; the high percentage of one fatty acid precluding the possibility of all the glycerides being mixed esters, because there is not enough of the other fatty acids to "go round."

The glycerides of a sample of lard were found to be composed of palmitodistearin 3 per cent, stearodipalmitin 2 per cent, oleodistearin 2 per cent, oleopalmitostearin 11 per cent, palmitodiolein 82 per cent. Another investigation showed that 84 per cent of specimen of coconut fat was made up of mixed glycerides of saturated acids, dilauromyristin being the most abundant. Trilaurin and other simple (unmixed) triglycerides of saturated acids were absent. The glycerides containing both saturated and unsaturated fatty acids constituted 16 per cent of the total. They were composed chiefly of esters containing one oleic acid radical and two radicals of saturated acid (or acids): dioleoglycerides were present to the amount of 4 per cent. Little or no triolein was present.

TABLE 2—ANIMAL OILS

Name of Oil	*Iodine No.*	*Method of Recovery*	*Industrial Uses*
		FISH OILS [a]	
Menhaden [b]	139-180	Pressing	Paints and varnishes
Sardine	161-193	Pressing	High-grade soaps
		LIVER OILS	
Cod	167	Pressing	Medicines and tanning
Haddock	154.2		Adulterant for cod-liver oil
		BLUBBER OILS	
Seal	127-145		Soaps
Whale [c]	115-155	Expelling	Soaps and leather dressings
Dolphin	99.5		Lubricant
Porpoise			Lubricant
		TERRESTRIAL ANIMAL OILS [d]	
Sheep's foot	74.2	Boiling sheep hooves with water	Lubricant
Horse's foot	73.8-90	Boiling horse hooves with water	Lubricant
Neat's foot	69.3-70.4	Boiling cattle hooves with water	Lubricant
Egg	68.5-81.5	Pressed hard boiled yolk of hen's eggs	Tanning
Lard	73	Pressing	Tanning
Tallow	55.8-56.7	Pressing	Tanning

[a] The chief sources of supply are the coasts of Norway, Scotland, North America, Japan and Siberia.
[b] Reizenstein, L. J., Amer. Paint J. *22*, No. 44, 7 (1938).
[c] Brandt, K., "Whale Oil: An Economic Analysis."
[d] Levitt, B., Chem. Industries *42*, 319 (1938).

TABLE 3—VEGETABLE OILS

Name of Oil	*Chief Source of Supply*	*Iodine No.*	*Method of Recovery*	*Industrial Uses*
	DRYING OILS			
Perilla [a]	Manchuria, Japan	206.1	Pressing	Varnishes
Linseed [b]	Russia, India, Argentina, Canada, United States	175–202	Pressing, extraction, expelling	Paints, varnishes, resins
Tung [c]	China, Japan, United States (Florida)	189–197	Pressing, extraction, expelling	Varnishes, resins
Poppy Seed [d]	Asia Minor, Egypt, Russia	128–141	Pressing	Salad oil
Oiticica [e]	Brazil	179.5	Pressing, expelling	Varnishes, resins
	SEMI-DRYING OILS			
Soybean [f]	China, Japan, United States	122–134	Pressing, expelling	Soaps, varnishes, resins
Pumpkin Seed	Russia	123–130	Pressing	Salad oil
Corn	United States	113–125	Pressing	Salad oil
Cottonseed [g]	United States, Egypt, Japan	111–115	Pressing, expelling	Salad oil
Sesame	India, China, Japan	109–112	Pressing	Soaps, margarine
Croton	Malabou	111–112	Pressing	Medicines
	NON-DRYING OILS [h]			
Rape Seed	Great Britain, Germany	94–105	Pressing, extraction	Rubber substitutes
Castor	India, Java, Italy, United States	84	Pressing	Medicines, varnishes
Almond	Southern Europe, Southwestern Asia	93–103	Pressing	Medicines
Peanut	United States	88–98	Expelling	Salad oil, margarine
Olive	France, Greece, Spain, United States (California)	79–88	Pressing, extraction	Salad oil, high-grade soaps

[a] Scofield, A., Amer. Paint J. *22,* No. 44, 7 (1938).
[b] Ennis, C. P., "Linseed Oil and Other Seed Oils," D. Van Nostrand Co., Inc. (1909).
[c] Concannon, C. C., Amer. Paint J. *21,* 54 (April 26, 1937).
[d] Science Library Biographical Series No. 329, "Processing and Technical Uses of Poppy Seed Oil," Science Museum, London.
[e] Holdt, C. P., Natl. Paint Bull. *1,* 10 (March, 1937).
[f] Hausman, M. J., Soap *12,* No. 12, 27 (1936).
[g] Lamborn, L. L., "Cottonseed Products," D. Van Nostrand Co., Inc., New York (1904).
[h] McKinney, R. S. and Jamieson, G. S., Oil and Soap *19,* 289 (1936).

SUMMARY OF RECOVERY METHODS AND USES OF CERTAIN OILS, FATS AND WAXES

A detailed study of the properties of each oil is beyond the scope of this chapter. However, the more common have been listed in Tables 2-5. For a more complete enumeration, reference may be had to the exhaustive work of Jamieson.[6]

[6] Jamieson, G. S., "Vegetable Fats and Oils," The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), New York (1932).

With regard to the table proper, it should be noted that the drying oils have iodine numbers[7] of 130-200, the semi-drying oils, 95-130, and the non-drying

TABLE 4—FATS

Name	*Iodine No.*	*Method of Recovery*	*Industrial Uses*
		VEGETABLE FATS	
Coconut	6.2-10	Pressing	Butter substitutes, soaps
Cocoa butter	32.8-41.7	Hot pressing	Confections, medicines, soaps
Cottonseed, stearin	89-103	Hot pressing	Butter substitutes, lard substitutes
Palm	49.2-58.9	Pressing, fermentation	Soap, soldering flux
		ANIMAL FATS [a]	
Beef tallow	35.4-42.3	Pressing	Margarine, lubricants, leather dressing
Butter fat	26-28		Foods
Mutton tallow	48-61	Pressing	Soaps, shortenings

[a] Obst. W., Allgem. Oel.-u.Fett-Ztg. *33,* 468 (1936).

variety still smaller values. It should also be remarked that the term pressing, when unqualified, refers to expression processes undertaken in the cold or under

TABLE 5—WAXES

Name	*Chief Source of Supply*	*Iodine Number*	*Method of Recovery*	*Industrial Uses*
		LIQUID WAXES		
Sperm.......	Head of sperm whale	80–84	Pressing	Lubricant, leather finishes
		SOLID WAXES		
Carnauba....	Brazil	13.5	Boiling leaves of palm tree in water	Floor waxes, carbon paper
Candelilla....	Mexico, United States (Texas)	37	Boiling plant in water	Polishes
Japan.......	China, Japan	4.9–12.8	Pressing	Polishes, leather finishes
Chinese Insect	China	23–40.5	Boiling insect deposit in water	Polishes, paper sizing
Bayberry....	....	3.9–9.5	Boiling berries in water	Tallow candles
Beeswax....	....	8.8–10.7	Pressing	Salves, cosmetics
Spermaceti...	Sperm whale	3.5–9.3	Pressing	Candles
Shellac.......	....	....	Treating shellac with alkali	Polishes
Montan......	France,Germany	....	Extracting lignites	Polishes

slightly warmer conditions, while hot pressing designates temperatures of the order of 150-160° F.

[7] Iodine number—the number of centigrams of halogen, calculated as iodine, which under specified conditions react with one gram of substance under test.

OIL RECOVERY AND REFINEMENT

Recovery of Oil—There are three methods extensively employed in the industry for obtaining oil from animals and vegetables. The first consists in

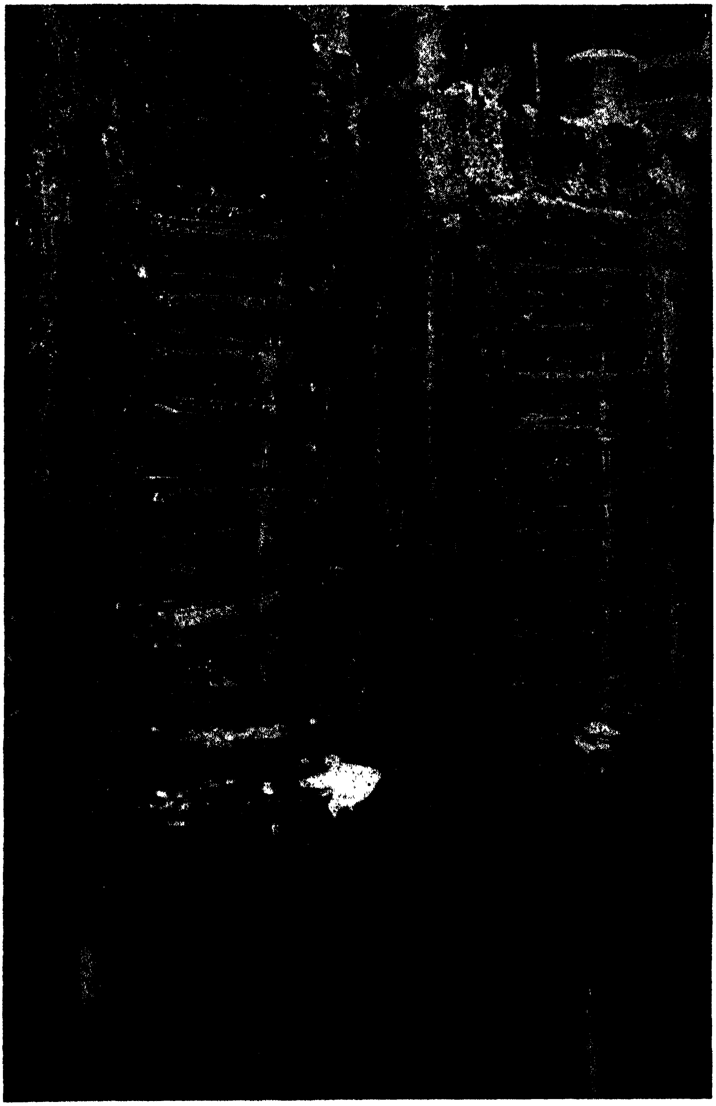

Fig. 1. Hydraulic Presses Removing Linseed Oil from Flaxseed. (Courtesy National Lead Co.)

crushing the material. The crushed material then is warmed and the oil removed by hydraulic pressure.[8] Such a press is illustrated in Figure 1. The residual

[8] Moss, W. W., Trans. Am. Soc. Mech. Engrs. *59*, 715 (1937).

solid material or cake may be employed as a fertilizer. When non-poisonous it is used as cattle fodder. A continuous extraction process of more recent origin uses the Anderson Expeller Mill. The meal is warmed slightly and is fed to a cylinder. Here the oil is expressed by a worm shaft and escapes through drainage holes while the cake is expelled at the end of the cylinder. Figure 2 illustrates such an expeller, and in Figure 3 may be seen the mechanical details of its

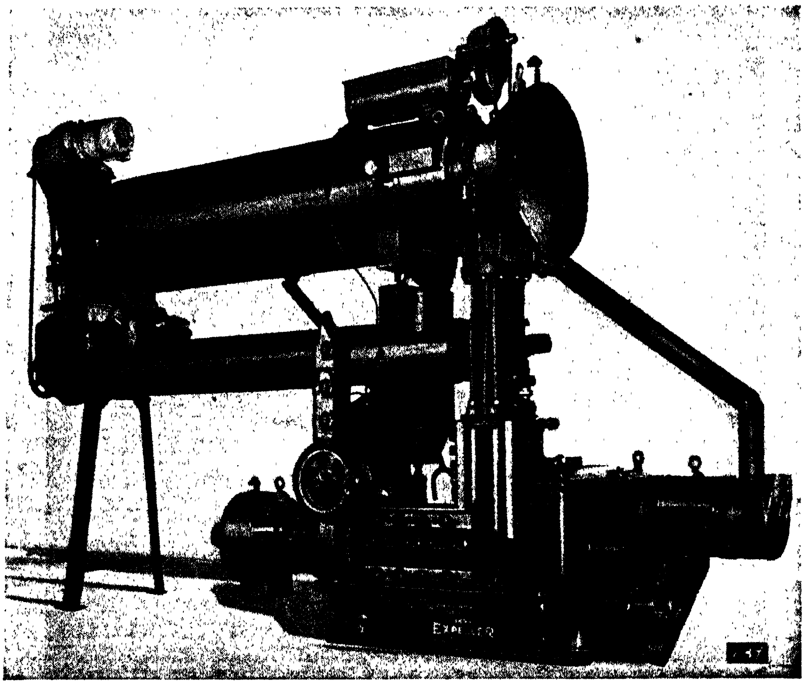

FIG. 2. Front View of Motor-driven Anderson Duplex Super Duo Expeller—Cooker Unit. (Courtesy V. D. Anderson Co., Cleveland, Ohio)

Equipped with variable feeder, cooler-dryer, conditioner, long vertical drainage barrel as well as horizontal barrel, automatic variable speed, vertical warm shaft, oil-cooling system. Capacity 16-25 short tons of raw material in 24 hours' continuous operation.

operation. The third process consists in extracting the desired oils with light petroleum naphtha or similar solvent. The naphtha extract is distilled, the naphtha recovered and used over again; the oil is obtained as a residue from this distillation.

The preparation of linseed oil from flaxseed is probably the most important of any with which the vegetable oil industry is concerned. The general method employed is discussed in Chapter 25 on Surface Coatings. Tung oil is prepared in a manner similar to that of linseed oil. The seed of the tree *Aleurites*, found in China, Japan and Florida (since importation) is shelled and the kernels are crushed. The kernels contain from 50 to 53 per cent of oil. On pressing they yield between 40 and 42 per cent of their weight in oil. The "white tung oil" of commerce is produced by cold pressing. It is a quick-drying oil, surpassing linseed in this respect. It is however inferior to linseed oil for ordinary paint purposes on account of the opacity and inelasticity of the film produced on drying.

Most oils, in order to satisfy the exigencies of rapid-drying paints and lithographic inks, must be bodied. The body of an oil designates the viscosity, consistency, density or covering power. The bodying may be effected by heating,

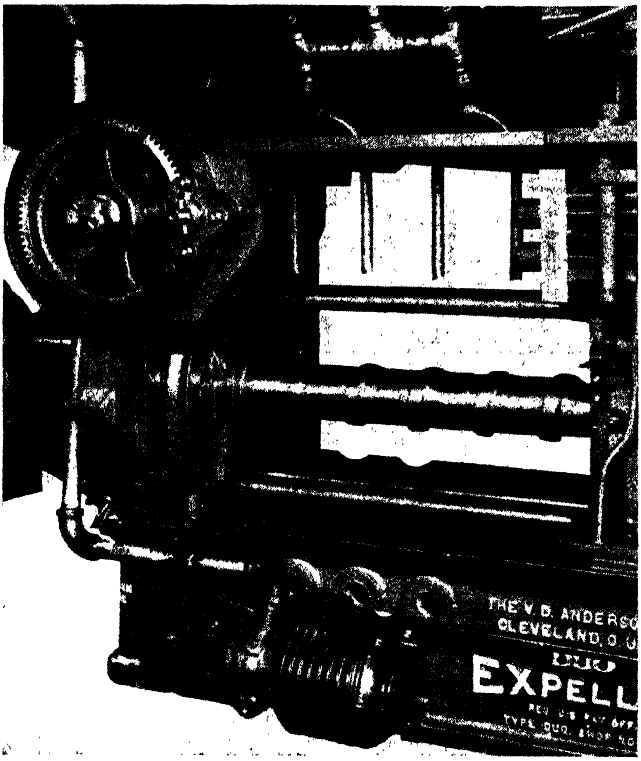

FIG. 3. Anderson Super Duo Expeller with Horizontal Barrel Removed, Showing Main Worm Shaft. (Courtesy V. D. Anderson Co., Cleveland, Ohio)

thus inducing preliminary polymerization. In some cases material is added which will increase the viscosity. Such substances as natural and synthetic resins as well as magnesia, rosin and starch are effective bodying agents.[9]

Refining Vegetable Oils—The following procedure is applicable for refining cottonseed, corn, soybean, peanut and other oils. The practice varies considerably in the hands of different operators but in general the method consists in adding to the oil a quantity of a solution of caustic soda just sufficient to combine with the free fatty acids and form a soap. The latter separates from the oil and in precipitating occludes and drags down much of the foreign matter, leaving the oil considerably lighter in color and substantially free from fatty acids.

[9] Ellis, Carleton, "Printing Inks—Their Chemistry and Technology," Chapter 3, Reinhold Publishing Corp., New York (1940).

The soap also carries with it a certain amount of unsaponified oil and this mixture of soap, oil, coloring matter, and impurities is called soap stock. It settles to the bottom of the refining kettle and is drawn off to be worked up into laundry soap or fatty acids. Recent practice provides for centrifuging the soap stock to separate oil. This step enables a recovery of about 60 per cent of the unsaponified oil contained in the soap stock. The refining kettle is equipped with a mechanical agitator or a coil through which compressed air may be admitted to the bottom of the kettle. It is necessary to stir the oil vigorously when the alkali is added as its even distribution throughout the oil is a matter of importance.

Kettles equipped with mechanical agitators are generally used. The type of

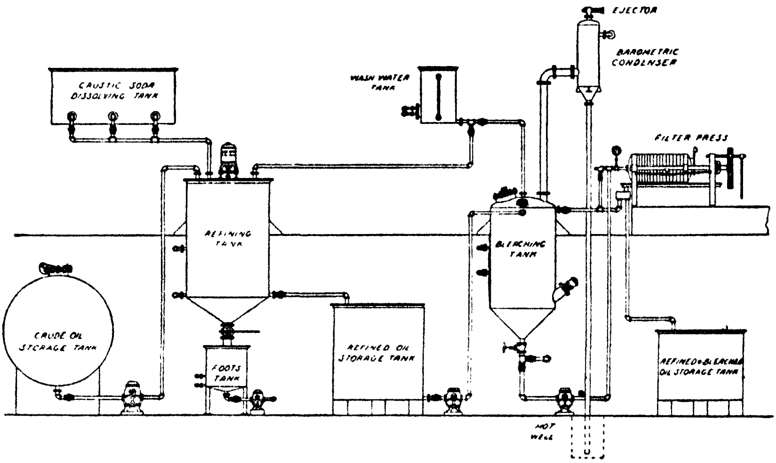

FIG. 4. Oil Refining and Bleaching Plant. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

stirrer varies from simple paddles to a vertically set spiral conveyor type of agitator which accomplishes a thorough mixing of the top and bottom layers. The amount of lye added to the oil is dependent upon the content of free fatty acids of the oil and an analysis always should be made in advance of refining for the purpose of calculating the quantity of alkali. The strength of the caustic soda solution will vary from 16°-24° Bé.; the lower the grade of oil, the stronger the solution, as a rule. An initial temperature of 70° to 75° F. should be maintained during the period of addition of the alkali. As the refining kettle is provided with steam coils, these may be used, when necessary, for cooling purposes. The caustic solution then is added with vigorous stirring and the agitation continued for a half hour before turning on steam and raising the temperature for the finishing stage. A few minutes after the introduction of the caustic solution the appearance of the oil changes. The oil becomes more fluid and turns to a brownish or black shade in the course of 15 or 20 minutes. When a sample shows a clear bright oil carrying a blackish floc, the oil has reached the stage of "breaking" which is an indication that sufficient caustic soda has been added. Steam is turned into the coils and the oil, undergoing gentle agitation, is heated to a temperature of about 120° F. The flocs or clots collect and settle readily. When refining a good grade of cottonseed oil, the temperature should not exceed 120° F. during the finishing operation but with poor grades of oil it is sometimes necessary to raise the temperature even as high as 140° F. The time required for the operations described above is approximately forty-five minutes to one hour.

After settling, the clear oil may be conducted directly to a storage tank. From the latter, the refined product is pumped to the bleaching tank. In some instances the oil is led from the refining tank to a washing unit, when the last traces of alkali are removed with water. The oil then is allowed to flow to the bleaching tank.

Figure 4 represents the arrangement of an oil refining and bleaching plant, showing the steps of the refining operation above described.

BLEACHING, DEODORIZING, AND WINTERING THE OILS

Fuller's Earth—So extensive has the practice of using fuller's earth as a bleaching agent become that this earth is by far the most important oil-bleaching medium employed at the present time.

Fuller's earth is a variety of clay that has high capacity for adsorbing basic colors and can remove these colors from solution in animal, vegetable, or mineral oils, as well as from some other liquids, especially water.

Analyses of various samples of fuller's earth vary so greatly that chemical analyses are now well understood to be no criterion whatever in determining whether or not a particular clay shall be classified as a fuller's earth. Like all other clays, fuller's earth is a hydrous aluminum silicate containing a higher percentage of water of composition than most clays, but this water is not an essential factor in the bleaching properties of all fuller's earths; some bleach fully as well after it has been driven off as before, and others lose much of their bleaching power when this water is removed.

Though samples of fuller's earth from different parts of any one deposit, or indeed from any one locality, are much alike, samples from different localities are so different in their physical properties that it is by no means easy to classify them. To determine whether or not a particular clay is a fuller's earth is no simple matter, for its bleaching power is practically the only characteristic by which it may be identified.

The range of specific gravity of fuller's earth is much the same as that of other clays, although the apparent specific gravity varies widely, owing to variations in porosity. As a rule, it is lighter and more porous than other clays. However, both the English earth and the Arkansas earth, when dry, are fully as dense as ordinary clay. The volume that a given weight occupies varies widely, and a cubic foot of dry, ground fuller's earth from Georgia or Florida weighs only a little more than half as much as a similar volume of English or Arkansas earth. This fact should be taken into careful consideration in applying this material to the bleaching of oils, for if the same measures are used in a comparative test of different earths no valid conclusions can be reached.

Most samples of fuller's earth give more or less taste and odor to edible oils but they vary greatly in this respect. For many years the English material was preferred, chiefly because it gave little such effect. Methods for removing taste and odor are now well known to all oil refiners, so that the question is not so important as formerly. Why taste and odor should be imparted to oil is not known, but it certainly is not generally due to any soluble material in the earth, but rather to some oxidizing action upon the oil itself. This property appears to be connected with the "acidity" of the earth, for if it is treated with lime water this action is greatly reduced. Unfortunately, the bleaching power is destroyed at the same time. Certain earths have so marked an oxidizing action on edible oil that they cause the oil to catch fire spontaneously when air is blown through the filter presses to remove the adhering oil, as is done in practice. This property is fatal to the use of a fuller's earth in refining edible oils, for beside fire risks to buildings it invariably destroys the cloths of the filter presses. Fortunately only earth from one or two deposits displays this vigorous oxidizing action.

Bleaching Practice—The method used in bleaching edible oils is essentially the same in general principle for all oils, but differs in detail. The temperature at which the bleaching takes place and the proportion of earth used vary not only with every oil, but also in the practice of the various refining plants as applied to similar oils. As cottonseed oil is by far the most important of those oils to which the process of refining is applied, it can best serve as an example.

Crude cottonseed oil is not affected by fuller's earth and it must first be subjected to the usual treatment with an alkali, which removes the fatty acids and at the same time converts the coloring matter into basic forms.

Partly refined samples of different cottonseed oils require very different quantities of the same fuller's earth to remove the color. Accordingly, in the best practice, the oils that will require the least quantity of earth are selected by laboratory tests for bleaching.

With the finest qualities of cottonseed oil as little as 1.5 per cent of the best fuller's earth may give an effective bleach; with others as high as 6 per cent is required. Probably 3 per cent is a fair average for bleaching cottonseed oil at the present time. The proportion of earth used also depends upon the temperature to which the oil is heated before treatment, although too great an increase in temperature may have a deleterious effect on the oil. In fact, it has been the practice of one plant to use in bleaching oils of special quality as much as 10 per cent of fuller's earth and a very low temperature.

In ordinary practice a measured quantity of the dry cottonseed oil is placed in a large vat containing steam pipes and heated to near the boiling point of water. The oil is then rapidly stirred by paddles and the necessary measured quantity of fuller's earth is added. Also, approximately 0.5-1 per cent of bleaching black is incorporated. Figure 4 represents a bleaching unit connected directly with the refining process. The quantity of oil for a single operation is so gauged that when all of the oil taken has passed through the filter press, the press itself is charged with fuller's earth and is ready to be opened. Before the press is opened, as much oil as possible is blown out with steam and the oil is generally further removed by blowing air also through the press.

The color of the oil after treatment with fuller's earth is greatly reduced and its standard is determined by means of the tintometer. Treatment with fuller's earth, however, besides reducing the color, also gives more or less taste and odor to the oil, which must be removed before the oil can be marketed. The earths that bleach oil the best almost invariably give the greatest taste and odor to the oil, but this is not now nearly so serious an objection as formerly, as methods for removing taste and odor from edible oils are now well known. In the treatment of lard and lard oil it is seldom, if ever, necessary to use more than 1 per cent of fuller's earth and generally the lard is not deodorized afterwards.

Testing Fuller's Earth—In determining the decolorizing power of fuller's earth for use for edible oils a quantity of oil should first be selected which is sufficient for all of the tests to be made, as different samples of oils are bleached very differently by the same earth. With cottonseed oil a definite quantity of oil is weighed or measured, placed in a beaker, and heated (preferably in a water bath) to 100° C. The sample of fuller's earth, unless already ground, is first carefully pulverized to pass a 100-mesh sieve. A portion of the pulverized sample, ordinarily 5 per cent of the quantity of oil taken, is weighed and stirred into the hot oil. The stirring is continued for three minutes. The mixture is immediately filtered into a sample bottle, such as is universally used in testing for oil color. If at the same time it is desired to determine the quality of the earth as regards its action in the filter presses, its filtration should take place on a Büchner funnel, using suction. If the question of filtration is not of moment, it is usually simpler to filter through an ordinary steam-jacketed funnel, using filter paper. A portion of the same sample of oil is then treated with a sample of standard fuller's earth, for which purpose the English earth is universally used, and the colors of the two oils obtained are compared in a colorimeter by means of Lovibond color glasses. The only glasses required are the red and yellow series.

Chemical Bleaches—Chemical bleaches likewise may be used, but these usually impair the flavor of the oil and are not generally looked upon with favor by manufacturers of edible oils. Sometimes the crop of seed is so poor that fuller's earth proves ineffective as a bleaching agent and has to be supplemented by a chemical bleach. Treatment with chloride of lime and mineral acid, followed by thorough washing, affords a bleached oil which satisfies many industrial requirements. Chlorophyll in small quantity is sometimes added to improve the color. To obtain a "red" oil for margarine manufacture affording the desired shade of yellow to the finished margarine, without use of dyes, the oil is treated with sulfur, or nitric oxide.

Deodorizing—Oil which is being prepared for edible purposes usually requires deodorization. This is effected by subjecting the well-refined oil to the action of superheated steam under reduced atmospheric pressure. The treatment is carried out in either vertical or horizontal tanks. A vertical type of apparatus is shown in Figure 5. A charge of oil is placed in the deodorizer. A heated mineral oil is circulated through a coil in the deodorizer until the cottonseed or other oil is heated to approximately 400° F. Superheated steam then is passed through the vegetable oil at such a rate that the gauge indicates a vacuum of 20 inches of mercury, or more.

When the oil has been freed from odoriferous constituents it is withdrawn through the vacuum cooling tank. From the latter the cooled oil is pumped to a filter press, the filtrate removed and conducted to a storage tank.

Wintering—The market brands "summer oil" and "winter oil" differ from each other in that the latter has most of the stearin removed; so that the oil does not solidify during the colder months. Winter oil is sometimes spoken of as "demargarinated." It is manufactured on a very extensive scale in this country by cooling the oil, filtering off the solid deposit and pressing.

Apparatus for wintering oil is shown diagrammatically in Figure 6. The refined, bleached and deodorized oil is pumped to a battery of graining tanks.

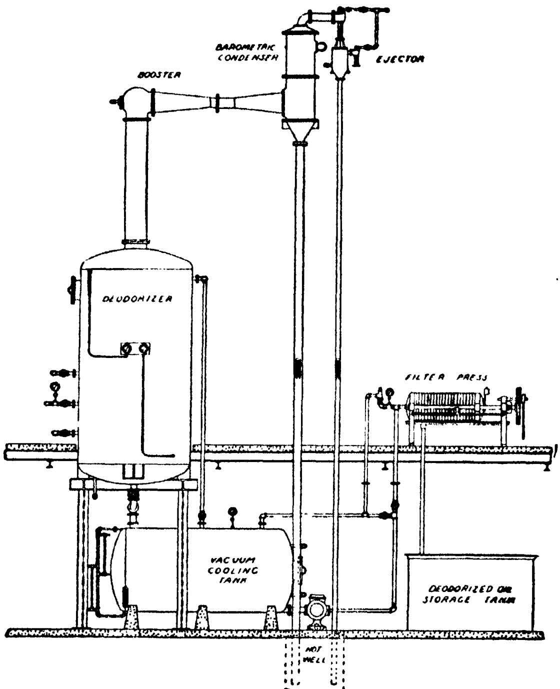

FIG. 5. High Vacuum Oil Deodorizing Plant. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

In the latter the oil is chilled by water, temperature observations being taken at regular intervals. Analogous to the titer test, control may be had by ascertaining the fall and subsequent rise in temperature which occurs during the operation. At first the temperature falls until stearin commences to separate, then a rise occurs due to such separation. At intervals, air is blown through the oil to agitate it thoroughly. Finally when the thermometer remains stationary for a sufficient interval the chilling stage is ended and the oil is discharged into the filter presses where the stearin is removed and winter oil collected.

The foregoing method is probably the most economical one in preparing winter oil. When large quantities of this oil are required, a somewhat different procedure sometimes is employed. The summer oil is exposed in tanks in a refrigerated room to a temperature of about 40° F. The oil is stored here for a period of about ten days during which time the stearin separates and settles.

The clear oil is removed by means of a suction swing-pipe and is pumped through a filter press to remove any suspended stearin. The filtered oil is winter oil and is conveyed to the deodorizer. Heated oil is run through the filter press to remove the accumulation of stearin. The tanks in the chill room are refilled with fresh oil without removing the stearin and the same operation is performed as before. When the quantity of stearin accumulated in the tanks is sufficient, it is removed by pumping and is usually employed in making lard compound; sometimes, however, it is deodorized and used as a cooking oil. The stearin obtained in this way should not be confused with the hard stearin products obtained from beef fat and by the hydrogenation of vegetable oils.

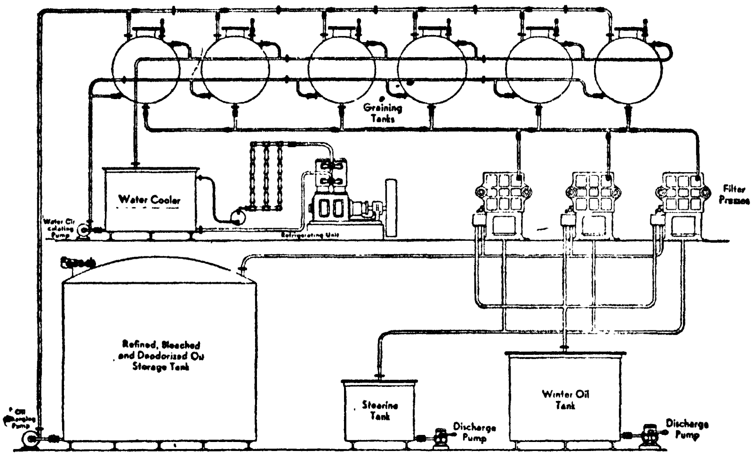

FIG. 6. Winter Oil Plant. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

HYDROGENATION

The market for many of the oils would be seriously handicapped were it not for the hydrogenation processes which effect hardening of the oils. These solids have been marketed as butter substitutes and shortenings. The chemistry of the reaction consists in the combination with hydrogen to saturate the double bonds in the esters. For example, in the presence of a suitable catalyzer oleic acid and hydrogen combine molecule for molecule to yield stearic acid according to the equation:

$$C_{18}H_{34}O_2 + H_2 = C_{18}H_{36}O_2.$$

Thus 282 lbs. of oleic acid require 2 lbs. (or about 0.7 per cent) of hydrogen for the production of 284 lbs. of stearic acid, and similarly the transformation of olein into stearin requires the use of about 0.68 per cent of hydrogen, equivalent to approximately 2500 cu. ft. of hydrogen per ton of olein (of 2000 lbs.). Thus, by weight, only a relatively small quantity of hydrogen is needed.

The analytical constants of oils of course change as hydrogenation proceeds, and aside from the increase in melting point, the progress of the reaction is indicated by a gradual reduction in the iodine number and index of refraction, while the specific gravity generally increases.

Apparatus—Several forms of treating apparatus are in use, all of which have the same object in view, viz., to secure intimate contact of hydrogen gas with the oil and the catalyzer. This is accomplished in various ways, one being to spray the oil mixed with catalyst into a chamber containing hydrogen, and to continue the spraying operation until the requisite degree of hardness is reached. By another method the oil and catalyst are agitated violently in a closed receptacle in the presence of hydrogen. In some instances, mechanical agitation has been omitted. Intimate contact of oil, catalyst and hydrogen is secured by bubbling the latter through the body of admixed liquid and contact agent, any unabsorbed gas being collected and re-used. A fourth process comprises packing the catalyst in an electrically heated vertical iron tube and maintaining an atmosphere of hydrogen in the tube. The oil then is allowed to flow over the catalyst and recycled until the desired degree of hydrogenation is secured.

Hydrogen—One of the problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The two methods most favored in the hydrogenation of oils in the United States are the iron sponge process [10] and the electrolytic method.[11] The hardening operation is described later. Hydrogen also is obtained from water gas by liquefaction of the carbon monoxide and separation of the hydrogen from the liquefied monoxide. This method, known as the Linde-Frank-Caro Process, has been employed in localities where electricity is too expensive to warrant its utilization for electrolysis of water. For further information on the production of hydrogen by the water gas reaction, see Chapter 19.

Catalysts—While platinum, palladium and certain other finely divided metals are capable of acting as hydrogen carriers or catalyzers, the essential constituent of all catalysts used in the hydrogenation of oils at the present time is *nickel*. In some cases nickel is used in conjunction with an auxiliary metal such as copper or aluminum. There are two methods of making catalysts by reduction: one, known as the dry process, involves the reduction of nickel compounds in the dry state; in the other, or wet process, the catalyst is prepared by reduction in oil or other suitable vehicle.

Dry Reduction—The dry process was used extensively in the past but now has been displaced to some extent by wet reduction. To prepare a catalyzer by dry reduction it is customary to precipitate an insoluble nickel compound on a carrier or supporting agent of a finely divided character. Inert mineral powders such as clay, fuller's earth, infusorial earth or kieselguhr, silex (a form of silica) and the like are customarily employed as supporting agents. The support is added to a solution of a nickel salt, usually nickel sulfate, and soda ash is added to precipitate nickel carbonate upon the carrier. The material is washed thoroughly by decantation, or in a filter press, then is dried and reduced in a current of hydrogen gas. For this purpose the nickel is placed in a closed receptacle which may be heated to a temperature usually ranging from 250°-500° C. and hydrogen gas is passed over or through the mass until water is no longer evolved. More rapid reduction is secured by agitating the material. This is ordinarily carried out by charging the raw material into a rotatable drum.

The most sensitive catalyzers are obtained by reduction at the lowest possible temperatures. Nickel carbonate begins to reduce below 220° C., but at 270° C.

[10] Hurst, S., Oil and Soap *16*, 29 (1939).
[11] Steinbecker, A. H., Oil and Soap *16*, 39 (1939).

the reduction is not complete even after long exposure to hydrogen. A temperature of 300°-325° C. gives fairly complete reduction and is a satisfactory working temperature. The lower the temperature at which the nickel carbonate is reduced, the more sensitive it is to various external influences, hence the preparation of this catalyzer should be conducted not only with respect to degree of activity, but also with respect to longevity. Nickel is easily poisoned by chlorine and by sulfur in the sulfide form. Copper is much less sensitive to poisons than nickel, but it is much less active.

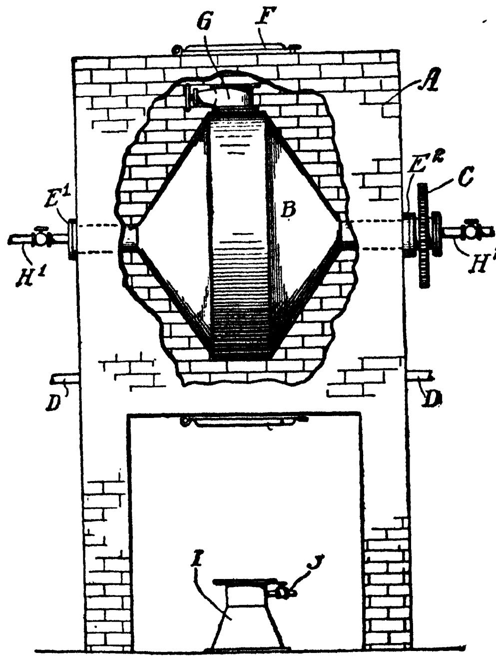

FIG. 7. Apparatus for Dry Reduction of Hydrogenation Catalyst.

After nickel has been prepared as described above, it should be kept out of contact with air, as it is extremely pyrophoric and loses in efficiency on exposure to the air. Consequently, when treating oil with such a catalyzer, it is advisable to free the treating apparatus of air by flushing with hydrogen.

Nickel-copper catalysts are prepared in much the same way as nickel itself, except that a mixture of nickel sulfate and copper sulfate is dissolved in water and coprecipitated with soda ash. Nickel-aluminum contact agents generally are made by alloying nickel with aluminum. Subsequently a portion of the aluminum is removed by washing the alloy in caustic soda.[12]

A simple type of catalyst-reducing device is represented by Figure 7. A is a brick structure which contains the reducing drum B. The latter is rotated by means of the sprocket C. E¹ and E² are stuffing boxes which permit the drum to rotate without disturbing the gas inlet and outlet. The catalyst is admitted

[12] Raney, M., Ind. Eng. Chem. 32, 1199 (1940).

and withdrawn through the gate G. The drum is filled about two-fifths full of the catalyzer and hydrogen passed in. When a test for oxygen shows that all the air has been expelled, the drum is heated to a temperature not exceeding 360° C. During reduction the hydrogen is passed through at a fairly rapid rate in order to remove the steam formed; thus reducing the partial pressure of the latter and facilitating the reduction of the nickel carbonate or hydrate. The gases issuing from the exit side of the drum may pass through a water seal, and after purification may be returned to the gas holders to be used again. When the issuing gases are found to contain no steam, the reduction is complete. The heating is then discontinued and the catalyst is allowed to cool in a current of hydrogen.

After the catalyst is cool, the hopper I is coupled to the flange of the gate G. The bottom of the hopper dips below the surface of oil contained in a receptacle beneath. Hydrogen is passed in at the valve J, expelling the air from the hopper. The valve of the reducing drum is now opened and the catalyst falls into the oil, with which it should be thoroughly mixed. Thus, it is effectively sealed from the air, and oxidation is prevented.

Wet Reduction—The method of reducing a nickel compound *in oil* to make a catalyst has proved simple and usually more reliable than the dry method. In addition, the operation is cleaner, there being less dust and dirt, and dangers from explosion due to hydrogen are minimized. Workmen constantly exposed to an atmosphere containing nickel dust may suffer injury to the lungs.

The wet reduction process is carried out very simply by adding a finely ground nickel salt to the oil, heating and introducing hydrogen gas until reduction is complete.

Nickel Formate. The most popular compound employed in wet reduction is nickel formate. When heated in a vegetable oil to a temperature of about 240° C. nickel formate breaks down, yielding finely divided, partially colloidal nickel. The reduction of nickel formate may be represented as:

$$Ni(HOOC)_2 \cdot 2H_2O = Ni + 2CO_2 + H_2 + 2H_2O.$$

The introduction of a reducing gas is not required. It is, however, a common procedure to introduce a slow current of hydrogen into the oil in which the nickel formate is undergoing reduction. The formate may be mixed with oil in such proportion that a catalyst concentrate is obtained on reduction. A temperature of 240° C. slightly affects the quality of the vegetable oil, e.g., cottonseed oil, used as the suspensory vehicle in carrying out the reduction, and if it is to be employed in making edible fat it is advisable to filter out the catalyst and wash it with fresh oil to remove the oil employed originally. The latter may be returned to the refinery or used for non-edible purposes.

Re-use of Catalyst. Well-refined vegetable oils do not impair the quality of the catalyst so rapidly as oils which have not been fully refined and which contain soap or other impurities. Fish and whale oils on the other hand impair it very rapidly. The catalyst therefore may be used repeatedly in hydrogenating refined vegetable oils. When employing 0.2 to 0.5 per cent of nickel, based on the weight of the oil taken, the catalyst ordinarily may be used to harden from five to ten batches of oil. No exact rule can be laid down, however, as variations in the kind and quality of the oils which are being treated, purity of hydrogen, and other conditions affect the life of the catalyst.

The separation of the catalyst from the hardened fat is effected by filtration. The oil is filtered in a press under such conditions that the filtrate is at a temperature of 49°-71° C. The catalyst remains in the press cake. If it is to be re-used this cake is dropped into the catalyst mixing tank, and the cycle repeated.

Bulking Agent. Catalysts prepared by the wet process are usually partly colloidal and the filtration of the catalyst from the oil is greatly accelerated by the addition of a bulking agent. This material may be fuller's earth, kieselguhr or other mineral powder which is capable of assisting filtration. Silex is useful and is less likely to impart an earthy taste to the oil than is the case with some other mineral substances. The bulking agent may be added to the oil with the catalyst or it may be introduced at any time prior to filtration. It has no value as a supporting agent as it does not function like the nickel-coated carrier employed in the dry process for the nickel particles are not attached to the bulking agent during the hydrogenation stage. After filtration the press cakes of catalyst and bulking agent may be churned with additional oil and the material employed for the hydrogenation of a subsequent batch of oil. This operation is continued until the catalyst has lost its strength. In some cases fresh catalyst is added from day to day in order to keep the material operative to substantially the same degree. In the handling of the catalyst there are small losses and the replacement of these losses from day to day will, in some cases, serve to keep the catalyst at a desired degree of activity.

Oils Difficult to Harden. Unsaturated free fatty acids are difficult to harden and this applies to glycerides having a high content of free fatty acids. Fish oil often has a high acidity. For hydrogenation of this oil a grade containing not over 3 to 5 per cent of free fatty acids should be chosen. The oil may be treated with, or filtered through, fuller's earth and one part of nickel catalyzer used to 100 parts of the oil. Additions of fresh catalyzer may be required. After a single exposure to fish oil the catalyzer usually is so impaired in activity that it is sent to the recovery plant.

The Hardening Operation[18]—The hardening (or hydrogenation) operation employing a catalyst reduced in oil will be described as typical of all procedures. The catalyst is conducted from the reducer to a catalyst mixing tank (Figure 8) where it is stirred into a portion of the oil charge. Also, nickel from the filter press at the end of the hardening step is transferred immediately to the mixing tank where it is incorporated in a part of the oil charge. Thus, the catalyst reducer need be employed only to furnish make-up catalyst as required when the plant is operating. The heated mixture of oil and catalyst is pumped from the mixer to the converter, where the balance of the oil charge is added. The contents of the converters are heated to a temperature of 120°-176° C. by means of superheated steam or hot oil coils. The temperature of the contents of the hydrogenator is registered by means of a recording pyrometer.

The pressure in the converter is then reduced somewhat to remove air and moisture. Hydrogen is then blown into the charge through a perforated inlet pipe. The hydrogen pressure usually is maintained at approximately 60 pounds

[18] Wurster, O H., Ind. Eng. Chem. *32*, 1193 (1940).

per square inch. Samples of oil may be withdrawn from time to time by means of a sampling cock and the melting point or refractive index determined.

Hydrogenation of animal and vegetable oils is an exothermic reaction, so that it generally is necessary to cool the oil during hardening. This may be

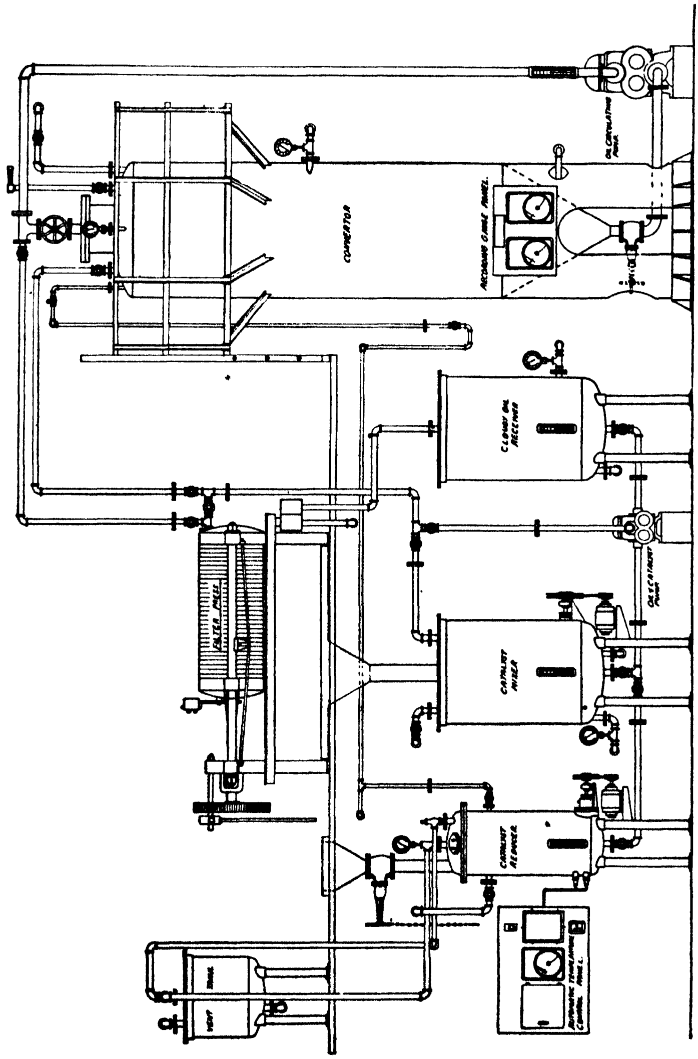

FIG. 8. Hydrogenation Plant. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

effected by allowing cold water to flow through a coil inside the converter. In some instances, reduction in temperature of the oil is accomplished by circulating the charge through an external heat exchanger, and returning the mixture to the converter through spray nozzles at the top of the converter.

When hardening has progressed to the stage desired (as indicated by the melting point or refractive index of a sample), the flow of hydrogen is discontinued.

Circulation of the oil is continued and the cooling coil operated until the temperature has been reduced to a point where filtration of the oil is possible. The charge is then pumped from the converter to a filter press, where hard fat is separated from the catalyst. The latter is removed from the press and returned to the mixing tank for re-use.

The method given above is capable of many modifications as oils of different character require different treatment and in consequence oftentimes call for equipment which varies considerably from that given by way of illustration.[14]

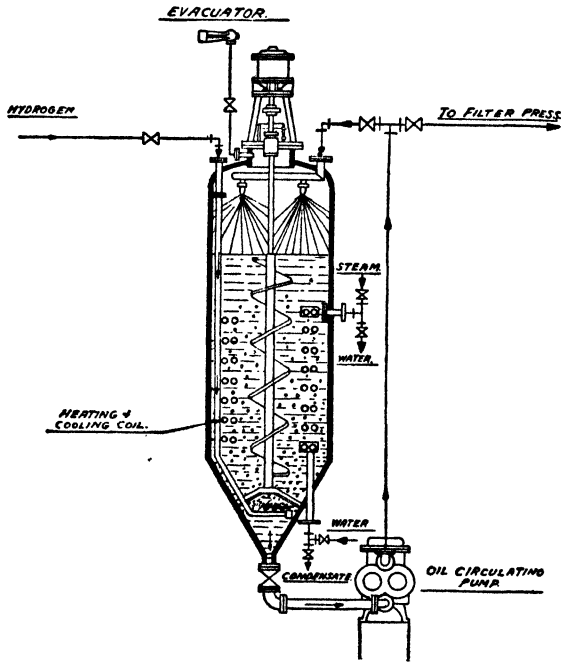

FIG. 9. Diagrammatic Elevation of Converter, Illustrating Method of Agitation. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

A simple type of converter now extensively used is shown in Figure 9. It consists of a closed tank equipped with a steam coil and stirrer. The vessel is charged with oil and catalyst and the charge is heated to the requisite temperature when hydrogen is introduced by the small pipes in the bottom of the apparatus. The oil is stirred vigorously during the operation. Sometimes preliminary heating by steam to 100° to 120° C. suffices to start the reaction after which the temperature rises rapidly. At 170° to 180° C. water may be passed through the coil to prevent overheating.

The simplest type of hydrogenator and one which, perhaps, is the most popular, consists of a tank and heating coil without any mechanical stirring device. See Figure 10. Using a partially colloidal nickel catalyst obtained by wet reduc-

[14] Ellis, Carleton, "Hydrogenation of Organic Substances," third edition, D. Van Nostrand Co., Inc., New York (1930).

tion and readily maintained in suspension, the introduction of hydrogen at the bottom serves to keep the charge well mixed. Unused hydrogen is collected in a gas holder and, after purification, is employed again.

A continuous method of hydrogenation has been devised, in which the catalyst is made in the form of a cage packed with nickel wool. The cages are packed, one above the other, in an iron chamber, and the whole heated to 180° C. Oil then is allowed to flow over the catalyst at a hydrogen pressure of 30-40 pounds per square inch. The oil charge is recirculated until hardened to the degree desired.

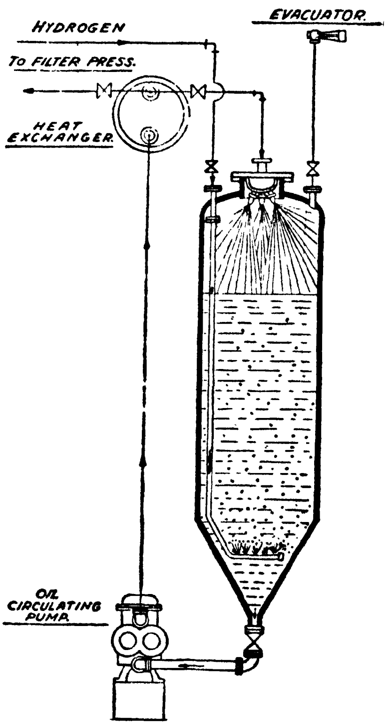

FIG. 10. Diagrammatic Elevation of Converter, Illustrating Method of Agitation. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

When hydrogenated products are intended for use as edible oils, it is customary to remove the "hydrogenated flavor" subsequent to the hardening step. Deodorization usually consists of distillation of odoriferous impurities with superheated steam, and is carried out under diminished pressure. The process is analogous to deodorization of refined oils as previously described. Hydrogenated oil is fed to a shell vessel containing a heating coil. A high flash mineral oil then is heated and circulated through the coil until the hardened oil has attained a temperature of approximately 200°-225° C. Pressure is reduced in the shell vessel, and superheated steam bubbled through the oil.

In place of steam deodorization, removal of hydrogenation flavor can be accomplished by bubbling a mixture of carbon dioxide and nitrogen through the oil for 45-50 minutes. During treatment, the oil is maintained at 145°-150° C. at atmospheric pressure.

PRODUCTS OF HYDROGENATION PROCESSES

Edible Hydrogenated Oils.—Since the addition of less than 1 per cent of hydrogen suffices to convert cottonseed oil or other vegetable oils into a fatty body of at least the consistency of lard, it follows that manufacturers of ordinary lard compound (that is to say, a mixture of about 85-90 per cent of refined cottonseed oil and 10-15 per cent or so of oleostearin) have promptly turned their attention to the production of compound by a "self-thickened" cottonseed oil. The hydrogenated product from cottonseed oil, if properly made, is stable in character. Unquestionably, the hardening process has increased the demand for cottonseed oil in the manufacture of edible fats.

By the hydrogenation process a lard substitute may be prepared in two ways. The entire oil may be simply hardened to the consistency of lard, care being taken to employ an oil as nearly neutral as possible to prevent excessive solution of catalytic metal, and to avoid a high temperature of treatment so as not to impair the flavor of the product. If the color and flavor are detrimentally affected, resort may be had to a further treatment with fuller's earth followed by steam vacuum deodorization. The addition of a small amount of coconut oil benefits the flavor.

The other method is that of making lard compound which, as indicated above, involves thickening a large proportion of normal oil with a small amount of a

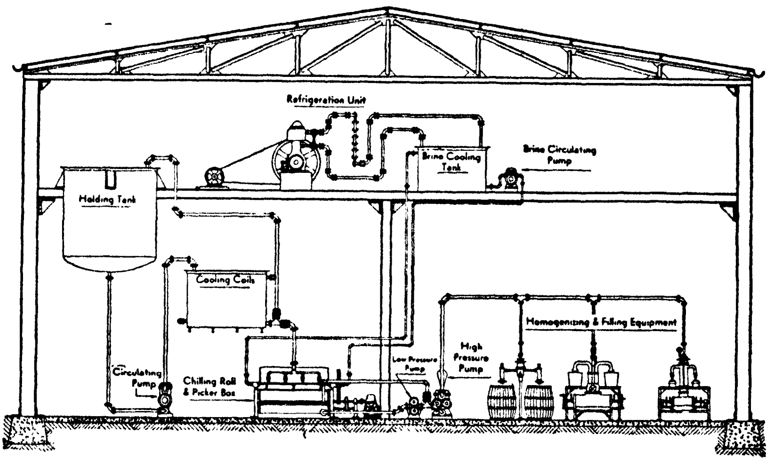

Fig. 11. Lard Compound Plant. (Courtesy Wurster & Sanger, Inc., Chicago, Ill.)

relatively hard hydrogenated product. This may be carried out as follows: After the oil has been hardened, it is freed of catalyst and then run into tanks containing the requisite amount of deodorized cotton oil, or other edible oil. If necessary the mixture is further clarified and filter pressed. With hardened cotton oil of 58 to 60 titer, only 7 to 10 per cent is required to thicken the oil to the consistency of lard, although in hot climates a somewhat larger proportion may be needed. The mixture is run on to a chill roll to cause rapid solidification and after slight aeration to improve the color it is ready to be packaged. Figure 11 shows a lard compound plant.

In this illustration the chilling roller is cooled by the circulation of brine, and is rotated slowly (6-10 R.P.M.). The warm liquid compound is pumped from the holding tank through a heat exchanger where it is cooled to 50°-55° C. The compound then is run into a feeding trough next to the chilling roll, from which the mixture falls on the chilling roll, forming a somewhat translucent film which quickly cools and solidifies. The solid fat is removed from the roll by a scraper and falls into a picker trough. The latter contains a shaft equipped with beating and conveying blades which churn the material and destroy the translucency, producing an opaque white product of lard-like appearance. The picker is run at a relatively high speed, say 175 to 180 R.P.M. Figure 12 is an end view showing chill roll, feeding trough and picker. The chilled compound is pumped from the picker box and forced through a pipe line to the homogenizing and filling equipment. Excessive speed of the picker blades incorporates an excessive amount of air in the product, rendering it "fluffy."

The speed of rotation of the chilling roll is governed by the rate of feed and temperature of the brine. The latter may be kept between, for example, −5 to

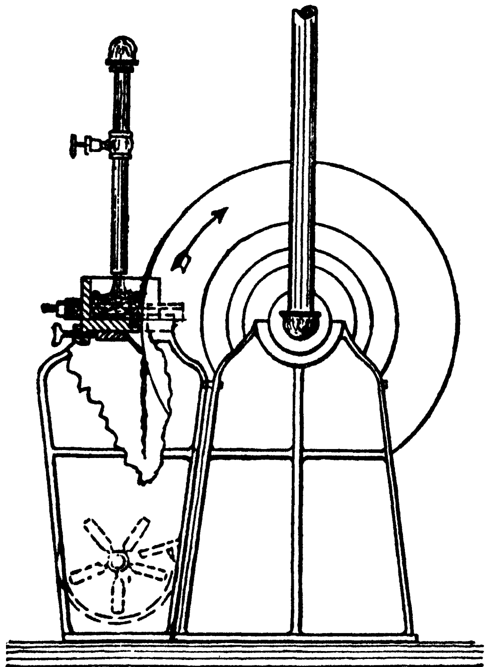

FIG. 12. End View of Chilling Roll, Feeding Trough and Picker.

+10° F. for good results. If the brine is too cold, the product tends to drop badly from the roll and the texture is not always satisfactory. This, however, may be largely remedied by increasing the feed. In winter the brine may be held at a slightly higher temperature to prevent brittleness. In the hottest weather, very cold brine should be used to aid in securing a product which will preserve its color and consistency for a considerable time.

When properly made, the compound derived by the hydrogenated oil thickener is excellent in color, texture, flavor and keeping qualities. By many it is considered superior in several respects to oleostearin compound.

Alcohols by Hydrogenation of Oils—Preparation of detergents from high molecular weight alcohols such as lauryl, myristyl, cetyl, stearyl and oleyl by treatment with sulfuric acid has been recognized as a possibility for some time. However, the former relative scarcity of the alcohols precluded any industrial application of this knowledge. Many oils and fats contained the raw material for these alcohols in the form of free fatty acids or glyceride esters. Research into hydrogenation of these oils proved the key that finally unlocked the door to industrial production of higher alcohols.

The hydrogenation of fatty acids to alcohols may be represented as:

$$RCOOH + 2H_2 = RCH_2OH + H_2O$$

where R represents the hydrocarbon portion of the fatty acid. In the case of a glycerol triester, the reduction may be pictured as

$$(RCOO)_3C_3H_5 + 6H_2 = 3RCH_2OH + C_3H_5(OH)_3$$

where R represents the hydrocarbon portion of the ester.

Among the oils that have been utilized for hydrogenation to alcohols are coconut, castor, sperm, as well as spermaceti. Since these substances contain a mixture of esters in which the acid portions are of different sizes, no unmixed alcohol is secured on hydrogenation. Rather, a composite of fairly close molecular weight and chain length is secured. On treatment with sulfuric acid, a blend of esters is obtained.

Relatively few accounts of this hydrogenation operation have been disclosed except in patent literature. It appears, however, that, in practice, oil is allowed to flow over a catalyst, the whole being maintained in an atmosphere of hydrogen. Pressures and temperatures are somewhat higher than in the hardening process, being of the order of 3000 lbs. per sq. in. at 350°-400° C. The flow rate of the oil is maintained at 2-8 volumes of fatty acid per volume of catalyst per hour. An excess of hydrogen appears to favor reduction of the fatty acids or esters. From 2 to 10 mols of hydrogen per mol of acid are used, depending upon the particular oil which is to be reduced.

Nickel catalysts utilized in hardening of oils are not effective for preparation of alcohols. Double compounds of zinc oxide and chromium oxide, designated zinc chromites, have been observed to be satisfactory contact agents for hydrogenation reactions leading to alcohols. In some instances smaller proportions of cadmium and copper chromites are added to the zinc compounds.

One of the most important properties of the sulfate detergents prepared from high molecular weight alcohols is their ability to form soluble calcium and magnesium salts. Thus, no precipitate or curd is formed on dissolving the sulfates in hard water. For these reasons the sulfate detergents have found industrial application as wetting assistants in the textile industry, as emulsifying agents and as detergents in shampoos and dentifrices. For further information on this class of detergents, see Chapter 42.

READING LIST

HISTORY

Weber, G. M. and Alsberg, C. L., "The American Vegetable-Shortening Industry," California Food Research Institute (1934).

CHEMISTRY

Jamieson, G. S., "Vegetable Fats and Oils," Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), New York (1932).

REFINING

"Chemie und Technologie due Fette und Fettprodukte, Second Edition, Bd. I, Chemie und Gewinnung der Fette," edited by H. Schönfeld, J. Springer, Vienna (1936).

"Chemie und Technologie der Fette und Fettprodukte, Second Edition, Bd. II, Verarbeitung und Anwendung der Fette," edited by H. Bönisch, Vienna, J. Springer (1937).

Schönfeld, H., "Neuere Verfahren zur Raffination von Oelen und Fetten," Allgemeiner Industrie-Verlag, Berlin (1937).

MANUFACTURE

Greene, L. W. and Richards, H. F., "Animal and Vegetable Waxes in 1939," Oil & Soap *17*, 191 (1940).

"Handbuch der Lebensmittel-Chemie, Bd. IV, Fette und Oele, Lipoide, Wachse, Harze, Ätherische Ole," edited by J. Grassfeld, J. Springer, Berlin (1939).

Lemmél, Hans H., "Gewinnung, Veredlung und Verarbeitung der Oele und Fette," Allgemeiner Industrie-Verlag, Berlin (1937).

HYDROGENATION

Ellis, C., "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York (1930).

UTILIZATION

Dean, H. K., "Utilization of Fats," A. Harvey, London (1938).

Guillaudeu, A., "Industrial Utilization of Fats and Oils," Ind. Eng. Chem. *31*, 158 (1939).

ANALYSIS

British Standard Specifications, No. 684, "Standard Methods for the Analysis of Fats" (Internationally Agreed), Brit. Standards Inst., London (1936).

Mason, R. D., "Fats, Total Solids and Moisture," A. Harvey, London (1939).

CHAPTER 42

SOAP AND GLYCERINE

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An exhaustive study of soap and glycerine would necessarily comprise the historical as well as the technical treatment, but inasmuch as the present study is directed primarily at the industrial phase of the subject, the historical phase, dealing only with the earliest developments, will be passed over lightly.

HISTORICAL ASPECTS

Soap of some kind was known to the ancients, for it is mentioned in the Bible and in some classical writings. However, little has been handed down to us that would form a good basis to enable us to judge just how much the ancients knew about soap. It is certain that they knew of the cleansing action of wood ashes, and that at times these were referred to as soap, and it seems equally certain that the emulsifying action of the alkalies in wood ashes on various kinds of fats and greases must have been known to them, and that at least some real soap must have been thus formed, in this way disclosing to them some of the virtues of soap as distinguished from mere alkalies.

Soap became a definite article of manufacture long before its chemical nature was at all understood. Some of the most successful manufacture of this kind was carried out in the Marseilles district of France.

In the early part of last century Chevreul, a distinguished French chemist, made a rather exhaustive study of the chemistry of fats and of soap and disclosed their true nature to such an extent that a scientific basis was thus established for the guidance of the soap industry.

Although this chapter does not purport to be a treatise on the chemistry of fats and oils or of soap it is nevertheless advisable that it shall embrace sufficient of the fundamental chemical principles relating to these materials to enable one more thoroughly to understand their essential chemical character, and to grasp more readily the various industrial processes employed in their manufacture, and even to have the clearer vision of the subject that is so helpful in devising new and improved processes.

THE SOAP MATERIALS

Soaps are made from fats and fatty oils by chemical action with some form of alkali. In the soap industry the term fat is commonly employed as embracing both solid and liquid fats and the liquid fats are generally referred to as oils.

The term "oil" as used in the soap industry refers almost exclusively to fatty oils and does not comprise the various hydrocarbon oils obtained in the refining of petroleum.

Constitution of Fatty Acids—Fats, as they occur in nature, are always mixtures of various members of a specific group of esters known as glycerides. Thus they may be considered as derived from glycerine,

$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH_2\text{—}OH \end{array}$$

a triatomic alcohol having three alcoholic hydroxyl groups, —OH, and one or more fatty acids, $R\text{—}C\begin{smallmatrix} \diagup\!\!\!\!\diagup O \\ \diagdown O\text{—}H \end{smallmatrix}$ each having one acid hydrogen.

In the above formula of a fatty acid the letter R represents an alkyl radical of the general formula C_nH_{2n+1} in which n is most commonly 11, 13, 15, or 17, since most fatty acids occurring in nature, either of vegetable or of animal origin, have an even number of carbon atoms. In addition to the above type of fatty acids, which when pure are solid at room temperature, the term "fatty acids" is now used very generally to include other acids with somewhat analogous physical properties which occur in fats, and especially in oils, having the general formula $R\text{—}C\begin{smallmatrix} \diagup\!\!\!\!\diagup O \\ \diagdown O\text{—}H \end{smallmatrix}$ in which R may represent an unsaturated radical of the general formula of C_nH_{2n-1}, or C_nH_{2n-3}, or a group with an even lower ratio of hydrogen to carbon.

The principal saturated fatty acids C_nH_{2n+1}—COOH found in nature are lauric, $C_{11}H_{23}COOH$, obtained from cocoanut oil, palm kernel oil, and several other oils derived from nuts or seeds from different species of palm trees; myristic, $C_{13}H_{27}COOH$, obtainable from many fats and oils; palmitic, $C_{15}H_{31}COOH$, occurring combined in triglycerides in many fats and oils both animal and vegetable; and stearic acid, $C_{17}H_{35}COOH$, obtainable from most animal fats and oils, and from many vegetable fats. Stearic and palmitic acids occur together in varying proportions in the harder acids derived from most animal fats. A number of other saturated fatty acids with even higher molecular weights occur in nature in combined form. Principal among these is arachidic acid, $C_{19}H_{39}COOH$, which occurs in arachis oil (peanut oil), which also contains some of the other high molecular weight acids.

Probably the most important unsaturated acid is oleic acid, $C_{17}H_{33}COOH$, having the general formula $C_nH_{2n-1}COOH$. Oleic acid, combined with glycerine as glyceride, occurs in considerable proportions in most soft oils found in nature, both animal and vegetable, and in appreciable proportions in most hard fats.

Other important acids with a higher degree of unsaturation occur in nature with the general formula $C_nH_{2n-3}COOH$. The commonest representative of this class is linolic acid, $C_{17}H_{31}COOH$, which is present in considerable proportion in cottonseed oil and in many other soft fats and oils.

Linolenic acid, $C_{17}H_{29}COOH$, with the general formula $C_nH_{2n-5}COOH$, is present in many soft oils and is an important constituent of most drying oils, such as linseed oil and menhaden oil.

In general, saturated fatty acids make harder soaps than unsaturated acids. Lauric acid sodium soap is reasonably soluble in cold water, but the sodium soaps from the higher molecular weight fatty acids are not readily soluble in cold water and therefore exhibit poor lathering quality except when used in warm or hot water. On the other hand they are exceptionally efficient when used in hot or boiling water.

DETERMINATION OF FAT PROPERTIES

Iodine Number—The degree of unsaturation of the various fatty acids is measured by the *iodine number*, which is the per cent of iodine they will absorb under certain standard conditions. The iodine number of a fatty acid is directly proportional to its degree of unsaturation, the pure saturated fatty acids absorbing substantially no iodine.

Titre Test—Mixed fatty acids in a given group may be judged by their *titre test*, which is the temperature measured in degrees Centigrade at which the molten fatty acids begin to show incipient crystallization on cooling. Thus a tallow with a titre of 43° C. will have more hard acids and make a harder soap than a tallow with 41° C. titre. The titre test was devised as a guide for the candle-maker to evaluate different lots of fatty acids, the harder acids being the more valuable. It was a very good test for this purpose. In the old days most candle-makers were also soap-makers, hence the titre test was adopted by soap-makers, and adhered to as a fetish, even though it frequently leads to wrong conclusions when acids from different general origins are under consideration. Consideration of titre alone may lead one far astray for cocoanut oil having a titre of about 23° C. makes a very much harder soap than cottonseed oil having a titre of about 35° C., and olive oil with a titre of about 20° C. makes a soap of about the same hardness as cottonseed oil soap.

The degree of unsaturation of various soap materials as measured by the iodine number is a much better guide than titre to the quality of soap that may be made; the fats with lower iodine numbers making the harder soaps, and those with higher iodine numbers making not only the softer soaps but also ones which are more prone to oxidation and darkening by absorption of oxygen from the air.

Saponification Number—There is no single simple test that will tell the character of a fat and the kind of soap that it will produce although much can be learned from an intelligent joint consideration of a number of separate physical and chemical tests. In addition to the titre and iodine value, a test well worth making is the *saponification value* expressed in per cent KOH necessary to completely neutralize and saponify a given fatty material. This test is usually expressed in an arbitrary illogical manner as the "saponification number" and is measured in milligrams of KOH per gram of fat. If the so-called "saponification number" is divided by 10 it gives per cent KOH absorbed. Most fatty acids used in soapmaking, with the exception of those derived from cocoanut oil and similar oils, have saponification values in the neighborhood of 20 per cent KOH, and, when pure, have free acid values nearly equal to their saponification values. On the other hand, cocoanut fatty acids absorb about 30 per cent more alkali, or about 26 per cent KOH. This test alone generally gives an accurate indication of the amount of cocoanut oil, or similar oil, used in the manufacture of a given soap.

Although the physical and chemical tests commonly used as guides in soapmaking are fairly simple it should be understood that the tests and separations involved in an exhaustive study in any part of the fat field may, and generally do, require most painstaking and exacting research methods such as fractional crystallization in special solvents, and fractional distillation under very low pressures. Often from the knowledge obtained from such research work simple improvements in commercial processes are indicated and may be put into practice, though previous factory procedure gave no inkling of the possibility of such improvements.

CONSTITUTION OF THE FATS

Although fatty acids and glycerine are actually generally obtained from fats by chemical splitting actions of saponification or hydrolysis, the simplest method of explaining the chemical nature of a fat is to consider the reverse of such a reaction, thus:

$$\begin{array}{lcrcrl}
RCOO{-}H & & HO{-}CH_2 & & RCOOCH_2 & \\
 & & | & & | & \\
RCOO{-}H & + & HO{-}CH & = & RCOOCH & +3H_2O \\
 & & | & & | & \\
RCOO{-}H & & HO{-}CH_2 & & RCOOCH_2 & \\
\text{3 Fatty Acids} & + & \text{Glycerine (Glycerol)} & = & \text{Glyceride (Fat)} & + \text{ Water}
\end{array}$$

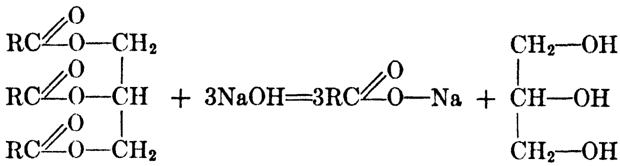
There are three general types of glycerides: triglycerides in which the three glycerine hydroxyls are each esterified with a fatty acid, as shown above; diglycerides in which two of the glycerine hydroxyls are esterified by two molecules of fatty acids and one glycerine hydroxyl remains free; and monoglycerides in which two of the glycerine hydroxyls remain free and one is attached to a molecule of fatty acids. Even though most of the glycerides occurring in nature are triglycerides, an understanding of diglycerides and of monoglycerides is useful to the soapmaker. It is also helpful to realize that the fatty acid radicals (R in the above equation) in a given molecule of triglyceride are not necessarily all alike, and that they are commonly different and may contain either one, two, or three different fatty acid radicals in the same molecule.

The physical properties of fats and fatty oils are largely influenced by the distribution of various fatty acid radicals in the molecules and by the actual positions which they occupy, even when the aggregate amounts and proportions of fatty acids present are unchanged. One way in which the positioning of fatty acids in a molecule becomes manifest is in a change in fluidity of an oil when a rearrangement of position is brought about. A good example of this may be seen in palm oil. A good quality of palm oil which has not been subjected to any special treatment is commonly quite fluid at ordinary temperatures but the same oil after subjecting to special treatments, such as heating and bleaching, is apt to become thick or nearly solid even when the amount of free acids has not appreciably changed. These oils when saponified make substantially similar soaps, that from the liquid oil being quite as hard as the one from the harder fat

One important point illustrated by this phenomenon is the fact that the hardness or softness of fats is not in general a good indication of the hardness of the soap that may be made therefrom.

PRODUCTION OF SOAP AND FATTY ACIDS

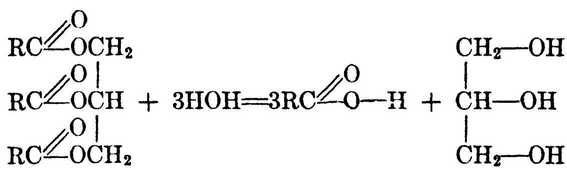
Saponification—When fats, as illustrated by a triglyceride, are acted upon chemically by an aqueous solution of caustic soda, soap and glycerine are formed, thus:



Triglyceride and Caustic Soda = Soap and Glycerine
(Fat) (Glycerol)

This chemical reaction of saponification was known and employed before the chemical nature of fats was understood and before glycerine had been discovered.

Hydrolysis—An analogous and perhaps equally important reaction is involved in the hydrolysis of fats by water to produce fatty acids and glycerine, thus:



Triglyceride and Water = Fatty Acids and Glycerine
(Fat) (Glycerol)

Under ordinary conditions at ordinary temperatures and over short periods of time this reaction is very slow, but it takes place to an appreciable degree when a long period of time is involved, and to a considerable degree at higher temperatures. Also the reaction may be considerably hastened by the employment of acid or basic catalysts or by the use of enzymes.

A careful study of the reactions of saponification and hydrolysis of fats shows that they are reversible reactions, though this is not commonly recognized as being so. Owing to the complex and varied natures of the different glycerides that may be involved, this reversibility is not realizable from start to finish and back again through all the same steps, as the reactions may and do take place at times through alternative steps leading over different courses. This reversibility of reaction thus becomes evident mainly in the *degree* of saponification or hydrolysis on one hand, or of esterification on the other.

Methods of Promoting Hydrolysis—It has been common practice for many years to hydrolyze fats in autoclaves with water with the aid of heat and pressure at the temperatures and pressures of saturated steam at about 125 pounds to 150 pounds per square inch. Under such conditions hydrolysis takes place at an appreciable rate, and at a more rapid rate with the aid of some catalyzer. In such cases some type of agitation to promote emulsification is necessary. This may be provided mechanically or by means of direct jet steam.

The presence of a small amount of sulfuric acid in the water hastens the hydrolysis, but tends to darken the material and necessitates the employment of acid-resistant equipment. Various bases have been used commercially as catalyzers; including lime, magnesia, zinc oxide, various alkalies, etc., with reasonably satisfactory results and with less darkening of the product than with the use of acid. In some cases the employment of only a fraction of a per cent of catalyzer, figured on the fatty matter, is sufficient to hasten the reaction to a considerable degree.

In order to avoid the necessity of operating under pressure in autoclaves at temperatures above the atmospheric boiling point of water a method [1] was devised of bringing about the hydrolysis in an open vessel at ordinary temperatures with the aid of an enzyme. An enzyme that has been used commercially for this purpose is present in castor beans and is prepared by grinding some of these beans with water and adding a per cent or so of the pulp thus obtained to a mixture of the fat and water. This treatment at best results in only about 85 per cent hydrolysis, owing to the retarding action of the glycerine formed. Although acids produced in this way have a fairly good color, the low degree of hydrolysis and the troublesome and wasteful separation of the emulsified pulp and oil have prevented this process from becoming used extensively.

The Twitchell Process for Hydrolysis—Another process [2] aiming to avoid superatmospheric pressures, and temperatures above the atmospheric boiling point of water, known as the Twitchell process, comprises boiling the fat and water at atmospheric pressure with a small amount of dilute sulfuric acid and an aromatic sulfonic acid emulsifying agent which is appreciably soluble in water and mineral acid, and even more soluble in fatty acids, though less soluble in the original fats and oils. Thus, as boiling continues and the reaction proceeds with the formation of a considerable proportion of free fatty acids, the emulsifying agent, or catalyzer, becomes more soluble in the fatty layer. After ten or twelve hours' boiling, the reaction, which is quite rapid at the start, gradually slows down as equilibrium is approached, with an increase in the concentration of the glycerine. The aqueous layer, after settling, may be removed and treated with lime for neutralization and removal of sulfuric acid and may be further treated for recovery of glycerine, while the fatty layer, now containing much of the catalyzer, may be boiled with fresh water, preferably with the addition of a little fresh catalyzer, and the boiling may be continued until the hydrolysis again slows down as the reaction approaches a new equilibrium point. In this way a degree of hydrolysis equaling or even exceeding 95 per cent may be realized with continued treatment. This process has been employed on an extensive scale both in America and in many foreign countries, and is still in use.

High Temperature-High Pressure Methods—It has long been known that when fats and liquid water are heated under pressure, either with or without catalyzers, the rate of hydrolysis may be considerably increased. Early work showed that if fat and water are contacted concurrently under pressure at fairly high temperatures, there is a considerable degree of hydrolysis.[3] In the

[1] Connstein, Seifenseider Ztg. 33, 198-200 (1906); Chemisches Zentralblatt I, 1679 (1906).
[2] Twitchell, U. S. Patents 601,603; 628,503; 1,170,468.
[3] Tilghman, U. S. Patent 11,766 (1854).

same way, fat and water heated to comparatively high temperatures under pressure in an autoclave have been found to result in a substantial degree of hydrolysis. Both of these treatments either result in, or approach, an equilibrium, beyond which they cannot be made to go without the removal[4] of the free glycerine formed. With the removal of the glycerine water and the further treatment with fresh water the hydrolysis can be carried further, again approaching the equilibrium point.

Countercurrent Liquid-Liquid Extraction—It has since been found that when fat and water, both in liquid phases, are heated in contact with each other to temperatures exceeding about 200° C. a considerable percentage of water actually becomes dissolved[5] in the fatty matter and that the proportion of water thus dissolved increases rapidly, causing an increase of the fatty layer and a diminution of the aqueous layer. At about 287° C., when cocoanut oil is used, the aqueous phase merges into the fatty phase, leaving but a single liquid phase.[5, 6] Other fatty acids dissolve water to very considerable, though varying, degrees.

This phenomenon of partial mutual solubility of fats and water makes it possible to devise a continuous countercurrent extraction system[5, 7, 8] which has many advantages for the hydrolysis of fats. If the apparatus is operated at temperatures and pressures where the two components show considerable mutual solubility but below temperatures when there is only one liquid phase, the glycerine which is formed can be continuously removed in the water stream. At the same time the resulting fatty acids in the non-aqueous phase can be removed in a separate stream. In this way substantially complete hydrolysis may be economically obtained without the use of a catalyzer. This type of countercurrent hydrolysis is already in extensive commercial use and bids fair to replace most other types, and even to revolutionize some of the older soap-making methods.

ANIMAL FATS

Beef Tallow—Perhaps the most important fat for soap-making purposes, if not for all purposes, is beef tallow. The best grades of tallow are obtained from suet and other fatty matter trimmed from fresh beef and rendered therefrom by melting at moderate temperatures above the melting point of the fat. Edible tallow is made in this way from carefully selected cuttings, and other grades of tallow, differing but slightly from one another, are also made whereby practically all available fatty matter is recovered for use. The better grades of tallow are nearly white when solid and have a light yellow color when melted and have an agreeable odor and contain only about one or two per cent of free fatty acids, whereas other grades have somewhat more color and somewhat more odor and may run up to as high as, or even higher than, 10 per cent free fatty acids for some of the poorer, darker grades.

Tallow is also obtained from some animals other than beef, notably from sheep. Mutton tallow is produced on a large scale. It makes soaps quite similar

[4] Tilghman, U. S. Patent 28,315.
[5] Ittner, U. S. Patent 2,139,589.
[6] Ittner, U. S. Patent 2,221,799.
[7] Mills, Can. Patent 365,544.
[8] For a discussion of the principles of liquid-liquid extraction, see Chapter 2.

in most respects to those made from beef tallow, the one important difference being that the soaps derived from mutton tallow are prone to have some objectionable odor which is apt to increase rather than diminish with age.

Lard—Lard, derived from hogs, is a fat of paramount economic importance. It is used on a tremendous scale as a food, in cooking, and as the quantity produced fluctuates, the surplus over that demanded for food finds a ready outlet in the soap kettle. Lower grades of fat derived from hogs are also recovered and come onto the market as "hog fat" or "hog grease."

Greases—The term "grease" is applied to fatty matters of mixed origin and to lower grades of fat even though they are derived mainly from one source. Very commonly a modifying adjective is used in the names of greases which tells the source of the grease; for instance, *garbage grease, house grease* or *kitchen grease, hotel grease, wool grease,* etc. Greases are generally darker in color, and possess more odor, and have a higher percentage of free fatty acids than other fats and for this reason usually undergo some preliminary decolorizing, deodorizing treatment such as bleaching, or hydrolysis and distillation of the fatty acids thus formed. In some cases the better greases may be used directly in lower grades of soap, with the employment of suitable lye washes to remove impurities and to lighten the soap.

PLANT SOURCES

Cocoanut Oil—Cocoanut oil is one of the most important soap-making materials. It is pressed or extracted from dried meats of the cocoanut, which yield about 60 per cent oil. This oil is not produced in the United States from home-grown cocoanuts but comes from tropical countries, chiefly from the Philippines. The production and consumption of this oil reached colossal proportions until a heavy tax was imposed upon it. Since then it has been used somewhat more sparingly but still in enormous quantities.

Cocoanut oil and a few other similar oils, including palm kernel and cohune nut oils, are unique among fatty oils in some of their properties. The average molecular weight of their fatty acids is appoximately 25 per cent lower than the average molecular weight of the acids from many of the other common soap-making materials and, for this reason, cocoanut oil soap is appreciably more soluble in cool or lukewarm water than most other soaps. It is not a good material to be used exclusively in soap for most purposes. On the other hand, it is an exceptionally good material to be used in conjunction with other fats and oils, as it imparts freer lathering qualities to soaps, thus giving more general satisfaction in the use both of toilet and of household soaps.

Palm Oil—Palm oil is derived from the pulpy matter of the fruit surrounding palm kernels. The palm fruit occurs in large bunches on certain palm trees that grow most luxuriantly in Africa, in the countries along the Gulf of Guinea and in the islands of the East Indies. The oil, if carefully extracted, is liquid at ordinary temperatures and possesses a deep yellowish red color and an agreeable odor. If saponified as received, it gives a very yellow soap that gives a yellow lather. Hence it is necessary to bleach the oil before making it into soaps. Palm oil is undoubtedly one of the finest soap-making materials to be found anywhere.

Olive Oil—Olive oil is produced mainly for food purpcses but certain grades of it develop more free fatty acids, more color, or more odor than is tolerated in edible oils, and these find their way to the soap kettle. It is a very good soap material. Formerly, olive oil soap was designated as *Castile* soap and this name applied only to pure olive oil soap. However, in later years soaps have been called "Castile," with or without some modifying adjective, even though they contained little or no olive oil soap. Olive oil, extracted by means of carbon bisulfide from the green olive pulp after expressing all possible oil, is green in color from the chlorophyll and is variously known as "olive oil foots," "green olive oil," and "sulfur olive oil." It is produced in large quantities and is used extensively in soap-making. Soap made from it has substantially similar properties to those made from the more expensive grades of olive oil.

Cottonseed Oil—Cottonseed oil is now used mainly for food purposes. It was formerly used extensively, blended with harder fats, in certain household soaps, notably in yellow laundry soaps. It is obtained on a large scale by cooking and pressing de-linted cotton seeds. The crude oil thus obtained is very dark brown in color and has a rather strong, characteristic odor. It is refined by stirring with dilute caustic soda solution containing 10 per cent, more or less, caustic and at a temperature of about 100° F. or a little above. In this way the caustic alkali unites with all the free fatty acids present, making a very crude, dark colored soap. To get good results the alkali must be used in slight excess. Agitation may be mechanical, or by means of air. Emulsifying influences like jet steam or pure water must be absent as they prevent a sharp separation of the refined oil from the soapy residue. After the oil and alkali have been thoroughly contacted by stirring, slight heat is indirectly applied until the soapy residue segregates into well defined flocks leaving a clear golden yellow oil surrounding them. The agitation is then stopped and the soapy residue known as "cottonseed foots" is allowed to settle, leaving a clear yellow oil above. When prime crude is used the oil thus obtained is known as "prime summer yellow" cottonseed oil. This is a grade of oil that has been used in household soaps when prices permitted.

Cottonseed foots obtained as described above and containing most of the coloring matter originally present in the crude oil are produced extensively and are used, after subjection to soap-making purification processes, in many cheap household soaps and particularly in soap powders mixed with sodium carbonate for coarse laundry work and many kinds of general cleaning.

Miscellaneous Oils—Soy bean oil was formerly imported very extensively from Manchuria. It makes a soap too soft for most purposes but when hardened by chemical treatment it makes good soap.

Corn oil like soy bean oil makes soap too soft for most uses.

Linseed oil, because of its high content of unsaturated acids, makes a very soft, almost liquid soap.

Menhaden oil obtained from certain fishes is very similar in its soap-making properties to linseed oil but, in common with all marine animal oils, it produces soaps with a very objectionable fishy odor which, though bad at the start, gets even worse with age.

Whale oil derived principally from blubber is at times produced on a large scale. It is used extensively in certain cooking preparations, particularly after being subjected to some hydrogenation. This same treatment makes it quite suitable for use in some soaps.

There is a very large number of other fats and fatty oils produced more or less regularly in different parts of the world, but in smaller quantities than most of the oils referred to above, which have interest to the soap-maker when and as they become available.

Rosin—Another important soap material must be mentioned here which, though neither a fat nor a fatty acid, behaves nevertheless much like a fatty acid. This is rosin, the common resin obtained from the gum of pine trees.[9] It is also procured extensively from the stumps of pine trees, remaining as a result of lumbering operations, by extracting the chips from these with gasoline and subjecting the solution thus obtained to suitable purification processes. The rosin so obtained is known as "wood rosin" to distinguish from the "gum rosin" obtained in the old, well-known way. A carefully prepared grade of wood rosin is as good for many purposes as the corresponding grade of gum rosin, and is generally better than the darker grades of gum rosin. Rosin consists chiefly of abietic acid which, when combined with alkali, gives a valuable cleansing body very closely allied to regular soaps in its properties. Rosin soap softens water and forms abundant suds with efficient cleansing qualities. Even in cold water it is readily soluble to a sufficient extent to form suds. For this reason the use of a certain amount of rosin in household soaps makes them more generally acceptable than if they were made without the use of rosin. Such soaps are yellow to golden yellow in color, though they give white suds. White household soaps cannot be made with rosin and for this reason they must be made with a fairly high content of cocoanut oil soap to provide free sudsing qualities comparable to those imparted to yellow household soaps by their rosin soap content.

HANDLING AND TREATMENT OF FATS

Handling—The large modern soap factory consumes many thousands of tons of fats in the course of a year. Most of this material is brought in in tank cars or in casks or tierces. Factories located on tidewater have the additional advantage of receiving foreign oils in ships' tanks. Tank cars and ships' tanks are connected to pipe lines and the contents pumped to storage tanks. Tanks used to transport or to store solid fats are provided with steam coils so the contents may be melted for pumping.

Casks and tierces are emptied in a melting room or "steamer." This is a room with a number of long sloping troughs about one foot wide set in the floor. At intervals of about three feet there are short steam pipes provided with swinging elbows. The casks or tierces are rolled into the melting room, the bungs knocked out and bungholes turned down over the troughs, and a steam pipe inserted into each cask. The room is then closed and live steam turned on until all the fat has been melted and run out and until each cask has been steamed free from fat. The melted fat runs along the troughs to tanks from which it is pumped to settling tanks. The melted, settled fat is separated from the water and removed to storage tanks which are provided with closed steam coils. All tanks should be equipped with carefully graduated gages and floats, to measure contents or amounts added to or taken from the tanks. It is an excellent prac-

[9] For a discussion of rosin production, see Chapter 17.

tice to have large weigh-tanks to check the movements of stock through the factory. It is always important to use every precaution to see that no water is pumped with the fat, for unless this is done grave errors may be made either with gages or weigh-tanks. In pumping fats, oils, or soaps it is always important to blow steam through all the pipes and the pump before beginning to pump. This is done for two reasons, to heat the line and prevent chilling or clogging, and to clean out other material. After pumping, the line should be blown out at once. Sometimes the bulk of the contents is blown out with compressed air to avoid getting water into it, but it is always best to end up with a thorough blowing with steam to leave the line clear and clean. It is not necessary to blow this steam into the oil tanks. Valves may be closed at the ends of the line, a by-pass opened and steam blown through and the cleansings blown into a blowout tank or some soap pan. Much of the material after steaming out and settling from water is ready for soap-making. This is stored in tanks until pumped to the soap pans.

Treatment—Some of the soap fats are not in a condition suitable for pumping direct to the soap pans but must go through some special treatment to remove color or other impurities. There is no set treatment that is best and applicable to all fats or oils. Each lot should be given preliminary laboratory tests which serve as a diagnosis, and determine the factory treatment.

Palm oil, for example, often contains some moisture and a small amount of sticks, fiber, and earth, especially the grades that come from West Africa. It also has a deep yellowish red color. Steaming and settling will remove the dirt. The oil is then subjected to bleaching. This is usually an oxidation treatment which destroys the color. Two of these are in vogue, dichromate and acid, and air blowing. The first is probably the better, though the latter is the easier. For the dichromate bleach, the oil is heated gently to a temperature just above its melting point and agitated with air or preferably with a mechanical mixer with about 1 per cent of sodium dichromate and 2 or 3 per cent of hydrochloric acid. It is best to avoid too much heat and too rapid action at the start. After all the dichromate has been used up, as can be seen by the absence of any reddish appearance in the aqueous layer (which should now have a clear green color) hot water is added and, after thorough mixing, the oil is allowed to settle. Sulfuric acid is sometimes used in place of hydrochloric, but it is slower acting, requires more patience, and has no compensating advantages.

For air bleaching it is quite important that the oil should be well settled, clean and dry. It is heated in a tank provided with a closed steam coil and a perforated coil for compressed air. Good oil bleaches readily; poor oil very slowly. A temperature somewhat above the boiling point of water is probably best though a lower temperature and longer blowing will answer. In this way a good oil may be bleached to a very light yellow color free from any of its original reddish coloring matter.

In all oxidizing bleaches of palm oil, especially in air bleaching, the oil itself undergoes some oxidation changes and the oxidation products thus formed cause the soap made from such bleached oils to take on a brownish hue which increases on aging.

It is well to know that the coloring matter contained in palm oil is destroyed at temperatures in the range of about 230° C. to 250° C., in the absence of air.

This change though rapid is not instantaneous. The countercurrent[5] hydrolysis treatment referred to above, which works very satisfactorily in this range of temperature, yields light colored fatty acids free from the original coloring matter when the raw material is a good grade of palm oil. The oil may also be heated to temperatures considerably above the boiling point of water in a closed vessel provided with a mechanical stirrer, with evacuation of air and agitation with about 3 to 5 per cent "activated" clay, which under these conditions absorbs the coloring matter. When the oil thus treated is reduced somewhat in temperature and filtered, a light colored oil is obtained that will yield a white soap.

Fuller's Earth. A very common bleaching treatment for fats and oils is agitation with fuller's earth at about 110° C. From 1 per cent to over 3 per cent of fuller's earth is used, as indicated by a preliminary laboratory test. After thorough agitation to obtain intimate contact between all parts of the fat and the earth and to allow time for absorption, the mixture is pumped to a filter press. The first filtrate is run back until a clear filtrate is obtained. When all the material has been pumped to the press, compressed air is turned on to drive as much of the last portions of fat as possible through the press. The discharge trough is now changed and live steam is driven through the press to steam out all the fat possible. The filter cake will contain approximately 20 per cent by weight of fat. This may be recovered by extraction with a volatile solvent.

Various fats behave differently with different natural bleaching earths and it is therefore advisable to test each fat with different earths to find the ones best suited to each. As a rule, earths that are well suited to the bleaching of cottonseed oil do not bleach animal fats at all well, and vice versa. This, and similar experience with other oils, leads to the conclusion that the coloring matters in vegetable oils on one hand, and in animal fats on the other are probably quite different, chemically. There are a number of efficient "activated earths" on the market. Their efficiency has generally been increased by treatment with strong acid and subsequent washing and drying.

Sulfuric Acid Treatment. Some greases yield to fuller's earth bleaching and some to dichromate treatment, while some do not improve with either treatment. Certain greases may be helped by heating them just above the melting point and mixing intimately therewith about 1 per cent 60° Bé. sulfuric acid. The mixture should be watched carefully to avoid any over-action. Hot water and steam can now be applied and the diluted acid then allowed to settle. The grease is often fit for use after this treatment. Or it may only be changed to a condition so that it will yield to fuller's earth or other earth bleaching treatment. Certain fats are treated dry with activated earth in a closed vessel with agitation and heat under diminished pressure to exclude air. It has been found that the addition of a small amount of concentrated sulfuric acid works considerable improvement. The acid collects rapidly in the activated earth, thus increasing its activity, and is removed with the earth by filtration, without resorting to any washing with water.

Miscellaneous Treatment. Carbon blacks, either alone or with earth, sometimes work well on fats. Some fats are treated with hypochlorites. This is rather a drastic oxidizing treatment and fats so treated are apt to revert, therefore some manufacturers follow this oxidizing step with a strong reducing agent such as one of the hydrosulfites.

CLASSIFICATION OF SOAPS

There are different ways of classifying soaps, but it is perhaps best to divide them into toilet soaps, household soaps, and industrial soaps. Toilet soaps comprise hand soaps, bath soaps, transparent soaps. Household soaps comprise laundry bar soaps, and a host of different kinds of comminuted soaps, both pure and compound, in cartons. Industrial soaps are made in a wide variety of compositions and are marketed in many forms, as bars, chips, flakes, beads, with widely varying compositions.

Toilet soaps are made for washing the hands and face and for the bath and demand the choicest materials. They usually contain some cocoanut oil soap to add to the free lathering qualities, but too large a proportion of this ingredient is objectionable and is believed to be hard on the skin.

The commonest raw materials are tallow and cocoanut oil, used together. Olive, palm, and cocoanut oils mixed or separate are also used extensively. Transparent soaps are made from tallow and cocoanut oil or from tallow and rosin.

Shaving soaps are a special branch of toilet soaps. They are usually prepared from some kind of hard stock with the aid of potash lye. The potash adds to the free lathering qualities and to the lasting property of the lather, while the hard stocks give close lather.

Household soaps are made from a great variety of raw materials, the commonest of which are tallow, rosin, greases, palm oil, cocoanut oil, and other stocks that may be available on a large scale.

Industrial soaps include tallow chip soaps for laundries and large textile mills, green olive oil soap for silk washing and a variety of special soaps for special purposes.

It has long been customary to speak of soaps as *hard soaps* and *soft soaps* as synonymous with *soda soaps* and *potash soaps*. This classification is no longer a good one. Potash soaps are now of only minor importance. Most soaps are soda soaps and there are several classes of soda soaps, each more important than all potash soaps put together.

Potash soaps, other things being equal, are softer than soda soaps. However, some potash soaps are solid and hard, as for example those made from material with high titre and low iodine absorption. On the other hand, some soda soaps are soft and even liquid, notably those made from materials with high iodine absorption. Thus, soaps may derive more differences in their qualities from the kind of stock used than from the kind of alkali.

Formerly it was common belief that only potash soaps were suitable for the washing of certain fabrics, but now soda soaps are giving eminent satisfaction in many places where formerly nothing but potash soaps were used.

SOAP MANUFACTURE

Soap is made either by the saponification of fats and oils or by the direct neutralization of fatty acids. Those involving alkaline saponification are made either by *boiling* in a kettle or pan, or by the *half boiled*, or *cold process* by mixing the material in a "crutcher" and allowing the product to stand in frames

The boiling process is by far the most important and accounts for most of the soap made though it is probable that recent improvements [5, 6, 7] in the hydrolysis of fats and oils and in the purification of fatty acids by distillation [10, 11] will cause the manufacture of soap by direct neutralization of fatty acids to assume paramount importance in the not very distant future.

Boiling—Soap is boiled in "kettles" or "pans" which are large tanks provided with means for heating and for drawing off lyes and soap. Formerly soap was boiled by building a fire under the kettles, but now it is almost universal practice to provide the pans with both open and closed steam coils. Soap pans are of different shapes and sizes. Some are cylindrical with flat bottoms, others with conical bottoms, while some are square with flat bottoms and still others square with pyramidal bottoms. A good soap boiler can make good soap in any of them, if they are properly provided with open and closed steam for thorough boiling. A good shape of soap pan is a cylindrical tank about twice as deep as its diameter. There is a slight advantage in a conical bottom. There is a double advantage in large pans. They take less labor per unit of soap and give a better settle than small pans. Pans holding a million pounds of liquid that will give about half a million pounds of finished soap are in use in some factories. Large pans also lose less heat per pound of product. In any case a decided saving is effected by having pans insulated against heat losses.

In describing soap-making by the boiling process a definite procedure will be described, but it should be distinctly understood that the procedure is somewhat subject to modification both in order and detail as circumstances may demand, the main object in each case being to get a good finished product.

Saponification—The saponification or "killing" of the stock may be begun before all of the charge has been pumped to the pan and the process may be continued coincident with the rest of the pumping. The contents of the pan should be boiled up with open steam and kept in a good state of agitation and mixing at all times. At the same time caustic soda lye is run into the pan in such a way that it is rapidly emulsified in the charge by the boiling. Saponification starts at once and proceeds rapidly if a slight excess of unacted lye is always maintained and if the excess is never permitted to be sufficient to "grain" the soap already formed and break the smooth emulsion that promotes rapid saponification. Saponification proceeds most rapidly when only sufficient excess lye is present to keep the boiling mixture in a smooth, comparatively thin condition which promotes thorough mixing with the steam agitation. Even when the pan is so clouded with escaping steam that the soap can not be seen, the experienced soap boiler has no trouble in following the reaction by the sound of the splashing soap. The contents of the kettle should not be too thin nor should it be allowed to become thick and tough, indicated by a dull flopping noise like splashing mud. The first condition is due to too rapid addition of lye and the latter to insufficient lye. When the saponification is going well, the mass will be smooth and will turn over freely with the escaping steam with very little splashing. If a large excess of lye is permitted to accumulate saponification stops almost completely and may cause considerable delay. The free use of

[10] Gensecke, U. S. Patent 1,713,431.
[11] Ittner, U. S. Patents 2,202,007; 2,202,008.

open steam in this step greatly aids emulsification and saponification. On the other hand, a worse fault is to hold the lye back too long when the saponification is proceeding rapidly. This may cause a very troublesome thickening that sets in very rapidly and stops agitation so that steam must be turned off to prevent an explosive eruption when it finally breaks its way through the thickened mass. If this condition is ever arrived at through careless handling, all that can be done is to pump in some lye in excess and turn on the closed steam until the lye boils through and cuts the thickened soap.

Proper Concentration of Lye. The saponification is really a very easy change to carry through and it can be done with great rapidity so that it will be completed almost by the time the last fat has been pumped into the pan. Old-time soap boilers had their pet strengths of caustic soda. They often started with a very weak lye and gradually increased the strength of lye in several stages as the saponification proceeded. This is altogether unnecessary as stock can be saponified with lye of any strength from under 10° Bé. to lye of over 40° Bé. Weak lye will leave a very large amount of water in the soap pan after saponification, requiring more salt or "pickle" (brine) to salt out the soap, thus lessening the capacity of the pan and unduly diluting the glycerine lye, which, in turn, necessitates greater evaporation in the glycerine department. In any event, no matter what strength of lye is used, it is desirable to carry the change far enough to complete saponification, or closely approach complete saponification. This will necessitate at least some excess caustic soda and hard boiling, with open steam with such excess caustic soda, while the soap is together and smooth. The soap boiler will choose one of two procedures at this time. He may operate with only a slight excess of alkali so that the lye taken from the pan after killing will have very little free alkali and may be sent to the glycerine department directly, after little or no treatment for removal of such alkali; or he may intentionally add an appreciable excess of lye and depend on a later treatment with fresh stock or partly saponified stock for removal of excess alkali from the spent lye before sending to the glycerine department.

The soap boiler judges the completion of saponification by the smooth appearance of the free boiling soap and the fact that excess caustic lye is not used up by further boiling. This excess can be judged with considerable certainty by touching a small bit of the soap to the tongue. Caustic soda, even when present in small fractional percentage, gives a sharp characteristic "bite" when touched to the tongue. About a gram of the soap taken on the finger and pinched with the thumb until chilled, will now give a flaky shiny piece of soap which is a good guide to the practiced eye. It is unnecessary to apply chemical tests at this time.

Graining—Soap is almost completely insoluble in concentrated solutions of common salt or in concentrated caustic soda solution. This fact is used in the further treatments of the soap. The soap is grained with strong salt solution or by shoveling salt into the pan and boiling with aid of the closed steam coils, or in some circumstances by means of concentrated lye. The graining process consists in gradually increasing the salt content or caustic soda content of the soap mass until the soap becomes insoluble in the aqueous portion and separates therefrom in large curds. A pure tallow soap will be largely separated from a salt brine of about 8° Bé. and will separate thoroughly from a brine of about 10°-12° Bé., whereas soap containing much cocoanut oil may require 14°-16° Bé. or even greater concentration to separate well.

The glycerine formed during saponification, being more soluble in the lyes than in soap, is largely removed with the first lyes and brines, and all but a small portion may be removed with further "pickle washes." In some of these washes it is good to add some caustic soda, as this gives greater assurance of obtaining complete saponification before the soap is finished and also causes the lye to settle out better. Saponification and washes may be, and sometimes are, carried out in a series of countercurrent treatments that cause the glycerine concentration to increase and alkalinity to decrease as the lyes are passed from pan to pan before going to the glycerine department, thus minimizing the glycerine content in the finished soap, and appreciably lessening the amount of evaporation necessary for the recovery of glycerine.

Operation with Rosin—When rosin is used, it is usually introduced in one of the last changes after most of the glycerine has been removed, as it yields no glycerine and its early addition would unnecessarily increase the bulk of the soap to be washed. Rosin may be shoveled directly into the soap pan to which enough salt or pickle has been added to keep the soap open or grained. In that case enough alkali must be added to convert the rosin into soap. Or the rosin may be saponified in a separate pan with a solution of sodium carbonate. There is some advantage in this latter procedure, both because of the slight saving in cost of alkali (carbonate being cheaper than caustic) and also because of the opportunity it affords to separate the sticks and dirt that sometimes come in rosin. The rosin soap thus made may be pumped into the soap pan and the whole mass boiled thoroughly while in a grained or open condition until the rosin soap is thoroughly incorporated. The lye from the rosin change, if low in alkali and glycerine, may be run to the sewer.

Finishing Operations—The pan changes will be dictated largely by the demand for soap and the selling price of glycerine. With a high glycerine price an extra wash may be given, and with a demand for increased soap production a change may be omitted.

It is customary to give a *strengthening* change to insure complete saponification. This is done by boiling the soap with salt pickle and lye so the aqueous layer contains several per cent of caustic soda. The soap may be finished after removal of any of the lyes.

The last lye is drawn off as thoroughly as possible. Open steam is now turned on and water is gradually added. The soap curds left in the pan after removal of the last lye remain surrounded and wetted by the lye that had not dropped to the bottom of the pan and could not be removed. This lye becomes diluted by the addition of water until the solubility of soap therein becomes appreciable and the viscosity of the soap mass approaches a minimum. Great care should be observed not to add enough water to cause the soap phase and diluted lye phase to coalesce. A two-phase system should be maintained, giving at the end, a soap phase containing most of the soap with a small amount of dissolved alkali and a diluted-lye phase containing practically all the salt, alkali, and soluble impurities, together with only a small amount of dissolved soap.

Settling—When the soap is properly finished, it will slide clear and thin from a hot shovel or trowel and, if balanced on a hot shovel for a moment, will show slight surface cracks in the clear soapy liquor when the shovel is tipped, and will slide off slowly, leaving the shovel almost clean but without any visible trace of a watery lye in the soap or between the soap and shovel. When the soap has reached this stage after thorough boiling, the steam is turned off and the soap allowed to stand. The soap begins to separate into two sharp layers, the upper known as "settled soap" and the lower as "nigre." These layers would each be perfectly homogeneous except for outside influences, chief of which is cooling. The nigre that separates at first is boiling hot and very thin, but as it becomes cooler on standing, the solubility of soap in this diluted lye phase is lessened, with the result that after several days' standing and cooling a lye layer develops under the nigre which contains less dissolved soap at the lower temperature.

The settled material (upper layer) consists of a very pure soap containing only about one-tenth per cent free alkali and one or two tenths per cent salt. During the settling most of the insoluble impurities will have dropped to the bottom of the pan beneath the nigre. The settled soap will contain about 30 per cent water, the amount varying somewhat with the kind of stock used. There will be about 34 per cent in a pure tallow soap and around 30 per cent in a tallow-rosin or tallow-cocoanut oil soap. The time of settling varies with the size of the pan. It may be completed in one day in a small pan and require a week or more in a very large pan.

The settled soap is now pumped from the pan through a swing pipe that may be raised or lowered to skim the upper layer as thoroughly as possible from the nigre without drawing any of the latter with it. If the boil has been prepared for making toilet soap, it is pumped to a jacketed tank in the toilet soap department where it is kept hot and liquid until used, and if it is to be made into household soap it is pumped to a framing department.

FINISHING THE SOAP

There are many ways of finishing soaps from the preliminary stages of manufacture to the final salable products and a few of the more important ones which account for the bulk of the product will be described at this time. Hot molten soap made by the settled soap process, or otherwise, may be run in pure condition into frames and allowed to cool and solidify, or it may be mixed with certain materials which themselves possess some detergent or water-softening properties. Chief among these are sodium carbonate, sodium silicate, and certain sodium phosphates.

Fillers—The demand for pure settled soap for household use is very small in this country. Soaps containing sodium silicate and sodium carbonate constitute the greatest percentage of those for household use. These "filling" mixtures are inexpensive, so soaps containing them can be, and are, sold for much less than the price of pure soap; yet give more actual washing value for the money than the more expensive pure soap. The advantage of silicated soaps is more pronounced with hard water, though they also work well in soft water. Since much of the natural water of the country is at least moderately hard, they have widespread use.

Mixing—The fluid soap is pumped to a tank above the mixing machines or "crutchers" and is run in, in measured or weighed amounts, with definite amounts of the filling mixture and the whole is agitated until it becomes uniform. Two general types of crutchers are used: one with a vertical helical screw working in the central part to produce a circulation of the soap mass, and the other with a horizontal shaft provided with numerous short arms, pitched at an angle, revolving in a horizontal cylindrical shell. In either type, the machine must be kept full or considerable air will be incorporated into the soap. It is also possible to flow the molten soap and filling materials together in desired proportions and to effect their thorough mixing, either continuously or intermittently. There is an optimum framing temperature for each different soap which will give best results. This is very commonly in the neighborhood of 140° F.

Framing—It is very common practice to add some perfume to soaps, even to many laundry soaps, to impart a certain attractiveness and also because perfuming materials exert a preservative quality in soaps. The mixed soap is run out of the crutcher into frames, which are large molds that hold half a ton or more of soap. The sides of the frames are removable and when the soap has chilled to a solid block it is stripped and is ready for cutting into bars. The soap is ready for stripping in three or four days after framing, and for cutting in about five days after framing.

Cutting and Drying—Most household soaps sold in bar or cake form are cut from large blocks of soap. This work is done by machinery. The stripped block of soap, riding on a wheeled bottom, is pushed into a slabbing machine which operates by drawing a set of taut steel wires horizontally through the soap in order to cut it into slabs of equal thickness, usually nearly equal to the thickness of the cakes or bars that are to be made. The slabs are then put through a power cutting machine in such a way that the slab moving lengthwise is first ripped by taut wires into three or four bars that are as long as the slab and have a width nearly equal to the length of the finished cakes that are to be made. The partly cut slab is now pushed by a lateral motion through another cutting head holding many wires that cut the soap finally into pieces the size of the finished cakes or bars.

The soap is forced through these wires by two sets of pushing wooden "fingers." The fingers are alternately long and short with a difference in length equal to the width of the slab of soap. The shorter fingers thus push every other set of cakes through the wires on to a movable drying rack while the longer fingers push the alternate sets of cakes further so that they land on a second rack. In this way the cakes are spread so their surfaces are exposed to the air for drying. The racks, piled on a large wheel bottom that will hold several tiers of racks, are now passed through a drying room provided with means for circulating warm dry air. The object of this drying is to cause the formation by partial drying of a tough, non-sticky "skin" that will aid greatly in the pressing of the soap, yielding a good firm cake. Further drying in this way is entirely impractical where great production must be maintained, as loss of water in drying bar soap after the first 24 hours is exceedingly slow.

After passing through the drying room the soap is fed to automatic presses which stamp it with name and design and from the presses it passes directly to automatic wrapping machines and then to boxes and conveyors that take it away for storage or shipment.

Handling the Scrap—In all soap-making processes some scrap is formed. Other portions of the soap become soiled so they are not fit to make directly into finished soap. Scrap that becomes contaminated with dirt, or scrapings from floors and frame bottoms, requires separate treatment for removal of the dirt. This may even involve working over in a soap pan by itself with lye and pickle washes. In cutting soap a certain amount of scrap is always formed which, if kept clean, can generally be worked over into the same kind of soap by simple remelting.

Nigre Soap—The soap that goes into the nigre layer is not as good as that which constitutes the upper, or settled layer. The nigre soap resembles the higher quality material in a general way but it collects a somewhat larger percentage of the more soluble and the oxyacid soaps, as well as most of the dirt and mineral impurities that find their way into the pan. The nigre also tests rather high in salt and alkali, as it is really a diluted lye containing dissolved soap. After the good settled soap has been removed for framing, the nigre left in the soap pan is grained with salt and the grained nigre may be used over in the same kind of soap. Preferably, especially in the case of high grade soaps, it is sent to a pan in which a somewhat lower grade of soap is being made. It can be added to the pan at any time, but most advantageously in one of the last changes.

OTHER PROCESSES OF SOAP MANUFACTURE

Direct Neutralization—Reference has been made to the manufacture of soap by the direct neutralization of fatty acids with alkalies. This has long been recognized as a desideratum among the more progressive soap-makers, and now with the advent of satisfactory and economical countercurrent hydrolysis of fats with water to fatty acids and fairly concentrated aqueous glycerine solution, it is highly probable that this method of soap manufacture will gradually crowd out most other methods. Fatty acids obtained from good stock and countercurrent hydrolysis are suitable for immediate use for soap-making by direct neutralization for many soaps. When dark fats are the starting materials, and when very light colors are desired in the finished product, the fatty acids may be subjected to steam distillation [10, 11] under reduced pressure, under conditions which induce substantially no polymerization or tar formation. It is now easy to distill fatty acids at pressures below 10 mm. mercury, the temperature being below those which produce any substantial or harmful effect on the acids.

Fatty acids can be neutralized to soap both with caustic soda, and with sodium carbonate. The former of these reagents works more smoothly and has the advantage of acting on and saponifying any small amount of glyceride that may have escaped complete hydrolysis. The neutralization with sodium carbonate loosens a large volume of carbon dioxide gas which must be eliminated to attain complete neutralization. Generally, after the gas is removed, a final addition of a few per cent of the required alkali, as caustic soda, is resorted to, to assure complete neutralization and saponification. The fatty acids and alkali solution in controlled, chemically equivalent amounts may be run together into a common system provided with efficient mixing. When caustic soda is the alkali employed, the reaction is smooth and rapid. When it is carried out above the melting point of the resulting soap the product is sufficiently fluid to be propelled through a conduit to any desired place and to any suitable type of finishing apparatus.

Cold Process—In former times, when most of the soap on the market was made in a large number of small factories, a considerable proportion of soap was made by the "cold process," or "half-boiled process." A small amount of soap is still made in this way. The cold process works most advantageously with high-grade fats with low fatty acid content. Since the process effects no cleansing of the soap, as does the boiling process, it is really necessary to begin with good materials. The soap-maker weighs out a certain amount of fat or oil, heated to just above its melting point, and crutches into it a weighed amount of caustic soda lye containing just about the right amount of alkali necessary to combine with the fat to make soap. Caustic soda lyes ranging from 30° Bé. to over 40° Bé. may be used, but for most purposes a lye testing about 35° to 36° Bé. will be found to work well.

The melted fat and cold lye are mixed in a crutcher for a short time, until a very smooth emulsion is formed. This becomes milky in appearance and thickens until it is about the consistency of moderately heavy syrup; then the mixture is poured into a frame and allowed to stand at ordinary temperatures for a few days. The saponification reaction sets in rather quickly on standing. The heat of the exothermic reaction raises the temperature of the mass, which greatly increases the rate of saponification. If the fat used contains too high a content of free fatty acids this chemical heating may be so rapid in the early stages of the process that it causes a partial and undesirable separation of soap and lye in the frame. Even when it is well made, soap produced by this process contains all the impurities that may have been present in the fat and oil and it often contains a small amount of both uncombined fat and alkali. However, cold made soaps have a very fine texture, which gives them a good appearance. For this reason, this process is still used to some extent in making cheap toilet soaps.

Half-Boiled Soaps—The half-boiled process does not differ greatly from the cold process, except that the saponification is completed or nearly completed in the crutcher, with the aid of heat. Fatty acids are sometimes used in making half-boiled soaps and when this is the case some or most of the glycerine may be recovered.

Dry Saponification—Although the settled soap process, which has been described in considerable detail, is still the most important one in present-day soap manufacture, it is being partially replaced by newer developments. The direct countercurrent hydrolysis of fats, followed by saponification of the fatty acids (see pp. 1539-41), is becoming increasingly important. A still newer process[12] which is coming into use may be described as "dry saponification."

In this process, dry fats, dry soda ash, and dry, superheated steam are employed to produce anhydrous soap and concentrated glycerine. At temperatures above 235° C. fats when intimately contacted with superheated steam hydrolyze to a considerable degree. If, at the same time, they are brought into contact with caustic soda, or, even more advantageously, soda ash, soap is rapidly formed and glycerine is set free. Anhydrous soap thus formed melts to a thin liquid at about 290° C. to over 300° C. which does not suffer any substantial degree of injury if

[12] Ittner, U. S. Patent 1,918,603.

air is excluded and if it is agitated to prevent local overheating. The saponification[12] by this process is very rapid and, if the soap is always maintained in a thin liquid condition and agitated with steam, the glycerine which is formed, distills off almost as fast as it is produced and may be collected without suffering decomposition. The process may be carried out at atmospheric pressure, but under reduced pressure with steam agitation the glycerine passes over somewhat more rapidly.

Soap made by this process is practically odorless, and when used with oils which ordinarily give soft soaps, the process yields, in contrast, soaps which are generally quite firm and possessed of good keeping qualities, and generally improved lathering properties. The process gives good soaps from fish oils.

Soap from Petroleum—The soaps so far referred to are all made from natural fats and fatty oils. It is generally known in the chemical world that petroleum oils are made up almost exclusively of various hydrocarbons. These are stable neutral bodies and are not acted upon by alkalies to make soap. There has long been a desire among chemists and others to be able to change petroleum so as to make real soap out of it. This can be done and has been done.[13] However, the commercial success of any process to accomplish this result is dependent upon the price of natural fats, the prices of certain petroleum products, and various other economic influences, and it seems improbable that any considerable amount of soap from this source will come onto the open market in the near future.

No matter what method is employed for this purpose the petroleum hydrocarbons must be changed to acids and salts of acids. This may be done in several ways but the simplest and cheapest method is to heat the hydrocarbon and oxidize with air. It is surprising how readily this oxidation may be brought about. Unfortunately, this oxidation is not a simple chemical reaction such as the conversion of a $-CH_3$ group into an acid group such as $-COOH$. It is more complex and far reaching and it is probable that it is preceded by some type of thermal cracking. After the cracking has taken place, various parts of the molecule undergo oxidation, a variety of acidic compounds such as true fatty acids, hydroxy acids, lactones, a small amount of phenols, and some alcoholic bodies are formed. The oxidation step causes an increase in weight of about 10 per cent. The product formed is reasonably good in color but has a slightly disagreeable odor. However, when the acids are neutralized and made into soap, the product is very dark brown. It lathers poorly, and has a most persistent, objectionable odor which is not improved by any of the ordinary soap-making processes. The fatty acids may be distilled and improved in color but when the redistilled acids are made into soap the product is still very dark and has a very objectionable odor.

It has been found that under certain treatment the soap from these acids undergoes a simple chemical change which greatly improves its character. If the soap, either by itself or mixed with soap from natural fats, is heated with agitation[13] in contact with steam and in the absence of air to about 300°-325° C. and is at the same time subjected to distillation, preferably under diminished pressure, most of the unoxidized and unsaponifiable and unsaponified matter will

[13] Ittner, U. S. Patent 1,951,511.

distill off, leaving a soap which has but very little odor. At the same time the oxyacid soaps formed by the saponification of the lactones (which may amount to about 40 per cent of the acids) lose their alcoholic hydroxy group and give good lathering soaps which, on acidification, no longer form lactones. The acids thus formed may be improved by distillation and may be made into soap which, given a second heat treatment as described above, is reasonably free from most of the faults of the soap from freshly oxidized acids. Such soap may then be satisfactory for many purposes.

MISCELLANEOUS SOAP PRODUCTS

Soap Powder—The term "soap powder" as used in this country is applied to powders that contain some soap and a considerable amount of soda ash, which not infrequently exceeds the actual soap content. These powders were formerly made by agitating a mixture of hot liquid soap and dry soda ash in a powerful mill. The resulting powder contained from 10 to 20 per cent of water, depending on the ratio of soap and soda ash used. As soon as the powder became cold it set to a hard mass. It was reduced to powder by some type of disintegrating machinery, preferably one that did not resolve it all to fine dust. When this type of soap powder was put into cold or lukewarm water it would set, almost instantly, to a hard mass that dissolved only after much stirring and loss of time and patience. This was because the amount of water present in the powder was far short of that needed to supply the ten molecules of water of crystallization to convert the soda into sal soda. For this reason when these powders were dropped into water they passed almost immediately into a hard cake cemented together by the formation of sal soda.

It was found that the incorporation of more water, by the addition of sufficient water to bring about the formation of $Na_2CO_3 \cdot 10H_2O$ with the greater part of the soda ash used, gave a powder that dissolved rapidly without caking with a small amount of stirring. These powders contain about 35 to 40 per cent water and are more satisfactory to use than dryer powders. To facilitate disintegration to powder and solution in use, the mixture of soap, soda ash and water is crutched until greatly fluffed in volume, thus producing a bulky, fluffy product. When fluffy, hydrated soap powders were first introduced the consumer at once recognized the advantage of powders that dissolved quickly and easily, and the manufacturer liked them because they were cheaper and easier to make, and these powders now constitute the bulk of soap powders on the market.

The mixture of soap, soda ash and water may be run into frames until solidified or may be run over chilling rolls. In either case, when the crystallization of the soda has taken place, the mass may be disintegrated. The mills best suited for this purpose bring about forced screening with very little extra grinding. Soap powder is also produced by spraying the soap mixture under conditions that facilitate solidification and some drying.

Chips—The soap finishing processes thus far referred to have dealt principally with laundry bar soaps and soap powders. Both in commercial laundries and in the home, for washing machines and for dishwashing, soaps partly dried and reduced to chip or flake form by passing through powerful rolls are in great demand. Chip soaps for commercial laundries are usually made from tallow, whereas those for use in the home usually contain both tallow and cocoanut oil. These soaps are sold both with and without a content of water-softening "fillers."

Beads—It has been found that soap blown through spray nozzles in drying towers assumes a form that dissolves much more rapidly than chip soaps, and when the conditions for spraying are controlled to give small beads of soap, which are small spherical shells of dry soap, a form is obtained that dissolves with extreme rapidity; almost instantly if the water is slightly warm. Sprayed soaps have become very popular for home use both for dishwashing and laundering.

Final Preparation of Toilet Soaps—The soap-making part of toilet soap manufacture is substantially the same as is used in making soaps for household use except that great care should be exercised in the selection of high grade, clean oils and fats. Although good beef tallow is perhaps the most commonly used fat, it is probably safe to say that there is no very successful toilet soap that is made from animal fats alone. This is because soaps made from animal fats which would be suitable for toilet soap-making do not lather at all readily in cold or lukewarm water. For this reason practically all toilet soaps contain some free lathering vegetable oil soap. Toilet soaps made from tallow generally contain cocoanut oil soap to cause them to lather better in cold water.

The hot, liquid, settled soap which is to be used as a toilet soap base, is pumped to a steam-jacketed tank in the toilet soap department, where it is kept hot and liquid until used. This soap should be made so that it contains very little excess alkali. When proper care is used, the free alkali need not be over one-tenth of one per cent and the content of salt and other impurities will also be low. The settled soap base when made contains about 30 per cent water but it is customary to dry most of this out before working it up into toilet soap. The old way of doing this was to allow the soap to chill and solidify, to cut it into bars which were then cut into chips, and to dry the chips in the air or in a dry room after spreading on trays. This method of drying has been almost entirely displaced by a system of continuous drying.

Drying—In making toilet soap by the boiling process it is now customary to avoid framing and to dry the soap by some rapid continuous process which saves both time and labor and gives a more uniform product. One such method is to run the hot liquid soap from a storage tank to a hopper feeding on to some hollow metal rolls that are chilled by circulating cold water through them. Each roll runs next to another that revolves at a slightly higher speed. A soap film attaches to the first roll and passes in turn to each successively faster roll and thus becomes chilled to solid soap by the time it leaves the third or fourth roll. It is cut from the last roll in ribbon form by a knife that presents two rows of narrow chisel-like edges to the roll. Means are provided for collecting these soap ribbons and carrying them through a drying chamber through which hot dry air is rapidly circulated by powerful fans. One means for accomplishing this is to permit the soap ribbons to fall on a continuous wire belt, which in turn drops them to another belt carrying them back through another portion of the drying chamber. In a short time the soap emerges, dried to any desired degree. For making into toilet soap it is usually dried to about 10 per cent water content.

Another method of drying soap, which has considerable vogue, is to run the hot molten soap into a trough extending horizontally along an element of a large hollow steam heated cylinder, provision being made for distributing the soap in a thin even film on the cylinder as it slowly revolves. In this way the soap loses water rapidly and the film of dry or partly dried soap is cut from the roll by a blade after it has been carried around on the roll nearly to the starting point. By regulating the thickness of the film and the speed of the roll the soap may be dried to the desired extent.

Mixing—A weighed charge of dried soap is put into a mechanical mixing machine not unlike those used for mixing bread dough and the perfume and any color that may be used are added and distributed through the mass. It is then dumped into the hopper of a soap mill which consists of a series of heavy granite or steel rolls running close to one another at different speeds. In passing between the rolls it is not only squeezed but is also stretched by the action caused by the speed differential and adheres to the faster revolving roll from which it is taken in turn, and in the same way, by a still faster roll. In this way it is worked together intimately and finally becomes smooth and homogeneous.

Forming and Packing—The well-milled ribbons of perfumed soap are fed into a powerful continuous compressor called a plodder that works it, by a slowly revolving heavy screw, into a solid mass that flows through the machine under great pressure. The mouth of the plodder is fitted with a nozzle through which the soap is squeezed into a long, smooth homogeneous bar. In the ordinary screw plodder most of the air between the soap ribbons is gradually forced backward as the soap becomes compacted by pressure in its advance, but a small amount of air remains in the soap, broken up into tiny layers that are normally invisible to the eye. These are apt to cause "blistering" of the cakes at a later time and thus cause an unsightly appearance. Plodders are now built so that they are evacuated in such a way as to effectively prevent pocketing of air, giving a soap with a smoother, better texture.

The bars emerging from the plodders are cut into small blocks of soap of the desired weight and are then pressed in suitable dies into finished cakes of toilet soap. Automatic presses are now used extensively for this work and the various operations are more or less synchronized and made almost entirely mechanical. Even the wrapping of toilet soap has become largely a machine operation.

Floating Soaps—Floating soaps are made by crutching air into fluid soap until the amount of air incorporated increases the volume to such an extent that the solid soap has a density less than that of water. The crutching is performed while the soap is fluid. Ordinarily such soap is not subjected to any subsequent drying; so at the time that it is made it contains about the same amount of water as when crutched. This is normally about 30 per cent water, or a little less, but may be appreciably less if a higher temperature is employed for crutching the dryer soap. The amount of water in floating soaps is normally considerably more than that contained in milled toilet soaps which commonly contain about 10 per cent water.

Soaps Containing Abrasives—For special cleansing, where a more drastic action is required than is furnished by soap suds, certain abrasives are employed in conjunction with soap. These special soaps are manufactured both in cake form and in powders, the latter being by far the most popular. For this purpose various finely powdered abrasives have been employed, chief among which should be mentioned powdered quartz or silex, feldspar, and volcanic ash or "pumice," Volcanic ash is more effective as a cleanser and is extensively used. It is less drastic and scratchy than silex, which is appreciably cheaper. The soap content in these powdered cleansers is generally low.

SPECIAL DETERGENTS AND WETTING AGENTS

Thus far we have considered real soaps and materials and means for making them. It has been found that, for some of the uses to which soaps have been applied, other bodies possessing some of the qualities of soaps, though themselves actually not soaps, are equal to or even superior to real soap. One of these special uses is the even impregnation of fibers preliminary to or during dyeing.[14] Soap has served satisfactorily for this purpose in many alkaline dye baths. In such cases the fibers are "wet out" so that the dye might be absorbed quickly and evenly by all the fibers. On the other hand, some dyes are injured by an alkaline bath or will not work well in such a bath, and some fibers, wool, for example, dye best in an acid bath. Soap would be decomposed by an acid dye bath and would injure the dye solution itself. This has long been known and dyeing adjuncts other than soap, but possessing wetting out properties, have been sought after. Sulfonated castor oil has long been used for this purpose. In recent years, a large number of chemical preparations have been discovered which possess even better wetting out properties than soap. Some of these will work well either in acid, neutral, or alkaline solutions and are more stable and better than soap as dyeing assistants. Most of these bodies are sulfonates or sulfates of certain organic derivatives. It has also been found that some of these bodies possess notable detergent qualities. Those with the most pronounced wetting out properties are not the best cleansers, although practically all which possess good detergent qualities do have good wetting out properties. The number of these non-soap detergents is so large that no attempt will be made here to classify them. Their number is being added to rapidly. Some have little value in comparison with others, while some have value for special purposes and are being manufactured to supply special demands.

Gardinol—Perhaps the best known of the organic non-soaps is "Gardinol" which is spoken of as the "sulfonate" of lauryl alcohol. This is a loose description of the product as it is, strictly speaking, a *sulfate* and not a sulfonate. It can be made by reducing lauric acid with hydrogen under pressure. The commercial raw materials are the mixed fatty acids derivable from cocoanut oil, which are reduced with hydrogen under pressure. Thus, instead of pure lauryl alcohol, a mixture of isomeric or similar organic alcohols is formed. These alcohols are esterified with sulfuric acid to monolauryl sulfate, which has one free acid hydrogen. The organic sulfate esters are then neutralized with an alkali, caustic soda, for example, and a product is obtained which yields a substantially neutral solution. The sulfation [15] is performed with concentrated or fuming sulfuric acid, which acts on the mixed alcohols. Good mixing and temperature control are necessary. An excess of acid is employed in order to esterify all, or nearly all, of the alcohols. An amount of sodium sulfate chemically equivalent to the excess of sulfuric acid left uncombined by the sulfation is always formed in the neu-

[14] See Chapter 29.
[15] For a discussion of the Unit Process of Sulfonation, see Chapter 3.

tralization step. Fortunately, it has been found that the presence of this sodium sulfate does not detract from the value of the product for detergent purposes. On the contrary, it seems even to add thereto, when the product is used in hard water.

The reactions by which the aliphatic alcohol sulfates are made may be illustrated as follows:

$$\begin{array}{ccccccc} R{-}COO{-}H & + & 2H_2 & = & RCH_2{-}OH & + & H_2O \\ \text{Fatty acid} & + & \text{Hydrogen} & = & \text{Fatty alcohol} & + & \text{Water} \end{array}$$

and

$$\begin{array}{ccccc} R{-}CH_2{-}OH + H{-}OSO_2O{-}H + \left\{\begin{array}{c}\text{excess}\\ \text{sulfuric}\\ \text{acid}\end{array}\right\} & = & R{-}CH_2{-}OSO_2O{-}H + H_2O & + & \left\{\begin{array}{c}\text{Excess}\\ \text{sulfuric}\\ \text{acid}\end{array}\right\} \\ \text{Fatty alcohol} + \quad \text{Sulfuric acid in excess} & = & \text{Fatty alcohol sulfate} & + & \left\{\begin{array}{c}\text{Water and}\\ \text{excess sul-}\\ \text{furic acid}\end{array}\right\} \end{array}$$

$$\begin{array}{ccc} R{-}CH_2{-}OSO_2O{-}H\left\{\begin{array}{l}+\text{Sulfuric acid in excess}\\ +\text{Caustic soda}\end{array}\right\} & = & R{-}CH_2{-}OSO_2O{-}Na + X\ Na_2SO_4 \\ \text{Fatty alcohol sulfate} \quad + \quad \text{Caustic soda to neutralize} & = & \left\{\begin{array}{c}\text{Sodium salt of fatty}\\ \text{alcohol sulfate}\end{array}\right\} + \quad \text{sodium} \end{array}$$

As the product is an ester of sulfuric acid and not a true sulfonate, in common with similar esters, it will suffer gradual hydrolysis with loss of valuable qualities if it is used in solutions that are either decidedly alkaline or decidedly acid.

OTHER SULFATED DETERGENTS

Another organic sulfate, which possesses unusually desirable properties, is the mono-sulfuric acid ester of a fatty acid monoglyceride, the sodium salt of which possesses very good detergent and wetting out properties. It may be illustrated graphically as follows:

$$\begin{array}{l} R{-}COOCH_2 \\ \qquad\qquad\ | \\ \qquad\quad\ \ CHOH \\ \qquad\qquad\ | \\ \qquad\quad\ \ CH_2{-}OSO_2O{-}Na \end{array}$$

The product is being made from the mixed monoglycerides derived from cocoanut oil and can be made from other fatty monoglycerides.

A still different type of detergent is being manufactured which, though a true sulfonate, is also an ester. Its general graphic formula is as follows:

$$R{-}COO{-}CH_2{-}CH_2{-}SO_2{-}O{-}Na$$

An analogous body which is not an ester has the following general graphic formula:

$$\begin{array}{l} R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}CH_2{-}CH_2{-}SO_2{-}O{-}Na \end{array}$$

All the above non-soap detergents, including sulfonated castor oil or Turkey Red Oil, which are being manufactured regularly, are derived from fatty starting materials.

Other synthetic detergents which are being manufactured or are capable of being manufactured, have been derived from a variety of quite different raw materials, and also possess quite different chemical structures. Some of these bodies are derived from aromatic chemical raw materials or coal tar products, and others are derived from petroleum products.

In the refining of petroleum hydrocarbons a step that has long been employed for the removal of certain olefins is to treat the petroleum products with concentrated sulfuric acid, or even with fuming sulfuric acid, under conditions that will cause the acid to combine chemically with the olefins. This step generally results in forming sulfonates with the sulfonate group attached to a double-bonded carbon atom. Some of these sulfonates neutralized and purified have desirable wetting or detergent qualities.

Some detergent products have been made by introducing long aliphatic side chains into aromatic rings and sulfonating the aromatic nucleus, the acid product thus obtained then being neutralized with alkali or even treated with alkali in excess when an alkaline product is desirable.

Some effective wetting agents, possessing very little cleansing qualities, have been made by sulfonating phenols which carried side chains. These bodies all possess certain common characteristics. One portion of the molecules mixes readily with water and aqueous solutions and is known as "hydrophylic," while another portion of the molecule mixes more or less readily with oils and materials that dissolve in oils. This portion of the molecule is described as "lipophylic." The sulfate or sulfonate salt portion of the molecule furnishes the hydrophylic character. This is augmented, if, in addition, there are some free alcoholic hydroxyl groups. Hydrocarbon radicals, particularly fairly long aliphatic radicals, furnish the lipophylic character. However, if these groupings are too long they may detract from the solubility of the product in water.

With these facts in mind it can now be seen why many of these bodies are extremely well suited to promote the emulsification of oily and aqueous phases, even when they are not inclined to form stable emulsions by themselves. This property causes this class of materials to be eminently suited to washing greasy articles.

Advantages and Disadvantages of These Detergents—The better non-soap detergents do not form objectionable precipitates with the calcium and magnesium salts in hard water as soap does. For this reason there is no deposition of calcium and magnesium salts on fabrics which are washed with them in hard water. However, the cleansing efficiency of these bodies is not equally good for all purposes. They are very good for washing woolen articles and work well on silk. For colored articles, with colors that are not fast, they are better than soap. They do not, however, have as high a degree of cleansing efficiency as soap, or soap reinforced by alkalies. Ordinarily they are not as satisfactory as soap for badly soiled articles.

It seems certain that for some purposes these detergents will continue to be used in place of soap, but it is equally certain that, for many uses, soap is best and that for most general purposes soap will continue to be used.

Most sulfate ester salts must be used by themselves and can not be used in the same water with soap or alkalies because the alkali of the soap will saponify the sulfate ester, causing it to lose its virtue, while the soap will be simultaneously destroyed. On the other hand, the non-ester sulfonate detergents are not injured by moderate alkalinity and some of these can be employed advantageously in the same bath as soap. This use is expected to increase gradually in importance.

Some non-sulfated esters of polyatomic alcohols with fatty acids, monoglycerides, for example, have good emulsifying properties and are finding special uses.

THE ECONOMICS OF THE SOAP INDUSTRY

The present day soap industry produces some 290,000,000 dollars' worth of soap products annually. This represents a slight decline over the peak value reached in 1929. In addition to this production some 3,500,000 pounds of castile and other miscellaneous soaps are imported annually. In general the industry has undergone very few severe production fluctuations, the imports and production being fairly steady. The export trade is, however, steadily rising with over 35,000,000 pounds of soap exported in 1939.

LAUNDERING [16]

Although the use of soap is as old as the material itself, there was but little systematic study or control of its cleansing powers until recent years. The discussion which follows deals primarily with the use of soap in modern laundry practice. While this covers only a small part of the field of application of soaps, it does serve to give the most essential information about the uses of detergents.

THE EFFECT OF SOILS ON THE LAUNDERING PROCESS

The type and amount of soil in clothes presents a highly variable factor that complicates the process of complete and quick washing. In general soils may be divided into the following classes:

1. Albuminous matter is present in the form of perspiration stains, blood, and stains from some foodstuffs. Albumins are soluble in cold or lukewarm water when fresh but become more difficultly soluble when old and dry or when subjected to heat. In a fair proportion of cases, albuminous stains in clothes reaching the laundry are old and do not respond readily to the solvent action of lukewarm water. Highly alkaline solutions at elevated temperatures are required to soften the material to facilitate removal.
2. Soluble soils such as sugar, salts, and many foodstuffs are easily removed by the action of cold or hot water.
3. Insoluble solid soils consist largely of soot, clay, and street dust and must be removed by the formation of stable suspensions of these materials in water. Soap solutions exhibit the desired properties of "wetting" the soil, separating it from the cloth fibers, and suspending it so that it can be flushed from the machine.
4. Oils and greases originating from mineral, animal, and vegetable sources may all be present. A very small proportion of the fatty oils may be

[16] This section on laundering contributed by C. E. Lennox, Laundry Research Division, Swift and Co.

present as fatty acids and as such could be easily saponified by alkalies and thus removed, but the great bulk of all oils must be removed by the emulsifying action of soap solutions that disperse the oils and form stable emulsions. Solid fats require elevated temperatures to render them liquid so that emulsions may be formed. Partially oxidized vegetable oils are quite resistant but highly alkaline solutions at elevated temperatures will soften the oil films.

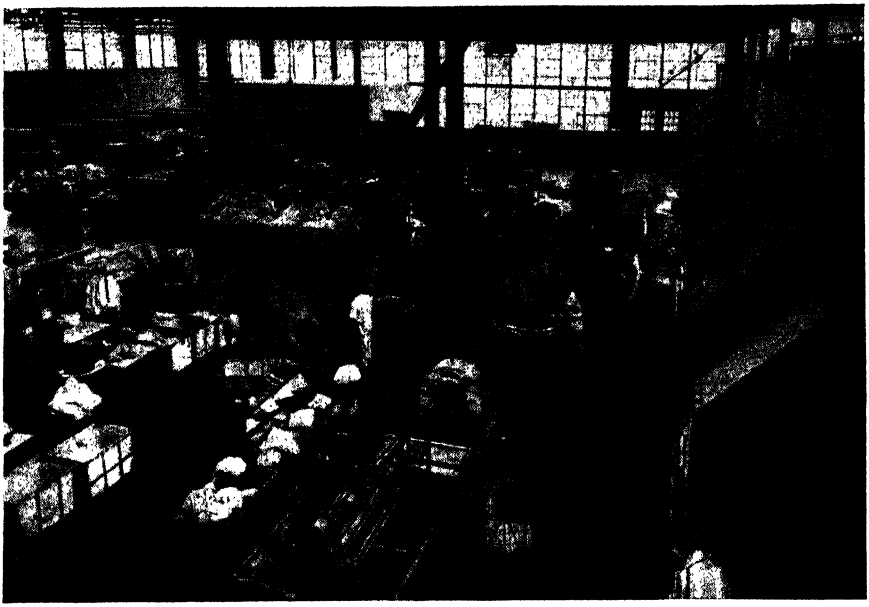


FIG. 1. Modern Laundry for One-Story Plant as Viewed from the Office Mezzanine. (Courtesy American Institute of Laundering)

5. Insoluble stains are considered to be materials not removed by washing with alkaline soap solutions. Hypochlorite bleaches and mild acid treatments remove some while a few others may be cleared up by special hand treatment. The balance remain since they may be as fast as a high grade dyestuff.

WASHING SUPPLIES

To remove soil from clothes, the primary cleaning material required is soap. In addition there are a wide variety of assistants to soap as well as various chemical specialties required for the removal of stains, for special washing treatments, and for supplying stiffness or body to fabrics.

Soaps for the Laundry—In the early days many laundries purchased supplies of tallow and grease and undertook to saponify these materials on a small scale with caustic soda. With a limited knowledge of soap-making and without means of control, the resulting crude soaps presented a highly variable material for washing. Later small soapmakers supplied well-made soap in the form of cutting scrap, bars, and solids but with the advent of large-scale chip soap driers almost the entire industry now purchases uniformly made soaps in the form of chips, flakes, or powders.

While the soaps consumed in the laundry industry are made from almost every available fatty raw material, the bulk of the production is made from tallow and grease since these materials are always plentiful and provide soaps of the desired characteristics. Nearly all of the washing takes place at temperatures between 100° F. and 160° F., and in this range tallow soaps provide most economical detergency. Neutral soaps of this type are covered by a Federal Specification and by an American Society of Testing Materials Specification [17] for chip soap. The important points of the latter are summarized as follows:

Moisture and matter volatile at 105° C., max., per cent	10.0
Sum of free alkali, total matter insoluble in water, and sodium chloride, max., per cent	4.0
Free alkali, calculated as NaOH, max., per cent	0.2
Matter insoluble in water, max., per cent	1.0
Anhydrous soap, min., per cent	85.0
Titre of the mixed fatty acids, min	39° C.

A similar A.S.T.M. specification [18] for powdered soap differs only in that the maximum moisture is 6.0 per cent and the minimum soap content is 89 per cent.

Soap Solutions—The majority of laundries purchase their soap requirements in chip form and prepare stock solutions of soap by dissolving the soap in tanks that range from 50 to 1,000 gallons in capacity. Appropriate quantities of alkaline builders are added to the soap to provide the desired alkalinities during sudsing.

For lower temperature washing many laundries use their regular stock soap but others prefer lower titred soap. Hence a moderate demand is found for soaps made from olive oil, distilled red oil (oleic acid), moderate quantities of cocoanut oil, and mixtures of these with tallow, grease, palm oil, and other of the common soap-making materials.

Powdered Soaps—Small laundries find that a ready-built soap in powdered form for direct addition to the washer is more convenient for their use since the preparation of a tank of soap is not warranted by their small consumption. A wide variety of such soaps is available, but the majority will conform to the types covered by an A.S.T.M. tentative [19] specification which is summarized as follows:

Moisture and matter volatile at 105° C., max., per cent	16
Sum of free alkali, total matter insoluble in alcohol, and alkaline salts, max., per cent	40
Matter insoluble in water, max., per cent	1
Anhydrous soap, min., per cent	50
Material passing a No. 140 sieve, max., per cent	20
Material retained on a No. 12 sieve, max., per cent	1.5

[17] A.S.T.M. D496-39, Chip Soap, Part III, 1939 Book of A.S.T.M. Standards; also 1938 Tentative Standards, 1520.

[18] A.S.T.M. D498-39, Powdered Soap, Part III, 1939 Book of A.S.T.M. Standards; also 1938 Tentative Standards, 1524.

[19] A.S.T.M. D533-39T, Built Soap, Powdered, Part III, 1939 Book of A.S.T.M. Standards.

In recognition of the need for various degrees of solubility, the above specification is divided to cover three types of products differing only in the nature of soap base used:

Type A.	Low	temperature washing........	Titre, max. 26° C.
" B.	Medium	" "	" , 26–39° C.
" C.	High	" "	" , min. 39° C.

The Type C is intended to cover the tallow type soap while Type A indicates the use of red oil and the softer vegetable oils. Type B represents various blends of high and low titre fats. While Type C soap is used to the greater extent by small laundries, the larger plants often supplement their stock solutions of strongly built tallow soap by Types A and B for colors and other less durable fabrics. Low titred powdered neutral soaps are most often used on silks and high grade woolens.

Synthetic Soaps—In recent years newly developed synthetic soap-like materials have been offered to the industry. The resistance of the synthetics to the formation of insoluble curds with hard water would indicate that they might be used to advantage with hard waters. However, these materials have not yet exhibited a sufficient degree of detergent power to properly wash white cotton cloth. Moreover, their use is not economically feasible at present. However, the ability of some of the synthetics to supply a limited detergent effect in acid solution has led to an improved means of handling hosiery and other colored knit goods that are fugitive to alkaline or even neutral solutions. Whiteness is not the measure of final cleanliness in such cases and the acid wash seems to be quite effective. Thus it would appear that the materials are finding a useful place in the laundry, but until better detergent properties are attained they will not be a factor in much of the work handled.

Alkali Builders—While soap is the primary detergent agent, the use of soap alone does not economically provide the best washing results. The soil in clothes represents in part a strong neutral buffer material that is acid to soap. Repeated tests on the soil found in the average clothes indicate that the soluble portion is in the range of pH 6.5 to 7.5. In dilute solution, neutral soaps have a pH of about 9.5 to 10.5. Assuming that soap functions best at its normal pH or higher, it is evident that alkaline materials such as soluble salts could be used to supplement and protect the soap by raising the alkalinity of the clothes. Practical experience has proved this assumption and so it has long been customary to add alkalies to the washing solution in appropriate quantities with due regard to the type of fabric washed, the amount of soil, and the type of water. The latter becomes a factor because of the variations in the sodium bicarbonate content of zeolite softened water.

In the early days of laundering before the advent of proper water treatment, the alkaline materials were also expected to act as water softeners. Since they acted as softeners only to a very limited extent, their use for this purpose required large amounts of alkali. When caustic soda was used in this manner, there arose various types of trouble including the yellowing and actual damage to cloth. This led to the development of what became known as modified soda or neutral soda, an approximately equal molecular mixture of sodium carbonate and sodium bicarbonate. This mixture is highly buffered in the range of pH 10.0

and hence provides safety to the fabrics no matter what quantity is used. Today the many phosphate compounds are preferred if water softening is expected, but since soap forms calcium compounds that are more insoluble than nearly any other known calcium compound, the softening of water in the presence of soap is not very practical and is invariably more expensive than if the water had been pre-treated by a zeolite unit. Hence the use of alkalies as water softeners is of little importance today.

Several basic alkalies are available to the industry. These will be briefly described in terms of their present application:

1. *Caustic Soda.* The standard flake or ground caustic is described in an A.S.T.M. Specification [20] which covers a commercial product with a 96 per cent minimum content of sodium hydroxide. In a limited way liquid caustic solutions of various densities are also used in some sections of the country. While the use of caustic soda was once frowned upon, the intelligent application in measured quantities has caused an increased use in recent years.
2. *Soda Ash.* The standard type is described in an A.S.T.M. Specification [21] which covers a commercial product with a 99 per cent minimum content of sodium carbonate. Soda ash is the most economical form of soluble alkali from the viewpoint of total available alkalinity, but when considered in terms of laundry application it becomes less desirable.
3. *Trisodium Phosphate.* The standard hydrated type contains 98 per cent or more calculated as $Na_3PO_4 \cdot 10H_2O$ and is covered in a tentative A.S.T.M. Specification.[22] Among the more alkaline salts, TSP offers the greatest water softening possibilities but is rather low in alkalinity.
4. *Sodium Metasilicate.* The standard pentahydrate form contains 98 per cent or more calculated as $Na_2SiO_3 \cdot 5H_2O$ and is covered by a tentative A.S.T.M. Specification.[23] An anhydrous form is also available. Greatly increased quantities of metasilicate have been used in recent years because of the ability of this non-caustic form of alkali to build up fairly high alkalinities. The benefits of soluble silica as a detergent aid have been presented in elaborate explanations but in the presence of soap it would appear that the meager colloidal properties of silicate are far outweighed by those of the soap.
5. *Modified Soda.* Also called neutral soda, this type of material may be in the form of a true crystallized sesquicarbonate described chemically as $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ or it may be in the form of a mixture of soda ash and sodium bicarbonate in approximate equal proportions. An A.S.T.M. Specification [23] places the following limits on this type of product:

[20] A.S.T.M. D456-39, Caustic Soda, Part III, 1939 Book of A.S.T.M. Standards; also 1938 Supplement, p. 240.

[21] A.S.T.M. D458-39, Soda Ash, Part III, 1939 Book of A.S.T.M. Standards; also 1938 Tentative Standards, 1518.

[22] A.S.T.M. D538-39T, Trisodium Phosphate, Part III, 1939 Book of A.S.T.M. Standards.

[23] A.S.T.M. D457-39, Modified Soda (Sesquicarbonate Type), Part III, 1939 Book of A.S.T.M. Standards; also 1938 Supplement, p. 241.

	Min.	*Max.*
Total alkalinity, as Na_2O, per cent	39	43
Sodium bicarbonate, per cent	35	50
Sodium carbonate, per cent	35	50

As previously indicated this type of product is self-buffered and mildly alkaline. Advancements in chemical control have caused much of this mild material to be replaced by the more efficient stronger alkalies.

Standardized Alkali Builders—In addition to the basic alkalies listed, there are standardized compounded products available that combine in part the properties of the basic materials. A few are listed as follows:

1. *Sodium Orthosilicate.* An anhydrous fused form is represented by the formula $Na_4SiO_4 \cdot H_2O$ which in effect might also be written as

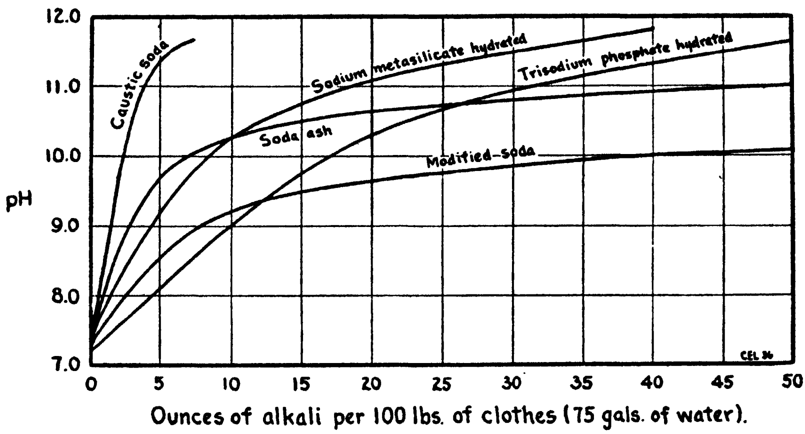


FIG. 2. Comparison of the Strengths of Laundry Alkalies.

$2Na_2O \cdot SiO_2 \cdot H_2O$ or $Na_2SiO_3 \cdot 2NaOH$. The orthosilicate is also marketed in a hydrated form.

2. *Sodium Sesquisilicate.* This is thought to be a crystalline salt represented as $Na_3HSiO_4 \cdot 5H_2O$ or $3Na_2O \cdot 2SiO_2 \cdot 11H_2O$. This might also be written as $Na_2SiO_3 \cdot NaOH \cdot 5H_2O$.
3. *Caustic Alkalies.* Fused or dry mixtures of caustic soda and soda ash are available over a wide range of compositions. The various types are commonly designated by a numerical value representing the per cent of sodium hydroxide in the mixture. Widely used products include 70 per cent, 45 per cent, 36 per cent, and 8 per cent alkalies.
4. *Laundry Compounds.* Mixtures of trisodium phosphate, metasilicate, and soda ash in varying amounts constitute the majority of the trade-named compounds outside of the products indicated in the previous paragraphs. In such mixtures the individual advantages of each basic material are assumed to be additive so that the compound presents the best possible material for building soap. In recent years the inclusion

of liberal quantities of caustic soda in such mixtures presents a hopeful sign that the desirable properties of caustic soda are being better understood.

ALKALIES AND SOIL

The neutral buffer effect of soil and the varying degrees of alkalinity supplied by the basic alkalies have been previously mentioned. Typical examples of the effects of soil on the several alkalies are shown in Figure 2.[24] In a Chicago laundry, regular lots of soiled family work were in effect titrated in the washer by the progressive additions of weighed quantities of the several alkalies. pH determinations were made colorimetrically. By this means comparative values of the several alkalies at various pH levels were established, and an indication of the buffer effect of soil thus estimated. Considering the pH 11.0 for discussion, it will be noted that approximately 3.6 oz. of caustic soda were required to raise the soiled load of clothes to this alkalinity while approximately 1 oz. of caustic soda would have raised an equal quantity of softened Chicago water to an equivalent alkalinity. Hence the soil neutralized or otherwise reacted with 2.6 oz. of caustic soda. To attain the same pH with the other alkalies studied, it would have been necessary to use five times as much metasilicate, eight times as much trisodium phosphate, or thirteen times as much soda ash. The self-buffered modified soda does not approach this pH level at all. Comparisons at other pH levels differ, but can be made from the chart. To indicate the relationship between the quantity of soap required and the amounts of alkalies required, it will be of interest to note that on the average approximately one-half pound of soap per 100 lbs. of clothes was needed to produce satisfactory suds. Soil conditions vary with different types of work and so do the alkali and soap requirements, but the relationship between the alkalies has been proved to be a fixed factor.

Soap Building—The previous paragraph tends to indicate the relationship between the quantities of soaps and alkaline builders required for washing. In a very empirical way, the industry has long used somewhat arbitrary proportions of soap and alkalies in the preparation of stock soap solutions. Modified soda is commonly used in equal quantities with soap. Other non-caustic alkalies are used in proportions of two parts of soap to one of alkali. In the absence of supplementary quantities of alkalies, such proportions would probably produce alkalinities of from pH 9.0 to 9.5 in the first sudsing operation. Tests made in the laundry verify this point, and with a growing appreciation of the need for higher alkalinities laundries have either used additional quantities of alkali builders on the first suds or have built their soap with stronger types of alkalies. At this point it should be pointed out that subsequent additions of built soap to later suds raise the alkaline values higher, but with the proportions mentioned in this paragraph pH 10.0 is seldom exceeded. If the washing time is long and the soil conditions are light clothes seem to respond satisfactorily to low alkaline sudsing, as testified by the fact that a fair proportion of laundry work is handled below pH 10.0.

New types of equipment designed for fast washing and the obvious need for more economical production methods have created a great interest in the possi-

[24] Lennox and Sandtner, Oil and Soap *13*, 257 (1936).

bility of substituting more chemical effect for mechanical action during washing. Higher alkalinities within the bounds of safety to fabric are one approach. Experimental evidence has proved that the cotton fiber is not harmed by alkalinities up to a pH value of 12.0. Practical experience has indicated that alkalinities higher than pH 10.0 are definitely desirable, but the point of optimum detergency for soap within this range is still open to speculation because of the difficulty of accurately measuring detergent efficiency in a complex, highly variable, and somewhat unknown system such as is daily presented in a load of soiled clothes. Current opinion would place the optimum range at about pH 11.2 to 11.5 with the higher bracket up to pH 11.8 set aside for specially resistant soils.

Again referring to Figure 2 it becomes obvious that this high range of alkalinity calls for the use of caustic soda or products containing liberal proportions of caustic soda. This is often accomplished by the addition of appropriate quantities of alkaline builders to the first suds while using a moderately built soap for the first as well as the later suds. Such a system allows the use of the same stock soap for fast colors where the alkalinity must be limited because of dyestuffs to about pH 10.5.

Concentration of Soap and Alkalies—Concentrations of soap are estimated visually by the appearance of the suds formed. The soap test for water hardness indicates that a good lasting lather is formed on soft water by a soap concentration of less than 0.005 per cent actual soap. The total quantities of soap present in the washer when a good suds is evident, range from 0.02 per cent for very light soil to 0.2 per cent for extremely heavy soil. The difference between the latter figures and the 0.005 per cent theoretically needed represents the soap consumed by adsorption on the cloth and by the formations of emulsions and suspensions. If a great excess of soap over these requirements is added, huge billowy suds are formed which roll out of the machine and are thus wasted. These heavy suds may also blanket the interior of the machine in such a way as to reduce mechanical action. Soap usage is thus regulated entirely by vision to keep the suds at a proper level. Alkali requirements are usually established by trial runs, but from the data of previous paragraphs it can be seen that the actual concentrations are quite low with an average of about 0.1 per cent in most cases. A good understanding of power laundry washing hinges upon appreciating the fact that all supplies are used at relatively high dilutions as compared to many other cleaning operations.

GLYCERINE [25]

It has been shown that when fats and fatty oils are hydrolyzed with water or saponified with alkalies in the presence of water to form fatty acids in one case and soap in the other, glycerine is always formed. Where hydrolysis is performed with the aid of a catalyzer suitable chemical treatment is employed to remove as much of the impurities as possible, including those introduced by the catalyzer, and to leave the glycerine solution in a nearly neutral condition. For example, where sulfuric acid has been employed, a common treatment comprises neutralizing with lime, which forms calcium sulfate which may be largely removed by filtration. Calcium sulfate is appreciably soluble in water and this

[25] This section was written by Martin H. Ittner.

portion may be removed by the subsequent use of suitable calcium precipitants such as sodium carbonate, which replace the calcium salts with soluble alkali salts.[26] Treatment with barium hydrate in place of lime gives an even better removal of impurities because of the greater insolubility of barium sulfate. It is desirable, in any case, to remove calcium sulfate, as this salt has the very objectionable property of precipitating in scale form on the heating surfaces in such a way as to greatly hamper evaporation necessary to produce crude glycerine.

Where countercurrent hydrolysis with water alone has been employed the glycerine solution, which may contain from 20 per cent to 30 per cent or more glycerine, is first allowed to settle thoroughly to separate it from any fatty matter. It will then be slightly acid from the presence of a small amount of soluble fatty acids, chief of which is acetic acid, and from the presence of a little suspended insoluble fatty matter. A small amount of sodium carbonate may be employed for neutralization and the glycerine solution may then be evaporated to somewhat over 95 per cent glycerine concentration prior to being subjected to distillation. The concentration is most advantageously performed in some type of vacuum evaporator.

GLYCERINE FROM SAPONIFICATION OPERATIONS

In the making of soap and glycerine by alkaline saponification of fats, the glycerine is commonly recovered in solution in the soap lyes. Many of these lyes, when removed from the soap pan, contain excess alkali which must be removed before the glycerine can be properly recovered. Neutralization with acid would be extremely wasteful as it would cause the loss of both the excess alkali and of the equivalent acid. The lye is therefore boiled with fatty matter, usually in separate kettles, until substantially all the excess alkali reacts to make more soap, after which it is sent to the glycerine department for treatment and recovery of glycerine. The spent lyes removed directly from the different changes may average around 4 to 5 per cent of glycerine but where the soap lye washing is performed countercurrently the glycerine in the lye may exceed 10 per cent. The lye also contains about 10 per cent, more or less, of salt and a small amount of soaps that are soluble in the lye.

Purifying the Solution—Soap lyes are given chemical and physical treatments that are calculated to remove as much of the objectionable impurities as possible while clarifying them at the same time. Any of several simple treatments may be employed for this purpose. Most or all of the caustic alkali should have been removed in the soap-boiling department, but the solutions will contain a small fraction of a per cent of sodium bicarbonate and a small amount of soluble soap. The lye may be advantageously brought almost to neutrality with a small quantity of mineral acid, sulfuric or hydrochloric. It can then be stirred and heated or boiled with some dissolved metallic salt which makes insoluble precipitates with soap and with carbonated alkalies. Salts of this kind which are available and which have been extensively used are ferric sulfate (crude), aluminum sulfate, or ferric chloride in solution. The addition of these reagents is performed under chemical control so that sufficient is employed to remove the last alkalinity and to precipitate any soap present as insoluble soaps, but so

[26] For an analogous procedure in water treatment, see Chapter 6.

there will be none of the unused precipitant left. These materials form gelatinous precipitates, either with alkali or with soluble soaps, so that after the precipitate has been removed by filtration in filter presses the lye is clarified as well as nearly neutral.

Evaporation of the Solution—The lye is now evaporated, preferably in vacuum evaporators. With the removal of water, the glycerine and salt concentration gradually increases until the salt saturation point is reached, after which salt begins to separate. Further evaporation should be performed in apparatus provided for salt removal. This can be done continuously by the continuous removal of a portion of the settlings from the conical bottom of the evaporator, or intermittently by providing the evaporator with a salt drum beneath, with a valve between the evaporator and drum so the salt contents may be removed at intervals.[27] The separated salt may be removed from the liquid portion of the concentrate either by filtration or centrifuging followed by a small amount of washing. The recovered salt is sent back to the soap boiling department to be used again, and the concentrated glycerine is boiled down, with the removal of more salt, until crude soap lye glycerine is obtained. This will advantageously contain about 80 to 82 per cent glycerine, along with about 2 per cent non-volatile organic matter; the balance being mostly salt and water.

Treatment of soap lyes with sulfuric acid and ferric or aluminum sulfate results in the formation of sodium sulfate which finds its way into the recovered salt and back to the soap pans. Sodium sulfate is not so good for graining soap and for lye washes as sodium chloride. Although the employment of hydrochloric acid and ferric chloride for soap lyes for glycerine recovery is somewhat more expensive than sulfuric acid and sulfates, the advantages obtained may outweigh the difference in cost.

In evaporating glycerine lyes there is very little actual volatilization of glycerine in the early stages. In the final stages, in bringing the concentrate up to crude glycerine, there is an amount of volatilization of glycerine which, though appreciable, need not be large. The actual volatilization of glycerine in evaporation from lye to crude is appreciably less where diminished pressure is employed. This is because the vapor pressure of glycerine, relative to that of water, is less at the lower temperature. Obviously, the use of diminished pressure at high glycerine concentrations is more necessary for preventing glycerine losses than at lower concentrations.

In spite of the fact that very little glycerine need be lost by volatilization in concentrating glycerine lyes to soap lye crude, there may be considerable losses in this operation due to excessive entrainment and poor separation of entrained material from the vapors.

Glycerine Evaporators—Glycerine evaporators are commonly heated by steam in tube calandrias within the lower portion of the evaporators. Diminished pressure is maintained by condensing the vapors with cold water in a barometric column.[28] Non-condensable gases are removed from the top of the barometric head either with a wet vacuum pump or an auxiliary steam exhauster.

[27] For further discussion of the technique of salt removal, see Chapter 9.

[28] For a more extended discussion of the unit operation of evaporation, see Chapter 2.

Many different types of evaporators may be used, but whatever the type, it should be such that the heating surfaces will not become coated with salt; and adequate salt removal must be provided. It is highly important that means shall be provided to reduce entrainment. For this reason it is customary to introduce one or another of various types of "catch-alls" between the evaporator and condenser. The "catch-all" should be located well above the liquid level of the evaporator so that any entrained liquor that is separated may flow back into the evaporator by gravity. An even more important precaution than the introduction of adequate catch-alls is that of avoiding sudden changes in the boiling temperature of the boiling liquor. These may be caused either by irregular introduction of the feed liquor or by unevenness in the pressure within the apparatus. When an unusually large amount of feed is introduced to a boiling evaporator, the feed, being more dilute and having a lower boiling point, will foam up badly and may even boil over so that a considerable portion of the contents of the evaporator will pass, as foam, with great rapidity through the catch-all to the jet condenser and be lost. A sudden increase in the vacuum may cause a similar disastrous condition. Holding back feed at times will cause the concentration and temperature of the boiling liquor to rise considerably. This will aggravate the foaming condition when fresh feed is again introduced. Evaporators should therefore be equipped with proper instruments to guide the operators in temperatures, pressures and height of contents at all times. When these are also of the recording type the management can have a check on the operation and find if and where this is at fault so that future operation can be improved.

In some cases, multiple effect evaporators are used in concentrating soap lyes but owing to the fact that the salt which separates is generally greater than the amount of glycerine present and may be irregular in amount, it is doubtful that such evaporators have much if any advantage over single stage evaporators.

The various types of crude glycerine, whether from aqueous hydrolysis with or without catalyzers, or from soap lyes, are not pure enough for most uses. In order to obtain good grades of refined glycerines the crude glycerine must be distilled.

REFINING OF GLYCERINE

Glycerine boils at 290° C. at atmospheric pressure. It is generally stated that glycerine boiling at this temperature is accompanied by decomposition. This is probably not correct, or at any rate the decomposition is inappreciable if air is effectively excluded and if local overheating is avoided and if a good excess of steam is present at all times. At a pressure of 10 mm. Hg. within the still glycerine boils at about 167° C.

There is such a wide difference in the boiling points of water and glycerine, a difference of about 190° C. at atmospheric pressure, that separation of water vapor from glycerine has long been practised by fractional condensation. In spite of these differences in physical properties of water and glycerine, glycerine refiners have been slow in deriving full advantage therefrom.

Glycerine distilled with open steam at atmospheric pressure is at high temperature and if a concentrated condensate is collected any vapor not condensed necessarily contains a large percentage of glycerine so that only a poor separation is made, and any attempt to recover all the glycerine necessitates the condensation of all the direct steam employed along with at least a substantial portion of the glycerine.

It is probable that the greatest improvement in glycerine refinement came from the joint use of direct jet steam and diminished pressure, in conjunction with indirect steam heating of the still contents. Distillation with direct steam at diminished pressure gave greatly improved results both in the quality of distillate obtained and in the ease and thoroughness of separation.

Van Ruymbeke Process—One of the most widely used and one of the most successful methods of distillation was the Van Ruymbeke [29] Process. By this process the crude glycerine was heated by indirect steam heat in a still maintained at a diminished pressure amounting to about two to three inches Hg. absolute pressure while a considerable amount of direct superheated steam was passed through the still contents. The mixed glycerine and water vapors were passed in turn through a series of catchboxes where most of the glycerine was condensed by air cooling of the exterior of the catchboxes, resulting in a number of condensates differing considerably among themselves in amounts of entrained impurities and glycerine concentrations. The first catchboxes contained appreciable amounts of color and entrained impurities but with high concentration glycerine, and the last catchboxes contained less entrainment but a higher percentage of water and appreciable amounts of volatile fatty acids. The vapor from the last catchboxes still carried a substantial amount of uncondensed glycerine, the recovery of which was accomplished by the complete condensation of these vapors in surface condensers. The "sweet waters" thus obtained contained anywhere from less than 3 per cent glycerine to over 5 per cent together with the greater part of the objectionable volatile fatty acids which pass over from the still contents, even though these be maintained on the alkaline side. In order to recover the glycerine from sweet waters it is necessary to evaporate off all the water, which is equal to the amount of jet steam used in the still. This necessitates a very decided loss of heat and an appreciable loss of glycerine. The glycerine collected in the last catchboxes is more dilute than desirable for most purposes, so this also must be concentrated by evaporation.

Improved Processes—There have been a number of other systems [30, 31, 32, 33] for distilling glycerine with direct jet steam under diminished pressure aimed either to improve the quality of the glycerine produced or to effect certain economies in steam consumption. A few of these which have been or still are used should be mentioned. All of these systems assumed as a matter of course that sweet waters must necessarily be produced, and much if not most of the "economies" realized in these systems consisted in utilizing the water vapor formed in evaporating and concentrating sweet waters as the direct steam employed in the still thus saving some heat over that employed in more wasteful processes. Unfortunately the water vapor generated by evaporating sweet waters carries the volatile fatty acids, which are perhaps the most objectionable impurities in distilled glycerine. The use of this impure water vapor returned and accumulated

[29] Van Ruymbeke, U. S. Patents 458,648; 522,132.
[30] Garrigues, U. S. Patent 774,171.
[31] Sanger, U. S. Patents 1,452,617; 1,743,488.
[32] Wood, U. S. Patent 910,440.
[33] Wood, U. S. Patent 1,089,383.

these objectionable impurities in the system, causing much of them to be retained in the finished distilled glycerine. Any economy that is effected in a process that lessens the quality of the product is of doubtful value even though its benefits are manifest in other ways. An attempt to improve this defect resulted in the utilization of the water vapor derived from the evaporation of sweet waters to evaporate distilled water, the vapor from which was in turn employed as direct steam in the still.

Another system,[33] which was at one time extensively used, employed a plurality of stills in series. Jet steam from the first still passed through a hot surface condenser, which condensed out the greater part of the glycerine vapors from the first still without condensing much of the water vapor, which in turn was then passed through a second still as the direct steam therein employed. In this way one charge of direct steam served as the direct steam for each of several stills, passing from one to the other. This system judged from a certain viewpoint seemed to effect substantial economies in heat but there is no doubt that the quality of the glycerine produced, especially in the stills that used recovered direct steam, was unnecessarily decreased by reimpregnation with the volatile impurities from the preceding stills. The distillate thus obtained after further concentration by heating under a vacuum in an evaporator was suitable for *dynamite grade* which contains about 98.8 per cent absolute glycerine, while by redistillations of the better fractions the *chemically pure* and *U.S.P.* grades were obtainable.

Attempts have been made to rectify glycerine in modified bubble cap columns somewhat like those employed in the alcohol industry but the rise in boiling point due to the increase in hydrostatic head introduced more objectionable than advantageous features.

A process[10] has been proposed and used for distillation at pressures lower than the pressure that maintains in an ordinary surface condenser system. This process has certain advantages but if all the glycerine is condensed at a temperature low enough to avoid substantial glycerine vapor losses the concentration of the condensate is undesirably low and the content of volatile fatty acids may be undesirably high, while if the condensation is at a higher temperature a portion of the glycerine vapors will escape unrecovered. These difficulties may be partly met by having more than one condenser in series.

A study of the complete liquid-vapor equilibrium data for the system glycerine-water shows that a separation of the two can be more readily effected at reduced pressure. Advantage has been taken of this fact in the most recent development for glycerine purification.

THE MODERN PROCESS

A system of glycerine refining[34] depending on this principle is now very extensively in use, in which substantially all the glycerine volatilized is condensed as distillate analyzing in the neighborhood of 99.6 per cent glycerine, without the collection of any sweet waters whatsoever and with no loss of glycerine through volatilization. All of the glycerine thus distilled is condensed directly

[34] Ittner, U. S. Patents 2,164,274; 2,164,275.

into salable glycerine except as it must be diluted afterwards with distilled water to meet the usual lower commercial standards, and over 80 per cent of the product is equal to or better than much of the twice or thrice distilled glycerine. The distilling rate that may be maintained is several times as great as may be obtained in other stills of the same size and the steam saving is considerable. The system is quite flexible inasmuch as it works well over a fairly wide range of operating conditions, and the conditions within the system which depend upon one another are largely self-adjusting so that a minimum of manual control is required.

Apparatus—An ordinary still pot, such as one 6 feet in diameter and 6 feet high with dished heads, may be provided with several steam heating coils located within the still in the lower outer portion; the coils being close enough to one another to supply a large amount of heating surface yet far enough apart to give ample room for free circulation of the liquid contents of the still. Five such heating coils may be employed advantageously.

A steam superheater coil may be placed within the other sets of coils for the purpose of superheating the direct jet steam used. The heat employed to superheat the jet steam within the still in this way amounts to only about 2 to 5 per cent of the heat required in the still, and is less than the heat that is lost by the use of a separate outside superheater such as Van Ruymbeke employed. Located in this position, the superheater coil derives its heat from the still contents, just after parting with the glycerine vapor set free, as the liquor circulates downwardly over the superheater coil before rising again between the heating coils, and does not sensibly lessen the operation of the still. The superheated steam passing downwardly through the superheater coil is distributed by a plurality of jets or ejector jets located under the five heating coils so as to discharge the steam with a tangential action. The tangential discharge of steam from the jets creates a slight circular motion around the still among the coils.

The mixed glycerine and water vapors are passed through an effective entrainment separator that is well insulated to prevent condensation. Then they pass through a special type of surface condenser which is called a boiler-condenser, because of the functions it performs. The vapors passing through tubes are cooled and glycerine is condensed. The outer sides of the tubes are surrounded by boiling distilled water being generated into steam through recovery of the heat of vaporization of the glycerine. The distilled water supplied to this boiler is the hot condensate from the heating coils employed within the still and when this is released to the lower pressure in the steam-water portion of the boiler-condenser (which may operate at any pressure over a wide range of pressures, but advantageously at about 5 lbs. gage), an appreciable amount of this water flashes into steam. A portion of the steam generated in the boiler-condenser, from distilled water, is led to the superheater coil within the still, after passing through a controlling valve and orifice.

It is advantageous to flash the hot, high pressure water from the condensate of the steam heating coils into a chamber maintained at an intermediate pressure at 25-30 lbs. gage and to use the steam thus generated in preheating the crude fed to the still.

This type of apparatus will condense somewhat over 80 per cent of the distillate as very high grade glycerine, testing a little over 99.6 per cent pure (and about 0.4 per cent water), when the pressure within the still is in the range of 10-15 mm. Hg. This glycerine requires no redistillation to comply with U.S.P. requirements, or to meet most of the special trade specifications for "C.P. Glycerine."

The mixed glycerine and water vapors passing through the boiler-condenser are now passed upward through a device [35] that might be called a "condenser-concentrator." It is essentially a shell and tube condenser with the vapor outside the multiple banks of tubes. Cold water flows through the top tubes and steam from the boiler-condenser flows through the bottom ones, while water at intermediate temperatures flows through the others. As the mixed glycerine and water vapor passes upward, some glycerine is condensed out on the hotter tubes, but the water vapor passes on. Part of the water vapor passes out of the top, but part of it, along with practically all the glycerine, condenses out on the top tubes. This liquid drips back down over the tubes which are staggered so drips from one row strike the next bank. The water in the liquid is revaporized before it gets to the bottom tubes. Hence, with proper regulation of temperatures and rates of flow, substantially pure glycerine is produced at the bottom of the condenser and substantially pure water comes off the top. This is really a continuous fractionation by repeated differential condensation. While it would not be satisfactory for separation of components with a small difference in boiling points it works very satisfactorily for the system glycerine water, where there is a great difference in boiling points.

A still of this kind operating on crude glycerine derived from a process like the countercurrent [5] hydrolysis of fats, where mineral residues are absent, might operate continuously night and day for over a week with unabated efficiency at a rate of over 3000 lbs. distillate an hour if the feed were available.

SYNTHETIC GLYCERINE

The structural formula of glycerine has long been established by various chemical reactions and even by laboratory syntheses, but up to a few years ago there has been no commercial synthesis of the product. Such a synthesis on a commercial basis seems now to be an accomplished fact through the work of Williams [36] and others of the Shell Development Company.

In the cracking of petroleum to form gasoline very large quantities of various gaseous hydrocarbons are formed.[37] These have been studied from the standpoint of their applicability as starting material for the synthesis of glycerine. Many efforts have been made to accomplish this result by the formation of 1,2,3-trichlorpropane and its subsequent hydrolysis to glycerine but the hydrolysis of this compound is not a smooth one and results in poor yields of glycerine and in large amounts of undesirable products. The hydrocarbon that has proved best suited for this purpose is propylene, an unsaturated three carbon compound with one double bond. When this is subjected to treatment with gaseous chlorine at a temperature of about 500° C., an unexpected chemical reaction takes

[35] Ittner, U. S. Patent 2,164,276.
[36] Williams, E. C., Trans. Am. Inst. Chem. Engrs. *37*, 157 (1941).
[37] See Chapter 3 and Chapter 14.

place. Ordinarily, when an unsaturated carbon compound is chlorinated,[38] the chlorine becomes attached to the carbons that were situated adjacent to the double bond. However, in the high temperature chlorination of propylene, instead of adding to the molecule at the double bond the chlorine substitutes for one of the hydrogens in the terminal methyl group, leaving the double bond intact, thus:

$$\begin{array}{lclcl} \begin{array}{l} H_2\ H \\ C{-}C{=}CH_2 \\ H \end{array} & + \ Cl_2 = & \begin{array}{l} H_2\ H \\ C{-}C{=}CH_2 \\ Cl \end{array} & + & HCl \\ \text{Propylene} & + \text{ Chlorine} = & \text{Allyl chloride} & + & \text{Hydrochloric acid} \end{array}$$

By observing proper temperature, and other suitable conditions, including the maintenance of a proper excess of propylene, a high yield of allyl chloride is obtained.

Hydrolysis of Allyl Chloride—The next step is to hydrolyze[39] the allyl chloride into allyl alcohol. This may be performed with acid catalysts or more suitably by treatment with alkalies such as caustic soda or sodium carbonate. It has been found that the best yields are obtained when alkalinity is maintained at a pH of 8-11. For this reason, sodium carbonate is used with gradual additions of caustic soda. Yields of 90-95 per cent are thus obtained.

Production of Glycerine—The formation of allyl alcohol takes place as follows:

$$\begin{array}{lclcl} \begin{array}{l} H_2 \\ CCl{-}CH{=}CH_2 \end{array} & + \ NaOH = & \begin{array}{l} H_2 \\ COH{-}CH{=}CH_2 \end{array} & + & NaCl \\ \text{Allyl chloride} & + \text{ Caustic soda} = & \text{Allyl alcohol} & + & \text{Sodium chloride} \end{array}$$

The allyl alcohol is then subjected to chlorohydrination by subjecting it to hypochlorous acid and chlorine in water. In this way two new products are formed, monochlorohydrin and dichlorohydrin, both of which may be converted readily into glycerine. The chlorohydrination of allyl alcohol proceeds as follows:

$$\begin{array}{lcl} CH_2OH{-}CH{=}CH_2 + & HOCl & = \begin{array}{l} \qquad\ Cl \\ CH_2{-}CH{-}CH_2 \\ OH \qquad\quad OH \end{array} \\ \text{Allyl alcohol} & + \text{ Hypochlorous acid} & = \text{Monochlorohydrin} \end{array}$$

The conversion of the chlorohydrins to glycerine is as follows:

$$\begin{array}{lcll} CH_2OH{-}CHCl{-}CH_2OH + & NaOH & = CH_2OH{-}CHOH{-}CH_2OH & + NaCl \\ \text{Monochlorohydrin} & + \text{ Caustic soda} & = \text{Glycerine} & + \left\{\begin{array}{l}\text{Sodium} \\ \text{chloride}\end{array}\right. \end{array}$$

and

$$\begin{array}{lcll} CH_2OH{-}CHCl{-}CH_2Cl + & 2NaOH & = CH_2OH{-}CHOH{-}CH_2OH & + 2NaCl \\ \text{Dichlorohydrin} & + \text{ Caustic soda} & = \text{Glycerine} & + \left\{\begin{array}{l}\text{Sodium} \\ \text{chloride}\end{array}\right. \end{array}$$

The course of the reactions given above gives the smoothest steps and the best yields, but it is obvious that optional steps are sometimes presented. Thus, instead of proceeding from allyl chloride through allyl alcohol, treatment with hypochlorous acid gives dichlorohydrin direct from allyl chloride, which can then be converted into glycerine.

[38] A more complete discussion of chlorination will be found in Chapter 3.
[39] For a discussion of hydrolysis see Chapter 3.

Unless the various chemical reactions leading from propylene to glycerine are carefully performed under approximately optimum conditions, yields will be poor and the crude product obtained may contain objectionable impurities which will cause purification to be difficult.

Purification of the Glycerine—The aqueous glycerine solution is evaporated to about 95 per cent concentration and distilled *in vacuo*. At a suitable point in this rectification, purification by solvent extraction with xylene or other solvent is performed for removal of certain objectionable impurities.

GLYCERINE FROM FERMENTATION PROCESSES

Although the principal production of glycerine, that from fats and oils, has been described in considerable detail, as has the possible synthesis from petroleum, the story would not be complete without mentioning another potential source. It has long been known that glycerine is produced in small amounts in the fermentation of various sugars. In ordinary fermentation processes, where alcohol is the desired product, the glycerine formed is normally but a small percentage of the alcohol produced and, when the alcohol is distilled, the glycerine is lost in the still residue. Considerable research work has been done to change and direct the course of the fermentation of sugar in order to increase the amount of glycerine produced. Most of these methods depend upon the employment of sodium sulfite and most of them are done in alkaline condition but some of them have been carried out in acid condition. Some of these methods have been said to have produced glycerine to as high as 30 per cent of the sugar used, though many of the processes do not lay claim to such high yields. In these processes alcohol might be looked upon as the by-product. The quality of the crude glycerine produced by these processes is very poor in nearly every case and the difficulties of refining very great. In spite of this fact, Germany, faced with an actual deficiency of fats and with a pressing need for glycerine for explosive purposes, produced upwards of 1000 tons of glycerine monthly during the first World War, through the fermentation of beet sugar with sodium sulfite. At the present time, with Germany again at war, their production of beet sugar during 1940 has been reported at 4,000,000 tons. It therefore seems not improbable, with this bountiful supply of raw material on hand, and with their present shortage of fats, though not so acute as in the first World War, that they may have again turned to the manufacture of fermentation glycerine for military purposes.

ECONOMIC ASPECTS OF GLYCERINE PRODUCTION

Glycerine has not yet been made on a large commercial scale by the synthetic process, but has been made on a pilot plant scale and is said to have been produced in U.S.P. quality. It appears that no decision has been made, as yet, to increase production of glycerine in this way. The process is said to offer the possibility of supplying any probable increased demand for glycerine, should this be forthcoming, and eventually to reach large figures. If put into operation it is probable that price fluctuations would be greatly lessened. Anything looking to stability in glycerine prices would be welcomed not only by consumers but also by the soapmakers themselves who, in the long run, do not profit by sudden rises in glycerine prices.

In considering glycerine economics it should be borne in mind that it costs the soapmaker but a few cents a pound to produce glycerine in highly refined condition. When glycerine sells at a low price, soaps are comparatively more expensive to make and when glycerine sells at a high price, soap is sold cheaper than it otherwise would be. The two trends can not be separated. These facts strongly influence the market for both soap and glycerine and are really outside of any absolute control by the soap-maker. Glycerine left in soap does not improve the washing qualities of the soap and may even detract from them, so it is probable that considerable glycerine would still be recovered and refined even if its market price dropped close to the price of soap. With no corresponding drop in the cost of fats the price of soap would rise with drop in the price of glycerine. As the soap-makers are all in much the same situation with regard to soap and glycerine production, there is no competitive advantage in having glycerine prices either high or low. It would be obviously harmful to both glycerine consumers and producers to have the prices so low as to make it uneconomical to recover a good yield of glycerine from soap. Also, it is harmful to both consumers and producers to have prices go so high that glycerine can not be used with customary freedom for all old uses or adopted for new uses.

Therefore it is probable that synthetic glycerine could never hope to displace any considerable proportion of that made from fats by underselling. On the other hand a successful method for the commercial synthesis of glycerine, whether operated or not, must serve as a boon to both glycerine producers and to glycerine consumers, benefiting producers by encouraging new and wider uses, and consumers by guaranteeing that the product can be produced to meet all needs, and benefiting all by a tendency to stabilize prices.

Annual Production—The annual production of glycerine in the United States at this time is close to 150,000,000 lbs. of 100 per cent or "absolute" glycerine, the production having increased in substantial degree over the last fifteen years.

Glycerine is used on a large scale for the manufacture of nitroglycerine, a large part of which is made into dynamite [40] which is probably the most valuable single explosive. Dynamite is used extensively in mining, quarrying and in large construction work. At times, nitroglycerine is extensively employed for military purposes.

Glycerine has a multiplicity of technical uses such as a softening agent, stabilizer of consistency, solvent, dehydrator, lubricant, preservative, and a host of varied physical uses, in making plastics [41] and for many other chemical purposes. It is used extensively in making pharmaceutical preparations and medicinals and is used to a considerable degree in food preparations. Many if not most of these uses will expand if the supply and demand are such as to encourage new uses and more efficient recoveries and if prices can be maintained within a reasonable range.

[40] See Chapter 32.
[41] See Chapter 31.

READING LIST

SOAP MANUFACTURE

Hurst, G. H., "Soaps: A Practical Manual on the Manufacture of Domestic, Toilet and Other Soaps," third edition, D. Van Nostrand Co., New York (1922).

Martin, G., "The Modern Soap and Detergent Industry," second edition, 2 volumes, D. Van Nostrand Co., New York (1932).

Poucher, W. A., "Perfumes, Cosmetics and Soaps, with Special Reference to Synthetics," 3 volumes, D. Van Nostrand Co., New York (1936).

Simmons, W. H., "Soap: Its Composition, Manufacture, and Properties," fourth edition, Sir. I. Putnam & Sons, Ltd., London (1936).

CHEMISTRY OF SOAP

Fischer, M. H., McLaughlin, G. D., and Hooker, M. O., "Soaps and Proteins: Their Colloid Chemistry in Theory and Practice," J. Wiley & Sons, New York (1921).

GLYCERINE

Lawrie, J. W., "Glycerol and the Glycols," A. C. S. Monograph No. 44, Reinhold Publishing Corp., New York (1928).

CHAPTER 43

GLUE AND GELATINE

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Glue and gelatine are two products which have assumed a key place in industry both in their own right, and by their contributions to and uses in other fields. Essentially they are alike, since both are nitrogenous organic substances of similar chemical constitution. Broadly speaking, glue is impure gelatine. In fact, some very light-colored high-test glues (technical gelatine) so closely resemble gelatine that an investigation of the conditions of manufacture and the presence of certain chemicals is the only practical way to differentiate between them.

The derivations of the terms glue (from the unused Latin verb *gluere,* to draw together) and gelatine (from the Latin *gelare,* to congeal, a word allied to the English chill, gelid, jelly) at once call to mind the principal properties of these substances, for glue is chiefly used as an adhesive, whereas gelatine is valued mainly according to its stiffening, jellying, or emulsifying properties.

Both glue and gelatine are obtained by heating properly prepared animal matter, such as skins, bones, etc., with water and drying the resultant extract. In the manufacture of gelatine, however, it is necessary to use only certain selected kinds of bones and parts of skin which must be washed and treated with especial care, so that the resultant product is much cleaner and purer than glue. It is also extracted at a lower temperature, hence less of the fluid disintegration products of the stock are formed. As a result, the jellying power is greater than with glue.

These brief statements may serve to define the materials being discussed but in order really to understand them it is necessary to discuss certain of their distinctive properties.

PHYSICAL AND CHEMICAL PROPERTIES OF GLUE AND GELATINE

The Colloidal State—Glue and gelatine are typical colloids, which in contrast to crystalloid material, do not readily form visible crystals, or readily diffuse through membranes like parchment paper or skin.

It should be pointed out that colloids do not constitute a definite class of substances, but that the colloidal state refers merely to a condition of matter which accentuates the display of certain physical and chemical properties. Particle size is the criterion of the colloidal state; but the shape and structure of the colloidal particles, their chemical nature, and their relation to neighboring particles and to the medium in which they are dispersed, are all important factors. Many substances may exist in either the colloidal or the crystalloidal state, depending upon the nature of the solvent (*e.g.*, certain soaps) or upon the conditions governing their formation (*e.g.*, gold, silicic acid). It is well recognized that the same substance may pass from one form to the other.

The ultimate particles of colloids are much smaller than what we would ordinarily term a physical subdivision, but rather larger than most of chemical molecules; consequently their reactions stand midway between the physical and the chemical changes of matter, as may be seen by considering the properties of gelatine and glue.

Gelatine and glue absorb a considerable quantity of cold water and swell up, yielding jellies which, upon the application of heat, melt to a viscous solution that gelatinizes again upon cooling. When dried at medium temperatures, they can be again redissolved and redried indefinitely, and are therefore called *reversible* colloids to distinguish them from other colloids which, when once dried, are insoluble (*e.g.*, silicic acid). When superdried at about 130° C., however, both glue and gelatine become insoluble, their constituent particles having approached too close to be again separated by simple soaking.

Glue and gelatine are also termed *hydrophile* (friendly to water), or *lyophile* (friendly to solution), in contradistinction to such colloids as silicic acid, alumina, etc., which are *hydrophobe or lyophobe*. The dispersed particles of hydrophile colloids are termed *emulsoids,* whereas colloidal silica, gold, etc., having solid dispersed particles, are called *suspensoids.* In nature, transition forms exist, and indeed as gelatine becomes hydrated, its molecular groups become separated by the imbibed water and it passes gradually from the solid to the fluid state.

If two equal portions of the same sheet of gelatine are placed, the one in, for example, 20 times its weight of water, and the other in twice as much water, the latter will swell much more than the former. This curious effect is largely due to the fact that diffusible substances which promote swelling (*e.g.*, $CaSO_4$, and certain hydrolysis products which are present in glue or gelatine) are removed to a greater extent in the presence of the greater amount of water.

Glue and gelatine are especially powerful *protective colloids,* for they render sensitive and irreversible colloids stable or reversible, even if present in minute quantity. The effectiveness of glue and gelatine as protective colloids is shown by the tabulation of the "gold numbers" of various substances in Table 1.

Chemical Constitution—The present evidence is that gelatine and glue are not definite chemical entities, but rather adsorption complexes containing various incidental substances. They differ materially in chemical composition according to the origin of the stock from which they are made and the process used. Assuming that such a thing as "chemically pure gelatine" exists, no one has thus far prepared it; and the numerous experiments made with more or less pure gelatine must be considered in the light of the powerful influence exerted by even traces of impurities.[1]

Glue solutions will not diffuse through colloidal membranes (*e.g.*, parchment paper and bladder), and their jellies are practically impermeable to other colloids. The solutions are thickened by alum, formaldehyde and tannin, and also by

[1] "Glue and Gelatine," A. C. S. Monograph No. 11, pp. 38 *et seq.*

TABLE 1—GOLD NUMBERS OF GLUE, GELATINE AND OTHER PROTECTIVE SUBSTANCES

Substance	*Gold Number* *
Gelatine	0.005-0.01
Russian glue	0.005-0.01
Isinglass	0.01 -0.02
Casein (in ammonia)	0.01
Egg-globulin	0.02 -0.05
Ovomucoid	0.04 -0.08
Glycoprotein	0.05 -0.1
Amorphous egg-albumin	0.03 -0.06
Crystallized egg-albumin	2.0 -8.0
Fresh egg white	0.08 -0.15
Gum arabic	0.15 -0.25 0.5 -4.0
Gum tragacanth	2.0±
Dextrin	6.0 -20.0
Wheat starch	5.0±
Potato starch	25.0±
Sodium oleate	0.4 -1.0
Sodium stearate at 100°	0.01
Sodium stearate at 60°	10.0
Deutero-albumose	∞
Cane sugar	∞
Urea	∞
Stannic acid sol (old)	∞

* The "gold number" is the number of milligrams of a protector which just fails to prevent the color change from bright red to violet, of 10 cc. of a solution of pure colloidal gold upon the addition of 1 cc. of a 10 per cent solution of NaCl. A low "gold number" is an indication that the compound is an active protective colloid. The less the protective action, the higher the gold number.

chromium salts, upon exposure to light. But these coagula cannot be considered in a strict sense as chemical compounds, because their composition varies greatly with the conditions of their formation. They are nevertheless of great technical importance, forming the basis of the tanning process, and photolithography.

Since the material commonly known as "gelatine" is purer, that is, of a more constant composition, than glue, it might be expected to show an approximately constant atomic composition. The composition [2] of ash-free isoelectric gelatine of highest purity showed the following ultimate composition; *in per cent:*

Carbon	*Hydrogen*	*Nitrogen*	*Oxygen*
50.5	6.8	17.5	25.2

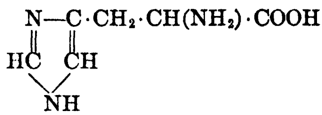
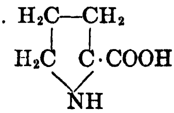
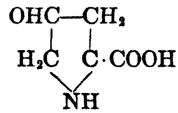
Such a formula would indicate that the material is essentially made up of proteins. This assumption is substantiated by the results of determinations of the cleavage products of gelatine, which show that it contains a number of the amino acids which are the recognized building blocks of natural proteins. The results of recent determinations are reported in Table 2.

Gelatine also contains small amounts of sulfur and phosphorus. This is to be expected as natural proteins nearly always contain greater or less amounts of complex compounds of these elements.

Though gelatine is an edible protein and hence can serve as food it is not a "complete" food protein, because it lacks the amino acids tyrosine and trypto-

[2] "Allen's Commercial Organic Analysis," fifth edition, Vol. 10, p. 131 (1933).

TABLE 2—AMINO-ACID CONTENT OF GELATINE * †

Amino Acid	*Per Cent*		*Formula*
Glycine	25.5	α-amino-acetic acid	$CH_2(NH_2)\cdot COOH$
Lysine	5.9	α-ε-diamino-caproic acid	$CH_2\cdot NH_2(CH_2)_3CH(NH_2)\cdot COOH$
Alanine	8.7	α-amino-propionic acid	$CH_3\cdot CH(NH_2)\cdot COOH$
Phenylalanine	1.4	β-phenyl-α-amino-propionic acid	$C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot COOH$
Leucine and Isoleucine	7.1	α-amino-iso-caproic acid	$CH_3(CH_2)_3CH(NH_2)\cdot COOH$
Aspartic acid	3.4	α-amino-succinic acid	$COOH\cdot CH_2\cdot CH(NH_2)\cdot COOH$
Glutamic acid	5.8	α-amino-glutaric acid	$COOH\cdot CH_2\cdot CH_2CH(NH_2)\cdot COOH$
Histidine	0.9	β-imidazole-α-aminopropionic acid	
Arginine	9.1	α-amino-δ-guanino-*n*-valeric acid	$NH{:}C(NH_2)\cdot NH(CH_2)_3\cdot CH(NH_2)\cdot COOH$
Proline	19.7	α-pyrrolidine-carboxylic acid	
Hydroxyproline	14.4	γ-hydroxy-α-pyrrolidine-carboxylic acid	
Methionine	0.97	γ-methylthiol-α-amino-butyric acid	$CH_3\cdot S\cdot CH_2\cdot CH_2CH(NH_2)\cdot COOH$

* Dakin, H. P., J. Biol. Chem. *44*, 499 (1920).
† Bergmann, M., ibid. *110*, 471 (1935); *115*, 77 (1936).

phane which are essential to maintenance and growth. These are found in milk (casein), eggs (ovalbumin) and wheat (gliadin, glutinin).

RAW MATERIALS

As was pointed out above, the sources of both glue and gelatine are essentially the same animal materials; only selection and treatment vary. Hence the raw materials for the manufacture of both products can be considered together. The principal raw materials are:

1. Skin or hide.
2. Sinew.
3. Bone.

The heads, bones and skins of fish are also sometimes used, but they are not considered here.

Hide Stock—Most hide stock is produced by tanners and as leather is usually considered more valuable than glue, only waste pieces ordinarily reach the glue-maker. However, it not infrequently happens that the demand for leather fails to keep pace with the supply and an appreciable portion of the usable hides may be diverted to glue manufacture. The condition of international markets and the increasing use of leather substitutes has definitely contributed to the greater use of hides for glue in recent years. This is striking evidence of the fact that the economic position [8] of any commodity must always be considered in the light of all events which might affect the situation.

The principal kinds of hide stock are: "pieces" or heavy trimmings from dried, salted or limed skins (yield 18 to 50 per cent of glue); "fleshings," representing the scrapings from the flesh side (yield 3 to 40 per cent of glue); "skivings," which are parings from the hair or grain side of the skin or hide. Very frequently the yield of grease from fleshings exceeds both in percentage and value that of the glue, especially in the case of "machine fleshings," which are usually thinner than those taken off by hand.

Calf, cattle, goat, sheep, deer, pig and horse skins are valued about in the order given. Good gelatine is now made from pig skin by treating the stock with acid.

A great variety of other kinds of hide waste also finds its way into the glue pot, as for example: *rabbit skin or coney stock,* a refuse produced by hatters who pluck off the fur for the manufacture of felt hats; *loom pickers,* representing discarded fragments of rawhide from textile machinery; worn-out Turkish rawhide moccasins, and many other kinds of rawhide and parchment waste. Tanned skin yields no glue, although patents have been taken out for extracting the tanning materials and making glue from the skin thus made soluble.

"Dry stock" may have been either uncured or salted or limed before drying; "green" or wet stock may be "green salted" or "green limed."

Sinews—These come into the market fresh or green salted from the slaughter houses; they are also imported in dried state from South America, in which case they are frequently mixed with dried bulls' pizzles. They are treated like hide stock, being first swollen in weak lime water.

Bone Stock—Quite a number of kinds of commercial glue stocks are produced from osseous tissue. The chief of these are enumerated below.

Green or Packer Bone. This consists of fresh sweet bone containing the marrow or bone fat and frequently adhering tendons, coming from the canning room, cutting room and killing floor. Such stock usually undergoes an immediate preliminary steaming at its place of production, by which part of the fat, miscellaneous tissue, and blood are separated and the keeping qualities of the bone so improved that it will stand transportation and storage. The long shin bones are sold to manufacturers of buttons, knife handles, etc. (whose refuse is later used), while heads, ribs, feet, etc., go direct to the gelatine or glue factory. The hoofs and horns are usually first removed, for contrary to the popular notion, perpetuated by many dictionaries, they are not used for glue. Hoofs and horns consist of keratin, a sulfur-bearing protein, which does not yield any glue-like substance on decomposition.

Country-bone, which is chiefly butchers' offal, and *junk bone,* consisting of old dry bone from any source, are used mostly for the production of low grade glues.

Ossein. This is also called acidulated bone, and its production is referred to later. It is prepared by leaching crushed bone in dilute (about 8 per cent) HCl, whereby the mineral constituents are dissolved, leaving a cartilaginous

[8] See Chapter 1, The Economic Pattern.

substance (collagen) in the original shape of the fragment of bone. Before this process the dry bones are usually degreased in a closed steel tank with a volatile solvent which is afterward distilled off from the grease and recovered. The actual solvent used depends upon cost and availability; it is generally gasoline, benzene or naphtha.

The collagen, after washing out the residual acid (using lime water to neutralize) may be made directly into gelatine, but it usually is dried at low temperature, yielding commercial ossein, which is used to manufacture gelatine.

Dentelles. The ossein made from button makers' bone is commercially known as "dentelles"; it is frequently called "spectacles" because of the fancied resemblance to eyeglasses, of pieces from which the round buttons have been cut.

Prepared Horn Pith. This is an ossein stock made from the cornillons or interior supporting bony core of the horns. As it is the only part of the osseous structure that does not come in contact with flesh, horn pith yields a singularly pure and high-class gelatine, and its porous structure renders easy its acidulation and subsequent extraction.

MANUFACTURE

General Features of Manufacture—The chemical aspect of glue and gelatine manufacture is really very simple. It apparently consists of a simple hydration of the collagen, or similar material, to give substances having new physical properties. Hence there is very little chemistry involved in the study of the manufacturing operations in this field. As a matter of fact, the chemistry is so simple that it is often unwittingly carried out on a kitchen stove. Thick soups which gelatinize when cold are really impure glue solutions.

Since strictly chemical reactions do not loom very large in glue and gelatine manufacture, most of the attention must be focused on the physical and mechanical operations. These essentially follow the pattern that has been developed as rule-of-thumb methods over hundreds of years. It would be a mistake, however, to assume that no advances have been made in recent times. Modern manufacturers have a good understanding of what is going on, they have introduced methods of careful control, and have made great improvements in the equipment used. Thus, though the principles of the old art of hundreds of years' standing still hold, the modern product is better and the costs less than in the past. This is characteristic of the type of progress which is made when scientific and technical knowledge is applied to the old manufacturing arts.

The manufacturing operations in the modern glue or gelatine factory may logically be divided into four divisions:

1. Preparing the stocks.
2. Heating the stock (misnamed "boiling").
3. Treating.
4. Drying the resulting glue or gelatine solution.

PREPARING THE STOCK

The last three operations listed above are essentially the same no matter what raw material is used, but the methods of preparation vary markedly, according to the stock used.

Washing and Liming—Hide, sinew and ossein stocks after a brief preliminary soaking or washing in water to soften them and remove dirt, salt, etc., are placed in successive baths of lime water of gradually increasing strength, in which the stock swells up and becomes "plump" so that it readily dissolves in the boiling kettle. The time required for liming varies with the stock and the season, always proceeding more rapidly in warm weather. Liming also removes hair from hide stock. Thick dry hide pieces may take as long as six months to lime, whereas fleshings or thin skivings from hides limed at the tannery are frequently all ready to cook, after washing and adjusting the hydrogen-ion concentration (pH). Coney stock, being very finely shredded, is usually "boiled" without liming. Hide pieces are often shredded or cut small to expedite the liming process, and the limes are sometimes "sharpened" with soda. The liming must not be too rapid, else a slimy mass results, which interferes with subsequent extraction. Practical experience is needed in this process, for an underlimed stock requires more time and heat to hydrolyze (thus injuriously affecting the quality of the glue), while overlimed stock is largely wasted in the washing process, which we will next consider.

The limed stock is taken from the lime pits (usually wooden vats sunk in the ground) and thrown into a washing machine, where it is thoroughly agitated in water until practically all of the lime is washed out, which may be determined by cutting open a piece of stock and testing the interior with indicators. The slight remaining alkalinity is neutralized by soaking in very weak acid. For very clear glues HCl is used, the resulting calcium chloride being very soluble; H_2SO_4 gives a precipitate of $CaSO_4$ which renders the glue more or less opaque. At this point sulfurous acid is often used to bleach and further plump the stock; alum is also used to bleach the stock and harden the jelly. After thorough draining the stock is transferred to the boiling tank or kettle. The stock is usually cooked at about pH 5.5, practice varying in different plants and with different stocks. (While conductivity water, especially purified and stored, has a pH of 7, ordinary distilled water, which has absorbed CO_2 from the air, has a pH of 5.5 to 6.) Some kinds of hide stock are now swollen in acid solution, and after regulating the pH are then boiled.

The "cone washer" is largely used in this country. The heavy wooden cone kneads, presses and turns the stock, effectively loosening the lime, which is carried away by a stream of water entering from a perforated standpipe at the center and flowing through perforated iron plates at the sides or bottom of the tub.

Fresh bone is sometimes boiled without even a preliminary washing; but if washed and degreased it yields a much clearer glue. Bones may be made into glue by the "sulfurous acid process," according to which bones are disintegrated by moist sulfurous acid gas or liquid SO_2 according to the equation:

$$Ca_3(PO_4)_2 + SO_2 + H_2O = Ca_2H_2(PO_4)_2 + CaSO_3.$$

Bones thus treated readily dissolve in the kettle; any acidity is neutralized with milk of lime, and the resulting "mud" after the calcium sulfite is oxidized by exposure to the air or by oxidizing agents, forms a valuable fertilizer.

Ossein. Preparation of the stock may also take the form of a leaching process. When crushed bone is treated with dilute HCl the mineral constituents of the bone are dissolved leaving behind "acidulated" bone, or ossein.

In the acidulation the main reactions are:

$$Ca_3(PO_4)_2 + 4HCl = 2CaCl_2 + CaH_4(PO_4)_2 \text{ (acid or monocalcium phosphate)},$$
$$Ca_3(PO_4)_2 + 6HCl = 3CaCl_2 + 2H_3PO_4,$$
$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2.$$

By careful control the amount of HCl is regulated to conform to the first formula.

From the acid solution the phosphoric acid is precipitated by the careful addition of milk of lime:

$$CaH_4(PO_4)_2 + Ca(OH)_2 = 2CaHPO_4 \text{ (dicalcium phosphate)} + 2H_2O$$
$$2H_3(PO_4)_2 + 2CaO = Ca_2H_2(PO_4)_2 + H_2O.$$

In both the solution and precipitation of the bone phosphate other secondary reactions go on at the same time. The "precipitated bone phosphate," as it is called, is calcined to produce "pyrophosphate" mainly $Ca_2P_2O_7$, which is largely used to line molds for casting copper, and to a lesser extent in the manufacture of "bone china." The "acid phosphate" is used in baking powders. In order to avoid an excess of lime, which would reproduce tricalcium phosphate, a filtered sample of the liquor is tested from time to time with molybdic acid solution, and the addition of lime stopped as soon as the failure of the ammonium phosphomolybdate precipitate to form indicates that no more free phosphoric acid or acid phosphate is in solution. Differential titration with phenolphthalein and methyl orange as indicators is a quicker method now used. If an excess of lime be accidentally added, the error can be retrieved by the addition of a suitable quantity of the acid liquor. The precipitate is pumped or forced by compressed air into a filter press and pressed free from calcium chloride.

The "Boiling" or Cooking Process—In the extraction (or cooking) of glue the prepared stock is subjected to the hydrolyzing action of hot water by which the collagen undergoes a change into glue. This process was formerly described as a "hydrolysis," proceeding in two stages according to the equations:

$$\underset{\text{Collagen}}{C_{102}H_{149}N_{31}O_{38}} + \underset{\text{Water}}{H_2O} = \underset{\text{Gelatine}}{C_{102}H_{151}N_{131}O_{39}};$$

$$\underset{\text{Gelatine}}{C_{102}H_{151}N_{31}O_{39}} + \underset{\text{Water}}{2H_2O} = \underset{\text{Semiglutin}}{C_{55}H_{85}N_{17}O_{22}} + \underset{\text{Hemicollin}}{C_{47}H_{70}N_{14}O_{19}};$$

but in dealing with substances of such variable composition, empirical formulae of this kind have no great significance. Indeed the whole boiling process seems rather to be the gradual breaking down of colloid complexes or "macromolecules" with accompanying changes in the amount of absorbed water, and to consist of physical as well as chemical changes.

The higher the temperature, and the longer the stock is exposed to it, the more rapidly these degenerative changes proceed and the lower the quality of the glue.

Hence it is desirable to extract the stock quickly and at as low a temperature as is commensurate with good operation.

Differences in stock necessitate the use of different types of kettles, or cookers, which may be grouped into two classes: 1. Open tanks; 2. Pressure tanks.

Open Tank. Hide, sinew, or ossein stocks are the ones usually boiled in the open tank. The open tank usually consists of a rectangular or round wooden tub having a closed steam coil over which a perforated false bottom of wood or iron is so placed to leave a circulating space between the two. Upon the false bottom is spread a layer of excelsior to serve as a rough strainer, and on top of this the stock is thrown to fill the tank. Sufficient clear water is then added to cover the stock, and steam turned into the coil. When the desired temperature is reached, the steam is cut down to the minimum needed to maintain it until a sufficiently concentrated "soup" or glue solution is obtained, which may be determined by chilling a sample in a small cup, or by taking the Baumé (specific gravity). After skimming off the floating grease, this solution, the "first run" as it is called, is drawn off for further treatment, the stock again covered with water and a second run made in like manner, the same process continuing as long as any glue is left in the stock. The last run or washwater is extracted at boiling heat and is usually so weak that it must be added to another kettle, or be mixed with a stronger preceding run or else be evaporated.

Hide, sinew and ossein stocks, since they are greatly softened by their preliminary liming, hydrolyze at comparatively low temperatures. As a rule three or four runs suffice to exhaust the stock; the residue is then dried for use as fertilizer. The tankage may contain fat or insoluble lime salts of fatty acids, in which event the grease is recovered by treating with H_2SO_4.

The temperature of "boiling" must in any event be above that favorable to bacterial growth, and usually begins at about 70° C. (158° F.), gradually increasing with each successive "run." The time required for boiling a "run" varies from one or two to six or eight hours, depending upon the pH and nature of the stock and the temperature used. Several new types of open tanks have been patented in which the water is caused to circulate through the stock by mechanical means (central standpipe), the object being to keep the temperature as uniform as possible throughout the tank; but with the ordinary tanks the stock is not disturbed, or, at most, occasionally stirred with a long pole to open it up to aid convection.

Pressure Tank. The pressure tank process of "boiling" glue is largely used with untreated bones. The tanks consist of vertical steel or iron cylinders capable of withstanding several atmospheres pressure, having convex ends and large manholes at the top for filling and at the bottom for discharging the steamed bone.

The bones may be heated with water under pressure (10-20 lbs.), the water may be allowed to trickle in from above while steam enters below (English process) or the condensation of the steam may supply the necessary water (French process). The successive runs of glue obtained are more concentrated than by the open tank method. They are drawn off from time to time through a perforated false bottom. With fresh bones a large quantity of bone grease is incidentally set free and skimmed off.

Treating the Liquors—With ordinary glues, the liquors, after adjusting pH and filtering, are concentrated in a vacuum evaporator if necessary, preserved with antiseptics (usually $ZnSO_4$), and run directly into galvanized iron pans or "coolers" where they set to a jelly, a process which frequently has to be assisted by artificial refrigeration if the "boilings" are weak or the weather warm. The Kind continuous chiller, cutter, and spreader receives the cooled liquor, chills it on a belt to a continuous sheet of jelly, which is automatically transferred to nets. (See Figure 1.) White or opaque glues are made by stirring in the desired quantity of zinc oxide, titanium dioxide, or other whitening material, before pouring the liquor into the pans.

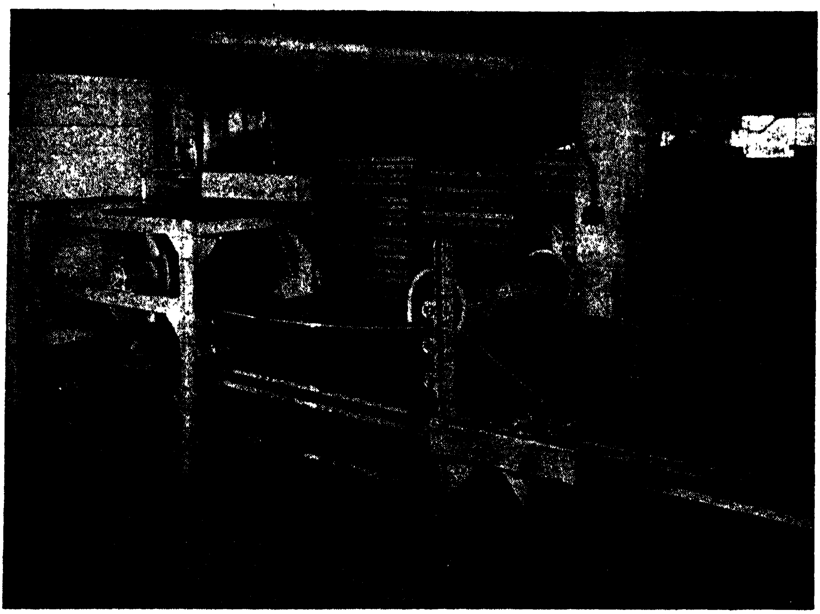
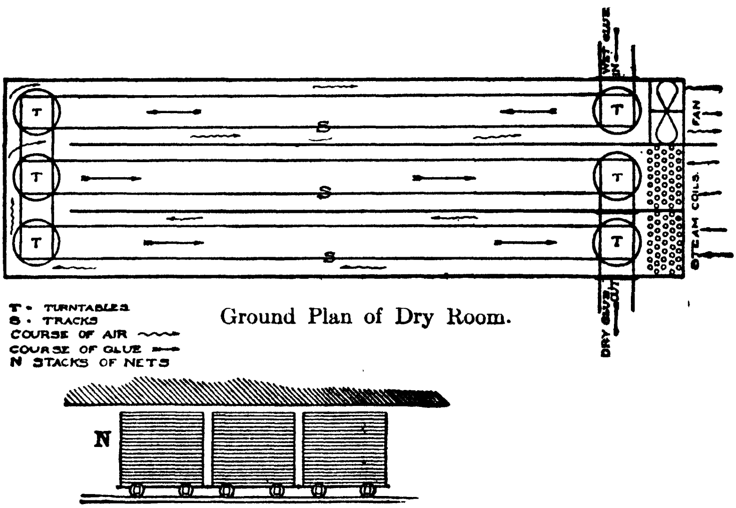


FIG. 1. The Kind Continuous Chiller, Cutter, and Spreader.

Clarification—Although ossein generally yields very clear liquors, in order to secure the extremely clear jellies required for some glues and food gelatines, both chemical and mechanical treatment of the liquors are resorted to. The chemical methods consist in forming within the liquor a flocculent precipitate which tends to absorb and carry down with it the turbidity-producing particles. Alum, phosphoric acid or sulfurous acid followed by milk of lime, and blood or egg albumen are among the substances which have been used. After the addition of albumen, the liquor must be heated to produce coagulation which has an injurious effect on its jellying strength. The modern method is to use a pressure filter, with a "filter-aid" like paper pulp or diatomaceous earth. The treated solution is filtered through a filter press or a paper pulp or bone char filter, and then run into the pans.

Drying—The "coolers" or molds are dipped for an instant into hot water to loosen the jelly blocks, which, by means of stretched wires operated by hand or arranged in special glue cutters, are sliced into sheets of desired size and thickness. In the older methods, these jelly slices are spread upon galvanized or linen nets, and high piles of the nets (called "stacks") are mounted upon wheeled trucks and are run into a dry room against a current of air which has been heated by a large steam coil. For forcing the air through the dryer, blower or pressure fans, and suction or exhaust fans are both used. (See Figure 2.)

As the drying proceeds and the glue "skins over," it can be pushed nearer and nearer to the hot coil in front of which it gets its final "baking"; the stack is then withdrawn through a side door and the finished dry glue taken from the nets to be broken, ground, and packed into barrels, bags or packets.



Side view of one alley.

FIG. 2. Side View of Dry Room.

Drying[4] frequently causes the manufacturer much concern, for weak jellies are apt to soften and stick to the nets or even run entirely through to the floor; and besides the fresh jelly is open to the inroads of bacteria whose action may result in black or offensive-smelling glue.

A variety of new methods for drying glue and gelatine have been patented, and some of these are now in use; for example, large drum dryers, on which a thin layer of liquor may be applied to the rising side of the drum and the dried glue scraped off before the revolution is completed. "Pearl" glue is made by dropping glue liquor into chilled liquid immiscible with water (*e.g.*, carbon tetrachloride and gasoline mixtures), drying the spheres of glue jelly that result, and re-using the chilling liquid. Residual vapors of the volatile chilling fluid may be trapped by adsorbents such as activated carbon or silica gel and recovered for re-use. Spray drying has been tried, but yields a rather bulky product. The success of such special processes must depend upon the skill applied in their operation, the cost of competing processes, and the form of finished product desired.

[4] See Chapter 2 for a discussion of this unit operation of drying.

More recently, modern air filters have been introduced, and also the use of ultra-violet lamps to "sterilize" the air. These improvements are important in the drying of gelatine, for whether this be used for food or for photographic purposes, extreme clarity and freedom from bacteria and molds are desiderata. Preservatives are forbidden in food gelatine, and if sulfurous acid has been used to bleach the stock, any traces of it remaining may be oxidized into harmless sulfate by hydrogen peroxide.

LIQUID GLUES AND GLUE SUBSTITUTES

By extension of the original meaning of the term, "glue" has acquired a general meaning. In popular parlance, anything that may be simply spread and binds surfaces together may be termed "glue"; *e.g.*, silicate of soda which is used in making corrugated paper, mucilages made of gum arabic or of dextrine,[5] and solutions of casein,[6] rubber,[7] and low-viscosity cellulose nitrate.[8] Many of the "liquid glues" used in the paper box and allied industries are based on solubilized starches[9] or dextrines; but the liquid fish glues are made from the fish stock previously referred to. Animal glues may be kept in a fluid condition by the addition to their solutions of various materials such as acetic acid, calcium chloride, etc. The "glue" on our postage stamps is a variety of dextrine. The total tonnage of glue substitutes used each year is enormous, and many of the substitutes are much more suited to their special uses than glue would be, besides being cheaper.

The question of the more general meaning of "glue" is by no means a purely academic one. For example, when a regulation stated that packages of a certain type should be "glued," a court at first held that only animal glue could be used.

While the joints made by glue are very strong when it is properly applied, they are readily ruined by water or extreme dampness. But for joints there is no largely used substitute for animal glue. In veneers, on the other hand, concentrated dispersions of starch (usually tapioca) in caustic soda solutions have been extensively used to substitute animal glue. Casein-lime dispersions, and solutions of soybean protein are also used, the former being quite resistant to moisture. More recently, synthetic resins have been used to produce plywood which is waterproof.

TESTING THE PRODUCTS

None of the so-called chemical tests for glue have much practical significance, but by experience it has been learned that glues made from certain stock and possessing certain physical characteristics give good results when used for certain purposes. The most important physical characteristics are the viscosity and the jelly strength of a solution of the glue, and in order to have some means of expressing these, numerically arbitrary standards have been selected which cover the wide range of commercial glues and gelatines. The following table gives the

[5] See Chapters 36 and 40.
[6] See Chapter 44.
[7] See Chapter 39.
[8] See Chapter 38.
[9] See Chapter 36.

viscosity and jelly strength of such standards, determined on solutions of 25 grams of glue in 100 c.c. of water.[10]

TABLE 3—THE VISCOSITY AND JELLY STRENGTH OF STANDARD GLUES

Standard	*Alexander's Grades **				*Equivalent Grades*				
					Peter Cooper	*Bogue*	*Nat'l Assn. of Glue Mfrs.*		
	Viscosities (in secs.) at 80° C. Solution 25-100	*Allowable Variation of Viscosities (in secs.)*	*Jelly Strength (in ozs.) at 10° C.*	*Jelly Strength (in gms.) at 10° C.*	*Grade No.*	*Grade No.*	*Grade No.*	*Jelly Strength in grams on Bloom Gelometer*	*Viscosity in Millipoises*
10	15½	±¼	......	......	......	......	1	10 or over	20
20	16	±¼	......	......	......	1	2	27 "	24
30	16½	±¼	......	......	2	2	3	47 "	28
40	17	±¼	60	1701	1⅞	3	4	70 "	32
50	18	±½	82	2324	1¾	4	5	95 "	37
60	19	±½	104	2948	1⅝	5	6	122 "	42
70	20	±½	126	3572	1½	6	7	150 "	47
80	21	±½	148	4196	1⅜	7	8	178 "	53
90	22	±¾	170	4820	1¼	8	9	207 "	60
100	23	±¾	192	5443	1X	9	10	237 "	67
110	24	±¾	214	6067	1	10	11	267 "	75
120	25	±1	236	6691	1 extra	11	12	299 "	83
130	26	±3	258	7314	A extra	12	13	331 "	92
140	28	±5	......	......	......	......	14	363 "	102
150	34	±8	......	......	......	......	15	395 "	113
160	40	±12	......	......	......	......	16	428 "	125
							17	461 "	138
							18	495 "	152
							19	530 "	167
							20	565 "	183
							21	600 "	200

* The tests here given in a series are strictly *comparative*, against *standard* samples, and slight variations of temperature do not materially influence the results. When using the official methods of the N.A.G.M. referred to, where *absolute* figures are taken, *extreme care* must be used in temperature control, when taking viscosities and jelly strengths.

Official Tests—The National Association of Glue Manufacturers have a Technical Division, which has established standard test methods. They decided on the following procedure:

Concentration of test solutions, 12.5 per cent, *i.e.,* 1 part by weight of glue to 7 of water.

Soak at 10-15° C. until soft (about 12 hours or overnight).

Melt at 62° C. within 15 minutes.

Take viscosity at 60° C. with a special pipette, calibrated so that its readings may be converted by a curve or table, into millipoises. The highest grades of commercial glue range from 200 to 220 millipoises and the lowest grades from 30 to 35 millipoises.

Jelly strength is taken with the Bloom Gelometer, an automatic machine measuring the weight in grams required to depress a plunger whose diameter is 12.7 mm. (½ in.) to a depth of 4 mm. into a 12.5 per cent solution chilled for 16 hours to a temperature of 10 degrees ± 0.001. The highest grades of glue take 440 to 460 grams, the lowest grades, 30 to 40 grams.

[10] See Alexander, J., J. Soc. Chem. Ind. *25,* 158 (1906).

The slightest difference in temperature and other conditions may greatly affect absolute determinations of this kind. In fact, the use of the instruments is limited to those who can take the extreme care which is essential to proper results.[11]

Other Tests—In addition to the physical characteristics already discussed there are several other properties of glue which serve as tests in determining the suitability of a particular glue. The glue solution may be "painted" on a piece of white paper with a little aniline color, and spots or "eyes" appear roughly proportional to the amount of *grease* present. *Foam* is determined by agitating the solution. Like grease, foam is estimated on a comparative basis. Generally, grease prevents foaming.

The *comparative set* of glue can be found by allowing hot solutions to cool and observing the speed with which the jellies harden. Very often it is desirable to allow glasses of glue to stand uncovered for several days under varying conditions to observe relative *keeping qualities* of the jellies. Notice is taken of the growth of mold, odors of decomposition, etc. If the keeping property under special conditions is desired, these conditions are simulated.

There is no one test that can have a general application to test the *binding or adhesive strength* of glue. The glue must be tried under actual working conditions. As before suggested, test figures must be read in the light of experience, and no one of them is sufficient to determine the value of a glue. The only test that can be accepted as conclusive is a practical trial of the glue under actual working conditions, which vary in each case.

USES OF GLUE AND GELATINE

The general public which does not use glue and gelatine directly, has little notion of their manifold uses. These class the manufacture of glue and gelatine as a key industry. Let us first epitomize the main uses of glue under several classifications.

Adhesive:

Wood joints in furniture, musical instruments, house-trim, toys, coffins, etc.
Veneers for furniture, ply-wood, shipping packages, etc.
Paper boxes and packaging—"setting up," covering, sealing, etc.
Leather goods and belting—pocket books, machinery belting, etc.
Bookbinding and padding—books, pamphlets, writing tablets, etc.
Gummed cloth and paper tape—for sealing packages, binding, etc.
Abrasives—making sand, garnet, and emery papers, belts, and wheels.

Sizing:

Paper—bonds, government currency, wall-, coated-, and writing paper.
Textiles—silks, woolens, carpets, shade-cloth, etc.
Calcimine—for walls, ceilings, etc.
Hats—straw hats are stiffened with technical gelatine or glue.

[11] For details, see Ind. Eng. Chem. *16,* 310 (1924); also Alexander, J., in "Allen's Commercial Organic Analysis," fifth edition, Vol. 10, p. 175 (1933).

Barrels—to prevent penetration of oil and alcohol in wood barrels.
Scenery—is sized and then painted with glue distemper colors.

Compositions:

Matches—to form and bind heads and reduce flare.
Fireworks—as adhesive, and to "tame" explosive mixtures.
Dolls' heads—including flexible "rubber" heads.
Printers' rollers—a glue-glycerine mixture, distributes ink.
Gas tubing—a glue-glycerine flexible tube covered by textile layer.
Moldings—for walls, picture frames, etc.
Flexible molds—to make plaster of Paris casts, etc.
Hectographs—made with technical gelatine and glycerine.
Spangles and millinery ornaments—for decorative purposes.

Colloidal Protector or "Colloidizer":

Electro-deposition of metals—electroplating, refining, to give fine-grained deposit and prevent "treeing."
Making colloidal precipitates—colors, insecticides, pharmaceuticals.
Photography—in film emulsions for X-ray, moving pictures, military and all other uses.
Inhibiting crystallization—gelatine in ice cream; glue in lead triazide to diminish sensitiveness to explosion.
Plaster of Paris—even in minute quantity glue retards the setting.
Making emulsions—in pharmacy.

Miscellaneous Uses:

Gelatine printing or "collotype"—technical gelatine and bichromates give plates from which printing presses can print.
Glass chipping—in drying, glue tears off the surface of glass, giving a rough "frosted" effect.
Pharmacy—for coating pills, making hard and flexible capsules, etc.
Bacteriology—gelatine is used in media, ultrafilters, etc.
Medicine—gelatine may be used intravenously in shock; also as an invalid food, and in special dressings.
Food—gelatine is extensively used in a variety of food combinations.

Since glues and gelatines may differ so widely in working properties, depending upon which of the many available grades or qualities is taken, it is obvious that for each particular use only appropriate grades should be selected. Apart from this choice of grade, proper preparation and skillful application are essential to good results. Glue is quickly hydrolyzed by acids and alkalies, and cold glue solutions are not adhesive. The following precautions help avoid trouble:

(1) Use definite proportions by weight. (2) Soften glue thoroughly by soaking in *cold* water. (3) Melt on a water bath, avoiding prolonged heating which injures glue. (4) Fit the strength of the solution to the work. (5) With joints, proper pressure (500-1000 lbs. per sq. in.) is necessary until the glue has set *and* dried. Glue must be applied hot.

FOOD GELATINE

Edible gelatine is made from carefully selected, clean, raw material under sanitary conditions, and is free from objectionable substances. Careful chemical control is necessary, for foods are protected by very stringent laws. Food gelatine is substantially free from taste and odor, and the stock is so highly purified that the resulting gelatine is nearly colorless. Even the clearest bouillon made at home would not, if dried, yield a salable food gelatine, for it would have too much taste, color, and odor.

Gelatine contains some of the amino acids essential to growth and repair, and has long been used for rebuilding tissue after wasting disease (*e.g.*, "calves' foot jelly").

The subjoined chart (Figure 3) shows some of the many uses of food gelatine. In marshmallow confectionery, it inhibits the graining of sucrose and facilitates incorporation of the leavening air. In ice cream, besides opposing crystallization of lactose and the formation of "gritty" ice crystals, it leavens the beaten mass and opposes curding of the irreversible colloid casein, thus favoring the digestibility of both casein and milk fat. Hence experienced pediatricians have recommended it as an addition to cow's milk in infant feeding; for compared to mother's milk, cow's milk is deficient in protective colloids.[12, 13, 14]

ECONOMIC ASPECTS OF GLUE AND GELATINE

Glue and gelatine are important raw materials in a wide variety of manufacturing operations, as reference to the listed uses will indicate. The U. S. Census figures show that in 1937 the total value of the glue and gelatine made in this country was over 41 million dollars, representing a total production of over 121 million pounds, of which over a third was green-bone glue and the balance hide and extracted-bone glue. The production of food gelatine for 1937 was nearly 23 million pounds, worth nearly 8 million dollars, and of inedible and photographic gelatine nearly 7½ million pounds, worth about 3⅓ million dollars. This takes no account of the importation and export figures, which are now apt to change materially. Imports of glue were only 4 million pounds in 1937, and have declined sharply since.

The price of glue and gelatine varies greatly in accordance with quality and with market conditions. In recent years, the price of bone glues has been roughly from 10¢ to 16¢ per pound, and of hide glues from 12¢ to 25¢ per pound. Gelatines have been worth from 30¢ to a dollar or more per pound, high prices being paid for very thin-cut gelatine sheets of high strength, very light color, and extreme purity.

While in many cases the peculiar physical and chemical properties of glues and gelatines render it difficult if not impossible to use substitutes, in other cases they have lost out to cheaper or more desirable substitutes. Thus vegetable glues are now mainly used in covering paper boxes with decorative papers, though for

[12] Jacobi, A., "The Intestinal Diseases of Infancy and Early Childhood, p. 62 *et seq*. (1890).
[13] Koplik, H., "Diseases of Infancy and Childhood" (1902).
[14] Alexander and Bullowa, Arch. Pediatrics *27*, 18 (1910).

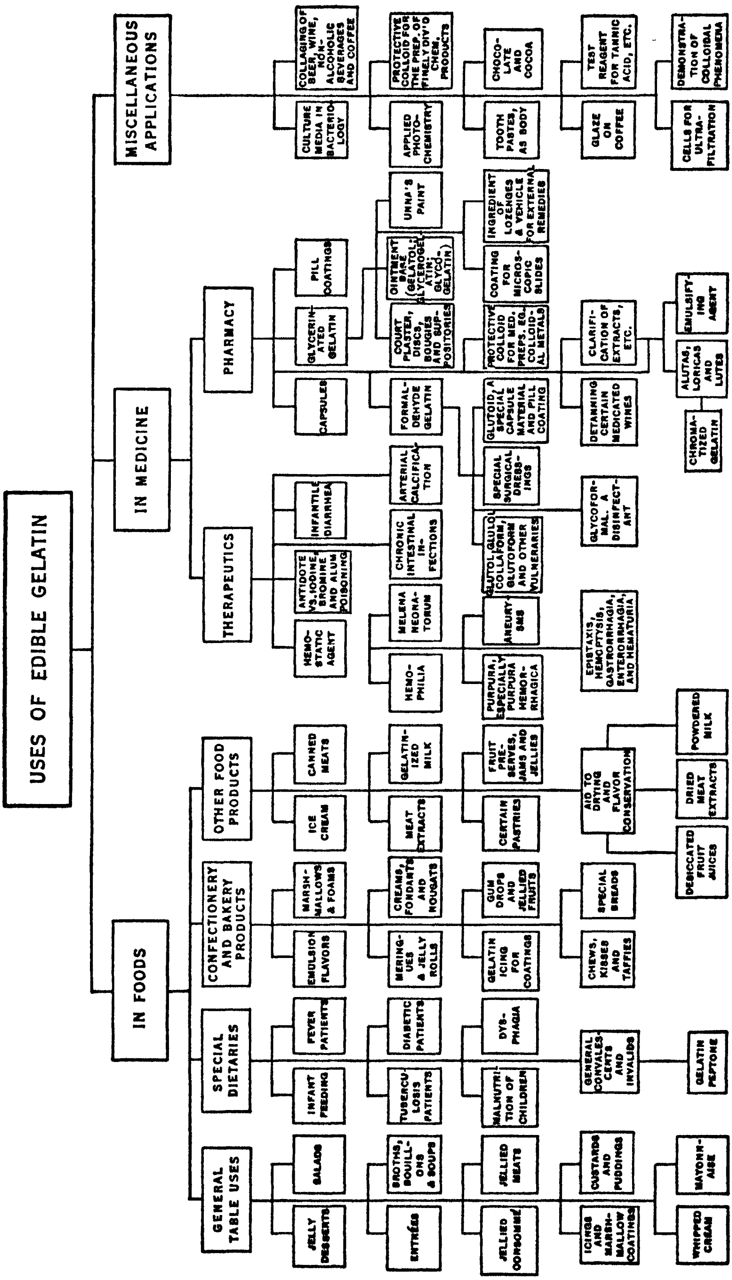


Fig. 3. Uses of Edible Gelatin.

"setting-up" and for high-speed folding box machines animal glue holds its own. The Census lists for 1937 a production of 330 million pounds of vegetable glue worth about 6½ million dollars, but this probably includes liquid vegetable glues containing much water, as well as certain starch-alkali glues used in making veneers, and perhaps labeling glues for bottle labeling machines and sealing glues for cartons. But the production and uses of glues and gelatines continue to expand.

READING LIST

GENERAL

Bogue, R. H., "The Chemistry and Technology of Gelatine and Glue," McGraw-Hill Book Co., New York (1922).

Lambert, T., "Glue, Gelatine, and Their Allied Products," second edition, C. Griffen & Co., London (1922).

Kissling-Bremen, R., "Leim und Gelatine," Wissenschaft. Verlag., Stuttgart (1923).

Alexander, J., "Glue and Gelatin," A.C.S. Monograph No. 11, Chemical Catalog Co., New York (1923).

MANUFACTURE AND USES

Cambon, V., "Fabrication des Colles et Gelatines, Traitment des Animaux Abbatus," Dunod, Paris (1924).

Davidowsky, F., "Die Leim und Gelatine Fabrikation," sixth edition, A. Hartleben, Vienna (1925).

Thiele, L., "Die Fabrikation von Leim und Gelatine," second edition, M. Jänecke, Leipzig (1922).

Goebel, E. and Gerngross, O., "Chemie und Technologie der Leim- und Gelatinefabrikation," T. Steinkopff, Dresden (1931).

Keghel, M., "La Fabrication des Colles," Gauthier-Villers et Cie., Paris (1926).

"The Manufacture of Glue and Gelatine," National Provisioner Co., New York (1928).

Sheppard, S. E., "Gelatin in Photography" (1923).

ANALYSIS AND TESTING

"Allen's Commercial Organic Analysis," fifth edition, Vol. 10, pp. 119-196, P. Blakiston's Son & Co., Philadelphia (1933).

Rideal, S., "Glue and Glue Testing," third edition, revised by H. B. Stocks, Scott, Greenwood & Co., London (1926).

Teesdale, C. H., "Modern Glues and Glue Testing," Periodical Pub. Co., Grand Rapids, Mich. (1923).

CHAPTER 44

CASEIN AND ALLIED MATERIALS

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INTRODUCTION

Occurring in the milk of all animals, casein belongs to the most complex group of nitrogenous organic compounds known as proteins. Of the industrially important animal proteins, casein is most highly standardized in composition, properties and applications. Indeed, it has been more extensively investigated from both the industrial and academic points of view than any other protein of technological importance.

Of increasing importance and potentially expanding industrial uses are the vegetable protein materials which are now being intensively investigated as raw materials for the preparation of proteins. In this group are the meals prepared from oil-bearing seeds, such as soybean meal, cottonseed meal, peanut meal and linseed meal. Also worthy of consideration is the protein, zein, isolated from the waste liquors of the corn starch industry, and the less important proteins from alfalfa and wheat.

In this chapter, these vegetable proteins of growing industrial importance are briefly compared in chemical properties and uses to those of casein, which due to its technological seniority will be taken up more thoroughly. As referred to in this chapter, casein is the protein obtained from cow's milk only.

HISTORICAL

Although casein has been known and used as a food by humanity from the earliest times, and although its uses in wood gluing and as a binder in house paints date back to the Middle Ages, its technical utilization in chemical manufacture did not occur until recent times. The manufacture of casein glue as an industry seems to have started in Switzerland or Germany in the early years of the nineteenth century.[1] The first commercial product of casein in the United States was made shortly before 1895-1900 when it was initially used in this country as an adhesive or binder in a cold water paint, and in water-resistant paper coatings.[2]

[1] Sutermeister, E. and Browne, F. L., "Casein and Its Industrial Applications," second edition, Chapter 8, p. 233, Reinhold Publishing Corp. (1939).
[2] Snell, R. M., "Superior Facts," Vol. 5, No. 3, The Paper Makers Chemical Corporation and Associates (1931).

During the years 1900-1916, its use in paper coating spread and became common practice. Improvements were made in the manufacture of cold water paints and the manufacture of casein was greatly improved and extended. Casein glues were used only to a limited extent in the United States before 1916-1917, when the need of water-resistant glues for airplane construction in the first World War led to their development.[1] The use of this protein in plastics started commercially in Germany shortly after 1900, while the first production of casein plastics took place in England shortly before the first World War, and in the United States a few years later.[3] From 1920 to the present, while its quality has been further improved and domestic production has trebled, casein has found application as a raw material in many industries.

THE RAW MATERIAL

Occurrence in Milk—Casein occurs in milk in the proportion by weight of approximately 3%, along with other substances as follows:[4] water 87%, butter fat 3.7%, lactalbumin 0.5%, lactoglobulin 0.05%, lactose 5.0%, citric acid 0.2% and inorganic substances determined on analysis as ash 0.7%. In milk, casein is present in colloidally dispersed micelles which have a mean diameter of only 90 $m\mu$ (1 $m\mu = 10^{-7}$ cm.) and a range in diameter from 8 to 200 $m\mu$.[5] These micelles in skim milk contain casein in combination with calcium as a calcium caseinate, and also other substances such as calcium and magnesium phosphates. The calcium caseinate and calcium phosphate in these micelles have long been regarded[6] as united not as a stoichiometric compound but as a colloidal aggregate such as a "calcium caseinate and calcium phosphate complex" or a "calcium phosphocaseinate." However, the extent of this union is uncertain since certain evidence indicates that the calcium caseinate and calcium phosphate are, at least in part, independently dispersed phases.

Chemistry—Composition and Structure—Casein is a phosphoprotein and so belongs to one of the more complex subdivisions of the proteins. It has the following typical elementary analysis,[7] by weight: carbon, 52.96%; hydrogen, 7.05%; nitrogen, 15.65%; sulfur, 0.72%; phosphorus, 0.85% and oxygen, 22.77%. Since casein is now believed to be a mixture[8] of three, or possibly four, proteins, its empirical formula is not significant other than as an aid to visualize the proportion of these elements. Hammersten formerly proposed the empirical formula $C_{172}H_{274}N_{44}SPO_{55}$.

It is well established that proteins are condensation products of amino acids, in which the latter are united through the peptide linkage, —NH—CO—, with the elimination of water. By means of acid or alkaline hydrolysis of casein, 23 different crystalline amino acids have been isolated[9] and doubtless others will be iso-

[3] Sutermeister, E. and Browne, F. L., ibid., Chapter 7, pp. 181-5.
[4] Associates of Rogers, "Fundamentals of Dairy Science," Chapter 1, p. 16, Reinhold Publishing Corp. (1935).
[5] Nichols, J. B., Bailey, E. D., Holm, G. E., Greenbank, G. R. and Deysher, E. F., J. Phys. Chem. *36*, 1303 (1931); Lait *12*, 748 (1932).
[6] Sutermeister, E. and Browne, F. L., ibid., Chapter 1, p. 13.
[7] Hammersten, O., Z. Physiol. Chem., 7, 227 (1883).
[8] Schmidt, C. L. A., "Chemistry of Amino Acids and Proteins," Chapter 3, p. 174, Charles C. Thomas (1938).
[9] Sutermeister, E. and Browne, F. L., ibid., Chapter 2, pp. 36-40.

lated in the future, since an appreciable fraction of the molecule is still unaccounted for.

Although it has undoubtedly been the subject of more chemical investigations than any other protein, until recently casein was considered as a chemical individual unusual because of its ease of isolation in a quite pure state. Researches during the past decade, however, indicate that it is not an homogeneous substance or chemical individual and so the term "molecular weight" is misapplied to casein sols—it is now regarded[10] as a mixture of protein particles of different micellar weights ranging in weight from 75,000 to 375,000, depending on factors such as the past history of the casein, its method of preparation, and pH.

Casein is converted into paracasein by the action of the enzyme rennin. Although no adequate explanation has been offered for this transformation, most theories postulate the formation of paracasein by a physico-chemical process in which the chemical composition of the casein molecule remains unaltered.[11] (The "rennet" casein and "acid" casein of commerce differ however in that commercial "rennet" casein has a higher ash content and is not as easily dispersed by alkaline "solvents".)

Properties—Casein is a non-crystalline, light straw-colored solid having a very faint, pleasant odor. Somewhat hygroscopic, its normal moisture content is about 8-10%. Prolonged heating to 200-275° F. in the absence of added water slowly brings about a loss in weight with accompanying decomposition and darkening, while heating at 400-450° F. causes charring. Like other proteins, it is susceptible to denaturation, a change in the protein resulting in decreased solubility. This may be produced by the action of acid and alkali, alcohol and acetone, heat, light, high pressures, or by other means. While heat results in decreased solubility of the protein, it does not produce irreversible coagulation as in the case of blood or egg albumin. However, heat will coagulate casein from skim milk or from sodium hydroxide solutions having pHs above 6.5.[12] The isoelectric point of casein is at pH 4.6, this being the pH of minimum electric charge and so the lowest stability of dispersion.

By virtue of its amino and carboxyl groups it is amphoteric and so can combine[13] with acids below its isoelectric point, or with bases above it. The salts formed are electrolytic and dissociate into ions in aqueous solutions, the casein being in the cation on the acid side of the isoelectric point and in the anion on the alkaline side.

Solutions of casein are not true solutions but are colloidal dispersions and are referred to as "sols." They are optically active, rotating the plane of polarized light to the left.[14] When casein dispersed in dilute alkali is allowed to stand for several days at room temperature (or better 37° C.) racemization occurs and the optical rotation of the solution decreases to a low, but constant value.[11] Casein lowers the surface tension of water and because of its property of form-

[10] Sutermeister, E. and Browne, F. L., ibid., Chapter 2, pp. 35-36.
[11] Sutermeister, E. and Browne, F. L., ibid., Chapter 2, p. 49.
[12] Zoller, H. F., Science *52*, 614 (1920).
[13] Grynberg, M. D., Biochem. Z. *262*, 272 (1933); Loeb, J., "Proteins and the Theory of Colloidal Behavior," Chapter 1, McGraw-Hill Book Co. (1922).
[14] Robertson, T. B., "Physical Chemistry of the Proteins," Chapter 14, Longmans Green (1918).

ing films at the surface of the water it is used as a protective colloid [14a] or stabilizing agent [15] for emulsions of either water-in-oil or oil-in-water types.

Aqueous solutions of casein are relatively viscous at comparatively low concentrations. The viscosity of commercial caseins varies widely according to the method of preparation, such as type of acid, acidity, and degree of heating used in the preparation, etc. Heating above 60° C. during its preparation or during the subsequent dispersion of it increases the viscosity of its solutions, though, due to hydrolysis, heating of solutions that are appreciably alkaline causes a decrease in viscosity.

Solubility and Salts—As casein contains [16] 2.3 times as many carboxyl as amino groups, its acid characteristics predominate. Thus it is more readily and completely dispersed in aqueous alkalies than in aqueous acids. It is a stronger acid than carbonic acid and will displace carbon dioxide from carbonates.

The degree to which casein is dissolved in alkaline solutions depends on the proportion of alkali present. It may be regarded as infinitely soluble when the amount of alkali is sufficient to convert all the casein to alkaline caseinate, though in this case the casein is only partly dissolved.[17] It is readily soluble in dilute aqueous solutions of the caustic alkalies, ammonium hydroxide, and the alkaline carbonates and phosphates. Solution in the alkaline earths takes place more slowly. Alkalies commonly used are ammonium hydroxide, 26° Bé. (5-10), borax (12-20), soda ash (7-10), caustic soda (3-6), triethanolamine (12-18), while others, including trisodium phosphate, sodium silicate, morpholine and other organic amines, or mixtures of these alkaline "solvents" are also employed. (The figures in parentheses represent the parts by weight generally required to disperse 100 parts of commercial casein of varying solubility.)

As casein is only sparingly soluble in aqueous acids, dispersions with acidities below its isoelectric point are not of technological importance. (A casein that can be dispersed in moderate concentrations at low acidities, e.g., pH 2.0-3.0, has recently been developed. These dispersions, however, are more viscous than those produced with alkalies, and jellies are formed at concentrations as low as 9% solids.) It is insoluble in most of the common organic solvents, but it is said to be soluble in alcohol [18] containing either hydrochloric acid or sodium hydroxide, and in certain anhydrous acids or mixtures of these acids.

Since casein has an indefinite "combining equivalent," caseinates formed from alkali, alkaline earths, heavy metals, organic bases, etc., are indefinite. Consequently, the term sodium caseinate, for example, does not imply a fixed ratio of sodium to casein. Numerous salts of casein in powdered or granular form have been prepared either by evaporation of their solutions [19] or by subjecting an intimate mixture of moist casein and the salt-forming chemical to high pressures,

[14a] See Chapter 43 for a discussion of protective colloids.
[15] Cheesman, D. F. and King, A., Trans. Faraday Soc. *34*, 594 (1938).
[16] Sutermeister, E. and Browne, F. L., ibid., Chapter 3, p. 81.
[17] Sutermeister, E. and Browne, F. L., ibid., Chapter 3, p. 78.
[18] Bancroft, W. D. and Ridgway, S. L., J. Phys. Chem. *36*, 1285 (1932).
[19] Sutermeister, E. and Browne, F. L., ibid., Chapter 3, pp. 84-86; Tague, E. L. "Casein, Its Preparation, Chemistry and Technical Utilization," Chapters 3 and 4, D. Van Nostrand Co., Inc. (1926).

followed by drying and grinding.[20] By the latter procedure, salts of casein with most of the common alkalies, alkaline earths and heavy metals have been formed.

Reaction with Formaldehyde—The ability of casein and its salts to be rendered water-resistant by the action of formaldehyde is made use of in most industrial applications of casein. This reaction, in which quite stable compounds are formed, has been studied by many workers.[21] Besides formaldehyde, other aldehydes, hexamethylenetetramine, soluble aluminum salts, and soluble chromates followed by exposure to light, are used to make casein water-resistant. Other reactions of casein that are of importance are those with carbon disulfide,[22] as used with lime for wood gluing; and iodine,[23] for the production of iodocasein. Casein can also be methylated,[24] and benzoylated.[25]

Hydrolysis—Moist casein or caseinates are subject to decomposition by chemical hydrolysis, by enzymatic hydrolysis, or by the attack of microorganisms. Hydrolysis progresses with the breaking down of the casein into smaller compounds. At each cleavage a molecule of water is added. The picture is as follows: casein $\rightarrow$ metacaseins $\rightarrow$ caseoses $\rightarrow$ peptides $\rightarrow$ amino acids. The degree of hydrolysis depends among other things on the concentration of acid or alkali, degree of heat and pressure, or enzyme used.

In order to prevent the attack of microorganisms, preservatives and fungicides such as para-chlor-meta-cresol, ortho-phenyl phenate, pentachlor phenol, other phenols, or their alkaline salts are generally incorporated with casein and caseinates in their industrial uses,—particularly if the solutions are to be kept for a few days or longer before using.

MANUFACTURING PROCEDURE

The manufacture of casein consists of its removal from skim milk (in which casein is present as a calcium caseinate, or "complex") in a form relatively free from calcium, or as paracasein; and further it consists of converting the curd into a more stable and commercially marketable dried product. The operations performed in the manufacture of casein are: precipitation, washing, de-watering, breaking up the curd, drying, and grinding and packing the product.

Coagulation—The casein micelles in skim milk can be coagulated[26] by the addition of alcohol or salts, by heating, by electrodialysis, by bringing the pH of the milk close to the isoelectric point of casein, or by the action of rennin. Casein

[20] Dunham, H. V., U. S. Patent 2,005,730 (June 25, 1935); 2,103,153 (Dec. 21, 1937); 2,108,582 (Feb. 15, 1938); British Patent 453,305 (Sept. 8, 1936); French Patent 784,-208 (Jan. 15, 1935).

[21] Sutermeister, E. and Browne, F. L., ibid., Chapter 2, pp. 57-58; Lloyd, D. J., "Chemistry of the Proteins and Its Economic Applications," Chapter 15, pp. 258-9, J. & A. Churchill, London, England (1926); Dyacheuko, P. F. and Shelpakova, K. F., Colloid J. (U.S.S.R.) *4*, 337-45 (1938).

[22] Aktiebolaget Lauxein-Casco, British Patent 376,748 (July 13, 1932); Davidson, G. and Laucks, I. F., U. S. Patent 1,691,661 (Nov. 13, 1928); Lindstaedt, F. F., U. S. Patent 1,833,527 (Nov. 24, 1931).

[23] Sutermeister, E. and Browne, F. L., ibid., Chapter 2, p. 53; Yaichnikov, I. S., J. Gen. Chem. *3*, 1-4 (1933).

[24] Skraup, Z. H. and Krause, E., Monatsch. f. Chem. *30*, 447 (1909); Geake, A. and Nierenstein, M., Biochem. J. *8*, 287 (1914); Edlbacher, S., Z. Physiol. Chem. *107*, 52 (1919).

[25] Kimura, H., Acta Schol. Med. Univ. Imp. Kyoto *11*, 117 (1928).

[26] Sutermeister, E. and Browne, F. L., ibid., Chapter 1, pp. 18-24.

is isolated from skim milk commercially in the United States by two of these methods, (a) changing the pH of the skim milk to approximately the isoelectric point, pH 4.6; or (b) by the addition of a small amount of rennin. When prepared by the former method the casein is referred to as an "acid" casein, and by the latter as "rennet" casein (paracasein).

The coagulation according to (a) is generally accomplished by adding muriatic or sulfuric acids to the previously skimmed milk, though other acids or an acidic or sour whey may be used. Much less commercial casein is precipitated by the action of rennet than by method (a), as rennet casein is used almost exclusively by the plastics industry. Due to its higher ash and relative insolubility in solutions of most alkalies it is unsatisfactory for use in the other manifold manufacturing operations in which "acid" casein is used. Whey from rennet coagulation is also satisfactory for production of milk sugar.

Careful control during the precipitation of the curd is necessary for the production of uniform casein of high quality. Only when the casein is properly precipitated can the curd be readily washed free from acid and constituents of the whey. The most important factor in precipitating the curd is the pH at which the separation from the whey takes place—although the original acidity of the skimmed milk, type and concentration of acid, temperature during precipitation and washing, and length of time the curd is left in the acid whey have an effect on the properties of the casein product.

Precipitation Procedures—Most of the casein manufactured in the United States is made by a discontinuous process in which the casein is precipitated from milk in small creameries,—though in the last decade continuous methods [27, 28] have been developed and more and more casein is being manufactured by them.

In the usual batch production of casein,[27] 6,000-20,000 pounds of skim milk are placed in a wooden or iron vat, generally having a sloping bottom and gate valve at the low end for removing the whey. The milk is then heated by direct steam to a definite temperature, usually within the range 94-140° F., while being suitably agitated (the exact conditions used depend on the acidity of the skim milk, acid used, type of casein desired, and other factors). Sufficient diluted acid, commercial sulfuric acid diluted with 5 or 6 volumes of water (or hydrochloric acid diluted with 8 or 10 volumes of water), or acidic whey is then added to bring the acidity to a pH near 4.6 (acidities from pH 4.1 to 4.9 are used). After the curd has settled it is pushed back from the gate valve, the whey is drained off and the casein washed two or more times with water. These operations generally take from 45 to 60 minutes. When a "cooked" casein having a higher viscosity is desired, the above method is modified slightly and higher temperatures are used, especially while washing the curd, when the curd and wash water are heated to 170-175° F. The curd is then pressed generally by means of either a hand press or a continuous rotary power press to reduce the water content to approximately 45-65 per cent.

When using an old-type curd press, the curd is wrapped in bundles in strong cloth, stacked between dividing and press boards, 24 inches square, and pressure is applied by manual operation of the press screw. Such a press is frequently

[27] Sutermeister, E. and Browne, F. L., ibid., Chapter 4.
[28] Stringer, W. E., Paper Trade J. *110*, No. 11, 46 (1940); Smith, R. W., Jr., Ind Eng. Chem. *26*, 819 (1934).

equipped with springs to maintain the pressure over a long period. The continuous presses consist of two revolving rolls, in which the upper roll is solid, and the lower roll perforated. By the pressure of a spring, the upper roll presses the curd against the lower roll, the water is squeezed out, and the de-watered curd is scraped free from the lower roll by a doctor blade. Certain types of curd may be sufficiently de-watered, however, by draining for a few hours in a drain vat or rack. After sufficient water has been removed, the curd is in a mealy form in which it can easily be spread on trays and in which it will dry rapidly in a tunnel or rotary drier.

In the continuous manufacturing processes now being used by the larger manufacturers, the coagulation of the casein takes place continuously in small acid-proof mixers such as stoneware cylinders containing baffles. The previously heated skim milk and diluted acid, or highly acid whey, are fed continuously into the mixer in the correct proportions so that on mixing the casein precipitates as a curd. The curd is subsequently separated from the whey as it is discharged over a screen onto a draining conveyor, and then continuously washed in a countercurrent stream of water, and pressed in a rotary press to remove excess water.

Rennet casein is made [27] from fresh skim milk of low acidity by heating it to 96° F. and adding sufficient (70-100 cc. per 1000 pounds skim milk, or less) rennet (an extract of an enzyme chymase, called rennin, isolated from the fourth stomach of young calves or lambs) to bring about the desired coagulation in 15-20 minutes at 96° F. The coagulation with rennet consists of two steps, namely, conversion of calcium caseinate into calcium paracaseinate, and the coagulation of the latter by the action of soluble salts of calcium in the milk. In practice, the curd is broken up (by slow stirring) shortly after the coagulation commences, and the temperature then raised to 150° F. After allowing the curd to settle the whey is removed and the curd washed two or three times with water at 75-85° F.

Drying [28a]—As soon as the curd has been sufficiently de-watered, drying should begin. The most commonly used method is to spread it on trays and dry it in a tunnel drier, though continuous rotary or wire screen conveyor driers may be used. When a tunnel drier is used the temperature is generally kept at 120-140° F., though higher temperatures may be used with well-washed curd.

After the moisture content has reached a normal value, 8 to 10%, the casein is ground (generally to pass a 20- to 30-mesh screen), screened, tested and bagged.

After being dried and placed in burlap sacks of 100-200 pounds capacity, casein may be stored without deterioration for long periods in well-ventilated, dry, clean rooms having a reasonably uniform temperature. Since the production during a few months of the year is much larger than that during the rest of the year, due to the surplus milk during that period, storage is necessary until there is a demand for the casein. Hence this stability of the dried casein is of great importance.

All of the above operations are not always carried out in one creamery or plant. The drying and grinding operations are frequently carried out in centrally located plants. In these cases the moist and drained or pressed casein is placed in

[28a] Drying as a unit operation is discussed in Chapter 2.

galvanized iron pails having removable bottoms and trucked to the drying plant.

Caseinates—Caseinates, many of them soluble in water without the addition of other chemicals, are manufactured either by dissolving ordinary casein and spray- or roller-drying the solution,[19] or by subjecting the mixture of alkaline modifying agent and moist casein to kneading or further mixing under high pressures and controlled temperatures.[20] Many different caseinates of industrial importance that have been developed during the past decade have found ready markets due to the fact that certain of their properties are different from those of regular "acid" caseins.

TESTING AND ANALYSIS

Since commercial caseins vary a great deal in certain characteristics which affect their practical uses, they must be carefully tested for uniformity and properties. The best method of determining the suitability of a casein for a given use is to test a sample of it in the formula to be used in practice. However, the casein manufacturer cannot generally do this, and so physical and chemical tests have been set up.[29] The physical tests include observations of color, odor, cleanliness, fineness, solubility in a standard alkaline solution, viscosity of a standard solution and the strength of the casein in adhesive or binding operations. This last test, particularly, varies according to the use to which the casein is to be put. It is also sometimes tested for foaming tendency. The chemical tests include analyses of the casein for moisture, fat, ash, nitrogen, and free or total acidity,—also determination of sugar, phosphorus and calcium are sometimes made.

TECHNICAL APPLICATIONS

Casein forms viscous dispersions that have good emulsifying and stabilizing properties, that are compatible with many types of materials and compounds, and that form essentially transparent and colorless films or coatings. Because of these properties and because of its good binding strength and adhesive powers, and the fact that it will react with formaldehyde or other tanning and hardening agents to form a water-resistant product, the industrial uses of casein are varied and manifold. Its relatively low cost, and the good stability of the dry product over long periods further enhance its usefulness.

In Paper Industry—It is estimated that 70%, or more, of the casein consumption in the United States is used in the preparation of coated or enameled papers.[30] First used for this purpose by William A. Hall in 1898,[2] the amount of casein used in paper coating far outweighs the combined consumption for this purpose of the two other chief adhesives, starch and animal glue.

Coated paper was developed commercially about 1880 to meet the needs of printers for a paper upon which fine half-tones could be reproduced. (See Figure 1.) Coated papers which are also called glazed, enameled or art papers are used for lithographic work, and book, magazine, advertising, and other print-

[29] Sutermeister, E. and Browne, F. L., ibid., Chapter 5.
[30] Sutermeister, E. and Browne, F. L., ibid., Chapter 13, pp. 401-402.

ing. They are prepared [31] by mixing mineral substances with a solution of casein and applying this "color" mixture in a thin even layer to the surface of the paper, the function of the casein being to bind the finely divided mineral matter to the paper so that it will not be "picked" off during the printing operation, while the mineral matters or pigments form a surface which is receptive to the ink by covering the fibers and filling in the hollows between them so that the paper will have smooth, semi-absorbent surfaces after calendering, or polishing. (For further information on the preparation of special papers, see Chapter 37, The Pulp and Paper Industry.)

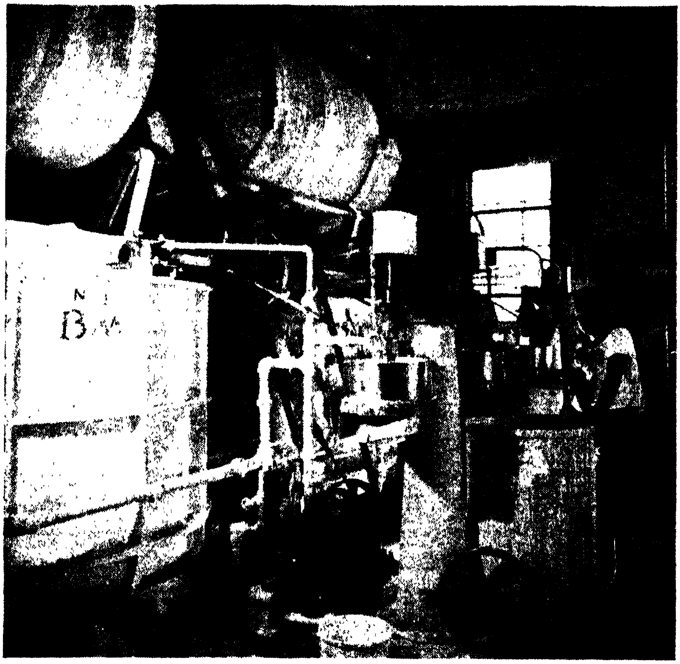


FIG. 1. Equipment Used in Preparing Coating Mixtures. (Courtesy Martin Cantine Co.)

In the preparation of coated papers the five operations performed consist of: dissolving the adhesive (casein), mixing this solution with the mineral matters and other substances, spreading the mixture on the surface of the paper, drying the paper, and smoothing or polishing the paper surface by calendering. The spreading of the coating is done by brushes, blades, rolls, or a blast of air. There are several types of coating machines,[31a, 32, 33] including single and double brush coaters, roll coaters, air-brush coaters, and machine coaters operating as part of

[31] Sutermeister, E. and Browne, F. L., ibid., Chapter 9.
[31a] Sutermeister, E. and Browne, F. L., ibid., Chapter 9.
[32] Massey, P. J., Paper Trade J. *109*, No. 16, 34-7 (1939).
[33] Clark, N. and Sutermeister, E., and co-authors, "The Manufacture of Pulp and Paper," Vol. 5, Third Edition, Section 4, Part 1, pp. 34-37, McGraw-Hill Book Co., Inc. (1939).

the paper machine, some of which coat the paper on one side only at a time, while others coat both sides in one operation. To make the coating water-resistant, formaldehyde is usually added to the coating mixture. (See Figure 2.)

Besides its use in the manufacture of enameled or coated papers, casein is used, though less extensively, as a binder or adhesive size in the manufacture of washable wall papers, box papers, gold, silver and platinum papers, mica coated

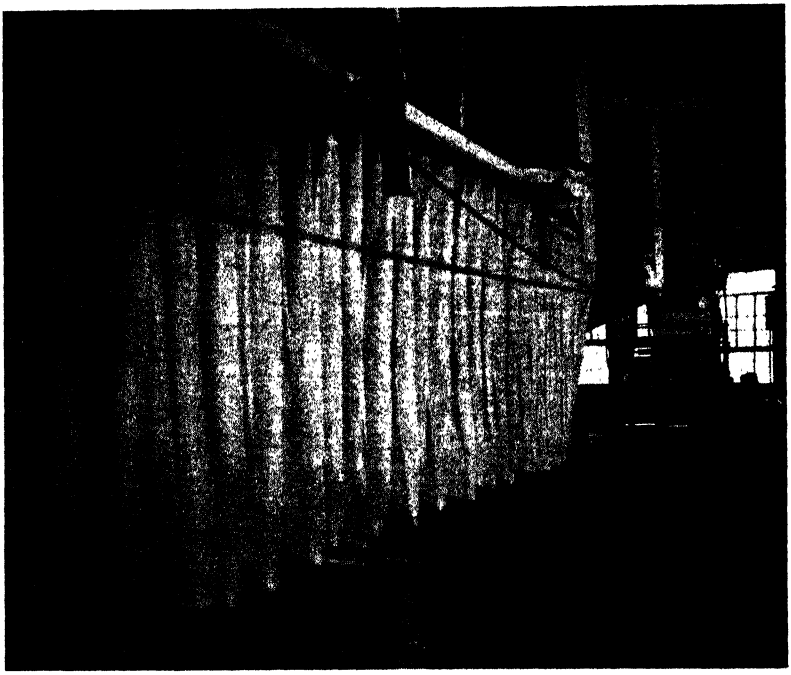


FIG. 2. Coated Paper Being Dried in a Festoon Drier. (Courtesy Martin Cantine Co.)

papers, water-resistant papers, oil- and grease-resistant papers, and playing cards. Also, it is used for beater-sizing of paper pulp for specialty papers and for top-sizing paper and paper-board. The paper industry offers an ever-widening field for the uses of casein.

Glues and Adhesives—Although casein was used as a wood glue in this country to only a limited extent until 1916-1917, its use has increased so rapidly since then that from 6 to 7 million pounds of casein glues are sold yearly in the United States. There are several reasons for this increased use, chief among which are: the improved formulas and gluing techniques fostering their use in place of the previously used and less water-resistant animal or vegetable glues, the development and growth of industries such as the plywood industry, and the needs and demands of various industries for better and more water-resistant adhesives and glues.

Prepared casein glues [34] are marketed in the form of dry powders containing all the necessary chemicals and ingredients except water. A few casein liquid adhesives are also marketed. Because of their convenience, the prepared casein glues are widely used at home as well as in industry. The user simply mixes the dry glue powder with water at room temperature in the proper proportions—usually 2 parts of water to 1 of glue by weight. Most casein glues take only 15 minutes to prepare, and are not only mixed without heat, but are also so used.

Prepared casein glues [34] are generally a mixture of casein, lime, and several alkaline solvents or salts. In gluing two solids together, the casein glue wets and establishes contact with each solid and then solidifies as the moisture is withdrawn to form a rigid layer in the space between them. The adhesiveness of the casein is believed to be due to both specific (by molecular attraction) and mechanical (by a grip in cavities of the surfaces of the solids) adhesion.

While it is not necessary that all casein glues be water-resistant, the property is usually desirable. They should only be referred to as "water-resistant," since any casein glue or product is affected by and will absorb water. Investigators have shown that as the strength of animal glue under tension decreases from 20,000 pounds per square inch to 8000 pounds and 500 pounds as the moisture content of the animal glue increases from 13% to 24% and 30%, the strength of casein glue at 30 or 50% moisture content is nearly as great as when it is dry, at least until hydrolysis of the casein starts.[35] Among the chemicals used to improve water-resistance of casein glues are lime, certain metallic salts, formaldehyde or other tanning agents, and carbon disulfide. Also mixtures of casein are frequently made with other colloidal materials, such as animal glue, albumin, seed meals such as soybean, peanut and cottonseed meal, rubber latex, and synthetic resins. This facility of formula manipulation makes it possible to adapt glues containing casein to a wide variety of industrial gluing needs.

Large use of casein glue is found in the woodworking industry. It is widely used for furniture making, gluing fancy veneers, veneered doors and millwork, laminated and block flooring, commercial plywood, in joint and core gluing, and for boat and marine work. (See Figure 3.)

Casein is also widely sold and used as a prepared glue, often as a caseinate (casein combined chemically with an alkali or a metallic salt, rather than a mixture of them), for the gluing of materials such as paper or cloth—for example, in the production of articles such as drinking cups and straws, and paper cones for textiles. Compounded with rubber latex, casein adhesives are used for gluing dissimilar materials where a flexible glue-line is desired. Jobs from gluing together leather or cloth, to those requiring higher strengths, such as the gluing of linoleum-type wall coverings to plaster or of stainless steel to fiberboard are successfully accomplished with these adhesives.

Casein Paints—As factory-made powder, casein paints [36] have been sold in the United States since 1895-1900, the casein paint business is almost as old

[34] Sutermeister, E. and Browne, F. L., ibid., Chapter 8; Dulac, R., "Industrial Cold Adhesives," translated by Rosenbaum, J. B. Lippincott Co. (1937); Hadert, H., "Casein and Its Uses," translated by Goldsmith, H., Chem. Publishing Co. (1938).
[35] Sutermeister, E. and Browne, F. L., ibid., Chapter 8, p. 237.
[36] Sutermeister, E. and Browne, F. L., ibid., Chapter 10.

as the "ready-mixed" oil paint business. The annual production of casein bound paint is still rapidly increasing. Manufactured and marketed by many paint manufacturers under various trade names, casein paints may be classified into two groups, (a) the dry powder paint, and (b) the paste paint.

The former is generally a mixture of a finely ground casein with alkalies, lime and pigments which produce covering power, light reflectance, and color when desired. A dry paint contains approximately 10% of casein by weight. A powder casein paint should not be confused with a calcimine (or Kalsomine) which is

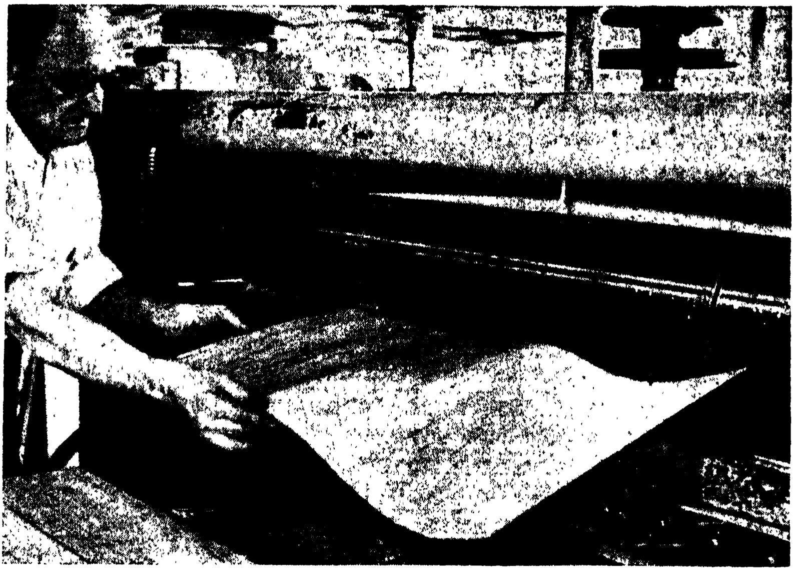


FIG. 3. Casein Glue Being Applied on a Sheet of Veneer.

essentially a dry mixture of animal glue or dextrine and whiting as a pigment, and inferior to a casein paint in that it is readily stained or damaged by water, and cannot generally be recoated and cannot be washed.

In a paste casein paint, there is enough water to hold the casein in solution. To prepare the paint for use, the user adds more water. Paste paints have recently been introduced that contain oils, and in some cases resins, lime not being used in paste paints to make the casein water-resistant. These paints are intended for exterior exposures, especially surfaces such as stucco, brick, and stonework. Although there is a wide difference of opinion as to the relative merits of the powder and paste forms, each type continues in use at the present time.

In cost and utility, casein paints stand between calcimines and flat oil paints. Still gaining ground rapidly at the expense of each, the main advantages of the modern casein paints over oil paints are considered to be: lower cost, less time to complete the painting job, freedom from lingering paint odors, high diffuse light reflectance and soft colors in pastel tints, and their applicability to new plaster.

Casein Plastics—Although casein has not been used for plastics as much in the United States as in Europe, this use[37] absorbs more casein than any use other than paper coating, and perhaps glue. Because of the impossibility of making casein completely insoluble, to the extent that it will not absorb any moisture, and because of the difficulty of hardening large objects, casein plastics are used only for small objects such as buttons, costume jewelry, poker chips and other novelty articles. Their brilliant, beautiful color effects and lustrous finish have made them very popular. Streaked and mottled effects, imitation horn, tortoise shell, and jade, are examples of the type of effects obtained. As casein plastics soften by heating to 200° F., they can be compression molded before treatment with formaldehyde, but injection molding is not feasible. Compression molding is only used occasionally for small objects, however. They machine well, though are very hard on the edges of cutting tools. Since their manufacture requires a large amount of hand labor and prevents the use of fully automatic machines, casein plastics are too costly except for the limited applications as described above.[37a]

Two Methods. Two methods have been used for the production of casein plastics, the "wet" process and the "dry" process. The one commonly used in this country is the newer and "dry" process. In this, rennet casein is commonly used, as it has been found to produce a better product.

In this process, the dry and ground casein is mixed with the dye or pigment to be used and moistened with 20-40% of water, based on the casein. After mixing and allowing the casein particles to swell, the powder is fed into a screw-press extruder, in which it is kneaded at elevated temperatures and pressures, and from which it emerges in the form of a rod or tube. Other types of machines such as steam-heated kneading machines, or rolls such as are used for milling rubber can also be used. These rods are then placed in cold water and removed to the hardening tank which contains a solution (approximately 6% concentration) of formaldehyde, where it is left for a period of time varying from several hours to weeks, depending on the thickness of the rod. However, when the rod or tube is to be cut into other objects, it is common practice to cut the objects or blanks from them before the hardening process. This procedure obviates excessive waste of hardened casein, since the non-hardened material can be re-extruded, while the hardened materials cannot be used again.

After the desired object is formed and hardened it is seasoned or dried slowly (drying generally requires from one-third to as long as the hardening operation depending on the size of the object) at about 130° F. to allow the excess water and formaldehyde to escape without setting up stresses and strains. The humidity is also controlled during the drying of large objects. The article is then straightened by warming and pressing if it has warped during the drying operation, and then polished by dipping it in a solution of sodium hypochlorite.

In the "wet" process, an "acid" casein is used in the form of moist curd or of a partially acidified alkaline solution. After mixing with the dyes or pigments, it is pressed or molded into the desired shape, hardened and carefully dried.

[37] Sutermeister, E. and Browne, F. L., ibid., Chapter 7.

[37a] For comparison of properties of casein plastics to other plastic materials see Modern Plastics, "Plastic Properties Chart," Breskin Publ. Corp., New York, N. Y. (October, 1939). Also Chapter 31, Synthetic Plastics.

A good deal of work has been done, and many patents have been granted, in which casein has been used as a filler or modifying agent for other plastic materials; and also for the incorporation of various resins or other plastic materials, with casein for the purpose of decreasing the hygroscopicity of casein plastics, and to permit their manufacture by more efficient methods.

Leather Finishes [38]—Casein is widely used in seasonings and pigment finishes in the leather industry. These are applied to almost all types of leather to make it more serviceable and attractive, conceal imperfections, impart various color effects, and provide resistance to water. They are applied in the last of the finishing operations which consist of coating leather with them, generally by hand with a swab, and then performing the mechanical operations of glazing, plating, brushing and ironing. When pigments are used they are called pigment finishes, otherwise they are called seasonings. Used in many combinations depending on the result desired and on the particular leather being finished, casein is probably the most important of all seasoning materials. (For further discussion of use in the leather industry, see Chapter 45, Leather.)

In Textile Industry—Although almost neglected by the textile industry in the past, the use of casein in textile printing, finishing and sizing operations is rapidly increasing.

As a finishing material casein imparts added stiffness to the cloth and so is being used for the finishing of light-weight materials such as organdies, and rayon and silk fabrics. These finishes are easily applied and are made reasonably wash-fast by the use of formaldehyde, which is added to the casein solution before applying it to the cloth. Casein may be softened as desired by the use of the usual textile softening materials such as sulfonated tallow, mixtures of raw coconut oil and sulfonated olive (or other) oils, lecithin, etc. As a substitute for albumin it can be used successfully in printing pastes to bind the white or colored mineral pigments to the cloth. The use of casein in place of albumin results in a saving in cost.

Casein is being used to a certain extent in place of gelatine as a size to impart strength and give protection to rayon warps, and attempts are being made to extend its use in this application. It is used with starch sizing compounds to improve the adhesion to fabrics subjected to abrasion and to increase the stiffening power and sometimes wash-fastness of the starch sizing. In conjunction with aluminum formate or acetate, either in separate or combined application, and generally in the form of a wax emulsion, it is used to make fabrics water-repellent and splash-proof.

Casein Fiber—The most recent commercial use of casein to receive widespread attention has been the development of a regenerated textile from casein. First obtained in the laboratory by Todtenhaupt,[39] or perhaps by Millar,[39] commercial development of these fibers (Lanital) was carried out by the Italian Rayon Company Snia Viscosa in 1935, through the work of Ferretti.[40] In the following few years casein fiber was produced under various names in many countries,

[38] Sutermeister, E. and Browne, F. L., ibid., Chapter 11; Mudd, J. S., "Leather Finishes, Their Formulation, Manufacture and Application," Chapter III, pp. 29-32, Chem. Publishing Co., Inc. (1939).

[39] Sutermeister, E. and Browne, F. L., ibid., Appendix to Chapter 7, p. 215.

[40] Mauersberger, H. R., Rayon Textile Monthly *21*, No. 11, 37 (1940).

Polan (Poland), Tiolan (Germany), Lactofil and Casolana (Holland), Cargan (Belgium) and Courtauld's casein fiber (England). Also, Cisalpha (Italy) and Fibramine (Belgium) were produced, these fibers being viscose fibers with 3-5 per cent casein incorporated to give wool-dyeing properties. In 1940, commercial production of a casein fiber in the United States under the name Aralac was announced by National Dairy Products Corporation,[40] at a price of 40-55¢ per pound. Numerous patents have been granted, and many investigations have been made on the production of a casein fiber.

The process consists essentially in dissolving casein in an aqueous alkaline solution, allowing it to stand for 1-3 days while the viscosity changes (probably with attendant racemization and molecular change of the casein), and forcing it through the small holes of a spinneret into an acid coagulating bath. The threads of filaments are then treated with formaldehyde and other agents in subsequent baths to harden or "set" them and render them water-resistant. An improvement in strength has been brought about by stretching the fiber at least 300-500% before the formaldehyde treatment,[40a] thus orienting the molecules in relation to each other and so imparting strength to the fiber. The fiber is cut into staple fiber, dried under controlled humidity and temperature conditions, and generally used in admixture with cotton, wool, rayon, or acetate. It is not regarded at present as a complete substitute for wool, but rather as a less expensive fiber to be blended with it. In this country it is being used in the felt hat industry in admixture with wool and rabbit fur.[40] Many patents have appeared on modifications of this process, utilizing other proteins than casein such as collagen, soya protein, or fish albumin, incorporating viscose, cellulose acetate, cuprammonium cellulose or resins in the casein solution and on the use of various modifying materials in the solution or precipitating or hardening baths.

Casein fiber dyes more readily than wool, but it is not as strong as wool in either the wet or dry state. It is reported[40] that the present fiber is about one-half as strong as wool, when dry, while its wet strength is about one-fifth of that of wool. Although it is too early to predict the future of this most recent casein product, it seems logical to assume that any developments in the production of fiber from the more abundant vegetable proteins will greatly influence its progress.

Casein in Foods and Medicine[41]—In nutritive value, it is said that casein compares favorably with the proteins of meat. It contains the proper amount and kinds of the essential amino acids for growth and nourishment, as well as phosphorus, 90% of which is utilized by the body. It is for these reasons, doubtless, and also because casein is readily acted upon by digestive juices, that casein has been so extensively used in foods and edible preparations. Their cost of production, however, is said to have prevented a wider use. Besides its use as a food in its modified form as cheese, casein is used as a component of various foods such as bread and baker's wares, baking powders, diabetic foods, sausages, reducing foods, soup tablets, and as a filler in ice cream. In these uses casein has generally been in the form of a readily soluble caseinate, referred to by various names such as Nutrose, Plasmon, and Protovac.

[40a] Meigs, F. M., U. S. Patent 2,211,961 (Aug. 20, 1940).
[41] Sutermeister, E. and Browne, F. L., ibid., Chapter 12.

In combination with heavy metals, iodine, or alkaloids, casein is used as a component of pharmaceutical preparations for the purpose of controlling and prolonging the medicinal action of the drug.

Miscellaneous Applications—An account of casein would not be complete without making mention of some of its many miscellaneous uses. It is used as a spreader and sticker as well as an emulsifier in insecticides and fungicides; as a stabilizer and thickener for rubber latex and to improve the adhesion of various materials to rubber (rayon to rubber in modern automobile tires); as a binder in printing inks, as an emulsifier for resins, fats, waxes and oils, in pigmented and unpigmented sealers and finishes for wood, plaster, and fiber-board; in soap to improve the texture and lathering properties, and as a clarifying agent for wines.

VEGETABLE PROTEINS

Soybean—There are several sources of vegetable protein materials of increasing industrial importance. Although these proteins are quite similar to casein in many of their present and potential uses, and so have frequently been erroneously referred to as "vegetable caseins," they belong to different protein sub-divisions and so differ from (milk) casein in their chemical properties.

The soybean is one of the most economical sources of protein, ranking among the first of the known vegetables in protein content. Raised primarily for the oil content, the domestic production of soybeans increased[42] nearly ten-fold during the period 1929-1939. Thus, it is not surprising that extensive researches of the potential industrial applications of the constituents of the soybean, the oil, the meal, and the protein, have been made during this period in the United States and abroad.

The production of the easily grown soybean is large and increasing yearly. Its uses in industry are due mainly to the large amounts and quality of oil and protein in the bean. It contains over four times as much fat and protein and about one-third as much carbohydrates as corn. Further it contains practically no starch. The average composition of the varieties grown for processing is approximately as follows:[43] Protein 40%; Fat 18.0%; Nitrogen-free extract 25.9%; Ash 4.6%; Crude fiber 3.5%; Moisture 8.0%.

Soybean protein consists principally of the globulin glycinin,[44] though a small amount of a more soluble globulin resembling phaseolin is also present. Unlike casein which is a phosphoprotein, glycinin is a simple protein and yields only amino acids on ultimate hydrolysis. Being a globulin, it is soluble in weak acids, alkalies and neutral salts. The isoelectric point of soybean protein is the same as,[45] or close to,[46] that of casein, pH 4.6. Its properties are in general similar to those of casein, though the present commercial product (it is now being pre-

[42] McBride, G. W., Chem. and Met. Eng. *47*, No. 2, 88 (1940).

[43] Kraybill, H. R., "Soybean Chemistry," p. 260 in "Proceedings of the Second Dearborn Conference of Agriculture, Industry and Science," Farm Chemurgic Council and Chemical Foundation, Inc. (1936).

[44] Satow, S., Tech. Rep. Tôhoku Imp. Univ. *2*, No. 2 (1921).

[45] Hsieh, H., Jen, T. and Chang P., Chiao-Tung Univ. Res. Inst. Ann. Rept. Bur. Chem. *3*, 63-70 (1936); Chem. Abstr. *31*, 8, 2709 (1937).

[46] O'Brien, W. J., "Soybean Proteins," p. 254 in "Proceedings of the Second Dearborn Conference of Agriculture, Industry and Science," Farm Chemurgic Council and Chemical Foundation, Inc. (1936).

pared and offered for sale [47] in quantities amounting to approximately 10 tons per day) differs from casein in certain characteristics such as color, viscosity and adhesive or binding strength. Up to the present, the isolated soybean protein of commerce has been darker and of lower binding strength than casein.[48]

Extracting the Protein. The direct source of soybean protein is soybean meal, which is obtained from the bean by crushing or extracting the oil. In the generally used procedure, the beans are dried to a moisture content of less than

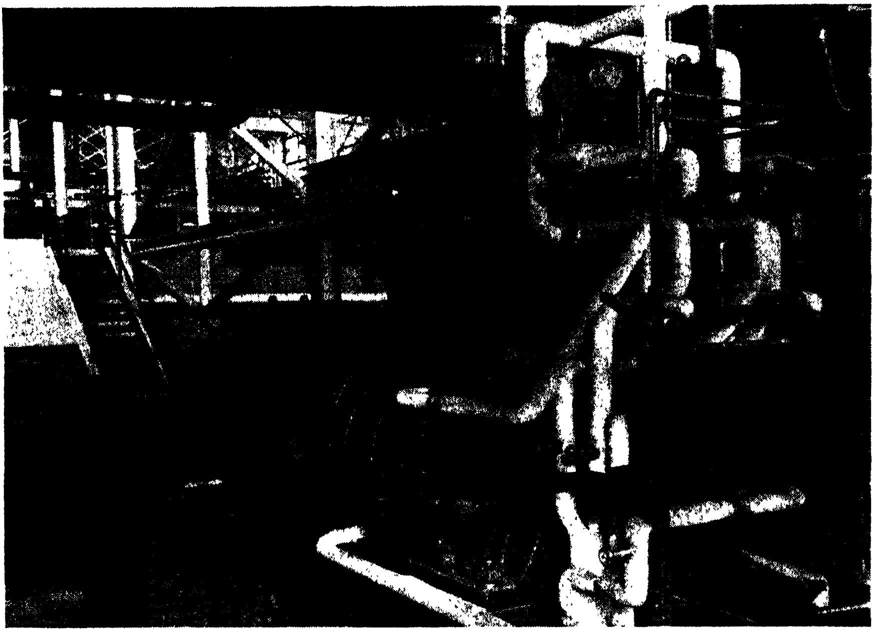


FIG. 4. Equipment Used in the Production of Soybean Plastic Material. (Courtesy Ford Motor Co.)

13%, partly cracked on coarse roller mills and further dried to 3-4% water content to prepare them for pressing.[49] When the oil is to be removed by crushing, the dried and heated beans are then fed into a press. In older procedures this was done by batch hydraulic pressing, though in 1939 [49] three-quarters of the crushing was done by a continuous screw or expeller pressing, the crude oil and press cake discharging continuously from it.

When the oil is to be removed by solvent extraction, this method accounting for about one-fifth of the oil produced in 1939,[49] the moderately heated beans which preferably have a moisture content of 10-12% are rolled into flakes to increase their surface area. Several types of continuous extractors have been

[47] Nickerson, R. F., Bieber, G. D. and Bass, L. W., Cotton Research Foundation, Mellon Institute, Pittsburgh, Pa., unpublished paper, "Economic Aspects of Industrially Significant Proteins" (1940).
[48] Roderick, N. F. and Hughes, A. E., Paper Trade J. *110*, No. 8, 104 (1940).
[49] McBride, G. W., Chem. and Met. Eng. *47*, No. 9, pp. 614-618 (1940); McBride, G. W., Food Industries *12*, No. 10, pp. 55-57 (1940).

found to be satisfactory for the removal of the oil, including the conveyor type, the screw type, the drum and press type and the column type.[50] The screw type is used by the Ford Motor Company.[49, 50] In this rapid and direct process the bean flakes are fed into the bottom of a pipe which is at a 10-degree angle to the floor and filled with hexane, which enters at the top of the pipe. The flakes are then carried by means of a screw conveyor to the top of the pipe where the extracted meal leaves the solvent chamber and has the solvent removed from it by steaming. As the meal leaves the steamer it hasn't any solvent odor. Meanwhile the solvent works down the pipe, carrying the oil with it. As it leaves the extractor at the bottom, it is filtered, and then the solvent is stripped from it. An extractor of this type of a size to handle 3 tons of meal in eight hours, requires about 100 gallons of solvent continuously flowing in the closed circuit. Anhydrous ethyl alcohol, benzene, and halogenated hydrocarbons have also received consideration as solvents for this operation.[50]

As solvent meal contains less than 1% residual oil while pressed meal contains 4 or 5% oil, the protein content of the former (about 50%) is higher than that of the pressed meal (41 to 44%). The solvent extracted meal is better adapted to industrial utilization and for the isolation of the protein from the meal, than the expeller or hydraulic meal. Solvent extracted meals have been found to be superior[50] in properties such as color, solubility, viscosity, adhesion, plasticity—and to yield proteins also superior in these properties. It should be pointed out however that the properties of the meal are dependent to a large extent on the past history and quality or variety of bean in addition to the conditions used in freeing the oil from the meal.

The isolation of the protein from the solvent extracted meal is a difficult step and much care must be used to produce a protein of desirable and uniform properties.[51] It is generally carried out[49, 52, 44] by extracting the protein from the meal by treating it with an alkaline solvent, though solutions of neutral salts may be used. Since the glycinin is easily hydrolyzed or denatured by too strong alkaline solutions and is easily oxidized by air, weak alkaline solutions having reducing properties, such as 0.1-0.2% sodium sulfite solutions, are frequently employed. More than one leaching is recommended. The protein solution is then clarified by filtration or centrifuging, the protein in the solution precipitated with acid, and the resulting curd washed and dried. Many methods are used to extract the protein, though the exact procedures used are kept secret. The pH and temperature during the precipitation are of importance, and affect the type of curd obtained as well as the properties of the resulting product.

The other constituents of the meal[52] that are water soluble (legumelin, proteose, soluble sugars) and mucilaginous substances (galactan and araban) that are partially soluble and easily carried into the solution as suspensoids are separated from the desired protein before precipitation, though only with difficulty. The water soluble materials may be separated from the desired globulin by extraction with dilute acetic acid solutions before solution of the desired globulin, while the mucilaginous substances are freed from the protein also by differences in

[50] Horvath, A. A., "The Soybean Industry," Chapters 6-10, The Chemical Publishing Co. of New York, Inc. (1938).
[51] Boyer, R. A., Ind. and Eng. Chem. 32, No. 12, 1549 (1940).
[52] Horvath, A. A., ibid., Chapters 16 and 17.

solubilities or are removed from a solution of the protein by filtration and centrifuging.[52] Published information on these methods, or the success of them is very meager. As the protein is discolored by iron, contact of the solutions or protein with iron is kept at a minimum.

Probably more than 90% of the soybean meal is at present used as a cattle food,[49] the proteins having been made available in digestible form during the heating in the press or extraction apparatus. In addition to this use soybean

Fig. 5. Bank of Presses Molding Soybean Plastic Parts. (Courtesy Ford Motor Co.)

meal is used[49] as a fertilizer, in adhesives, in plastics and in miscellaneous other applications such as a filler in sausages, and in insecticide spreaders or sprays.

Uses. As might be expected from the similarity of their properties, isolated soybean protein and casein potentially have similar industrial applications. Since the soybean meal and protein have been made available commercially in the United States, casein has been replaced to a limited extent by the meal or isolated protein in a few applications such as adhesives, water paints, wall paper sizings, etc., especially when the price of casein has been high. They have also found application in miscellaneous coatings and in plastics. In plastics,[53] in which use the Ford Motor Company pioneered, the soybean meal or purified protein that has been prehardened with formaldehyde is mixed in varying proportions with phenolic or urea molding compositions for the production of small molded parts, to be used in automobiles. The plastic properties of soybean protein have been

[53] Horvath, A. A., ibid., Chapter 18; Satow, S., Tech. Rep. Tôhoku Imp. Univ. *3*, No. 4 (1923); Taylor, R. L., Chem. & Met. Eng. *43*, No. 4, pp. 172-176 (1936); Brother, G. H. and McKinney, L. L., Modern Plastics (September 1938 issue).

found to be similar to those of a prolamine, such as zein from corn. Further, soybean protein hardened with formaldehyde has been shown to be thermoplastic.[54] As yet, the isolated soybean protein has not replaced casein in many applications, probably due in large part to its darker color and lower binding strength,—though improvements in these respects undoubtedly will result in a wider market for this vegetable protein. A summary of the production and use of soybean products for 1939 is given in Table 1.

Fibers. A potential application for this isolated protein is in the manufacture of regenerated fiber. Following the isolation of the protein from the solvent extracted meal, the process in general parallels the present processes for the production of casein fiber. A large amount of laboratory work has been done

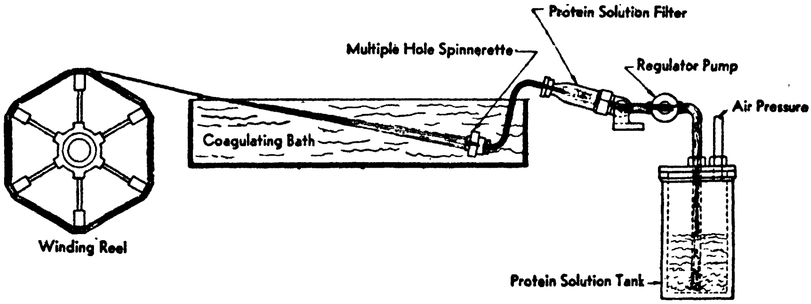


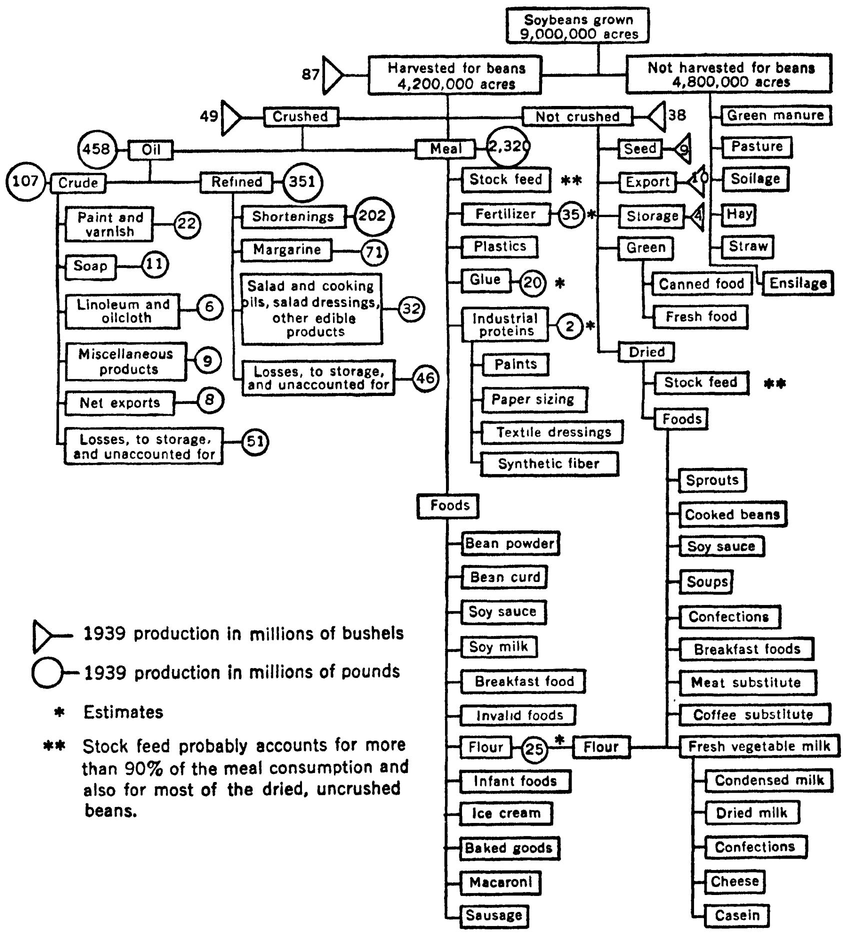
FIG. 6. Sketch Showing Layout of Soybean Protein Fiber-spinning Outfit. (Courtesy Ford Motor Co.)

by the Ford Motor Company,[51] which has resulted in the development of a stronger though slightly more yellow fiber than that of the present regenerated casein fiber, and in a continuous machine that will precipitate, harden and perform the after-treatment of the filaments continuously. The fiber has a medium luster, warm, soft feel, natural crimp and high degree of resilience. It can be produced in natural color or spun dyed with or without a highly permanent crimp. The tensile strength of soybean fiber is about 80% as compared to wool, while the dry elongation of 40% and wet elongation of 60% are much higher. The wet and dry tensile strength at the break are approximately the same, though the yield point of the wet fiber is lower. Claims are made that the soybean fiber is not wet as readily by water and is more resistant to the action of mold than casein fiber.

Fiber sizes of 1½-5 denier in staple lengths of 1½-6 inches have been produced.[51] These are handled on conventional cotton and worsted equipment. The fiber shows promise in wool blends for use in suitings and upholstery fabrics, with cotton and spun rayon in the development of many new fabrics—and perhaps with wool in felt manufacture. With plans being made for a plant to produce 1000 pounds per day of finished "top" fiber for blending in automotive upholstery, it is highly probable that the next few years will see the commercial development of soybean fiber in this country.

[54] Brother, G. H. and McKinney, L. L., Ind. and Eng. Chem. *30*, 1236 (1938); Brother, G. H. and McKinney, L. L., Brit. Plastics (October 1938 issue).

TABLE 1—PRODUCTS MADE FROM SOYBEANS IN COMMERCIAL QUANTITIES AND QUANTITIES OF MAJOR PRODUCTS PRODUCED IN 1939[49] (Courtesy of G. W. McBride)



Cottonseed—Although the supply of cottonseed has been much greater than that of soybeans, the extraction and commercial utilization of protein from cottonseed has received little attention. The availability of the cottonseed is regulated to a large degree by cotton fiber production. Approximately 80% of the yearly crop (1939 domestic production estimated at 2,000,000 tons) is crushed, largely by the hot press method.[47] The oil obtained is utilized largely for edible purposes, and the chief use for the meal is as a stock feed. No solvent extracted meal is produced commercially at the present time, though it has been produced on a pilot plant scale at the Mellon Institute of Industrial Research, where research on cottonseed protein has been carried on for the last few years under the sponsorship of the Cotton Research Foundation and the National Cotton Council.

The oil-free cottonseed meal contains approximately 50-55% protein,[55] of

[55] Olcott, H. S. and Fontaine, T. D., J. Am. Chem. Soc. 62, No. 6, 1334 (1940).

which about one-fifth consists of albumins and related substances, and is soluble in water. The globulin, which represents about 40% of the total protein, can be isolated from the meal which has had the oil and gossypol (a toxic pigment occurring in cottonseed) removed by solvent extraction and then being subsequently leached with water by (a) treating with alkali (pH 10.0) and precipitat-

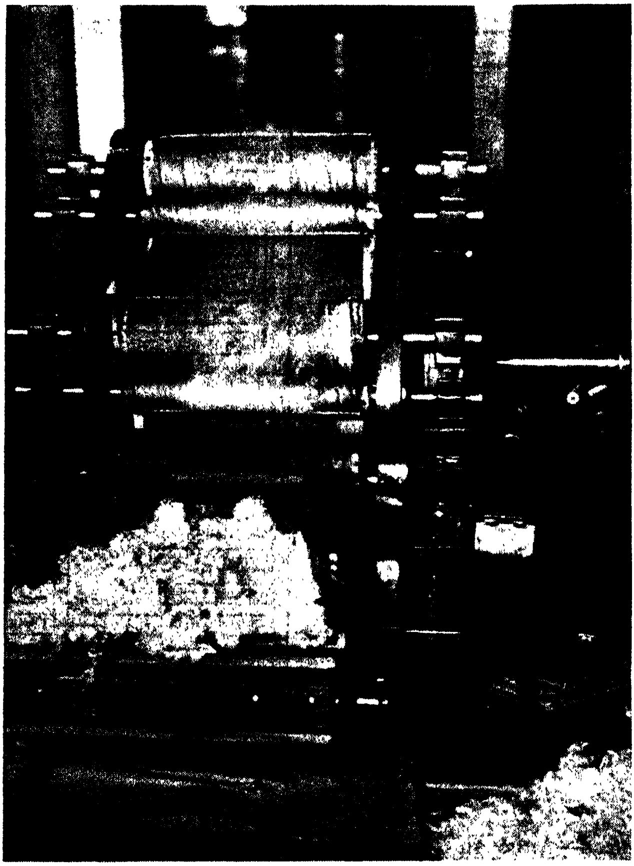


FIG. 7. Carding Soybean Protein Fiber. (Courtesy Ford Motor Co.)

ing the desired globulin from the alkaline solution by the addition of acid to the isoelectric point (pH 6.5-7.0)[56] or (b) by treating with 3% sodium chloride solution and precipitating the globulin by acidification[57] to pH 3.9-4.2. The residue of protein in the extracted meal, amounting to 40% of the residual weight, makes this spent product satisfactory for use in animal feeds. A disadvantage in the former method is that cottonseed pigments not removed during the solvent extraction of the meal are easily oxidized in alkaline solution, and yield brown products affecting the color of the globulin, while the protein prepared by the

[56] Nickerson, R. F., U. S. Patent 2,194,835 (Mar. 26, 1940).
[57] Olcott, H. S., U. S. Patent 2,194,867 (Mar. 26, 1940).

second method is said to be of lower solubility than the alkali-extracted protein. The protein has been produced by the former process on a pilot plant scale,[58] and studies on its applications have been started. The difference in the isoelectric point of this protein from that of casein or soybean isolated protein might lead to its use in different applications than those of casein or soybean protein.

Other Seedmeals—In addition to soybean meal and cottonseed meal, other seedmeals, such as linseed and peanut, are produced in appreciable quantities.

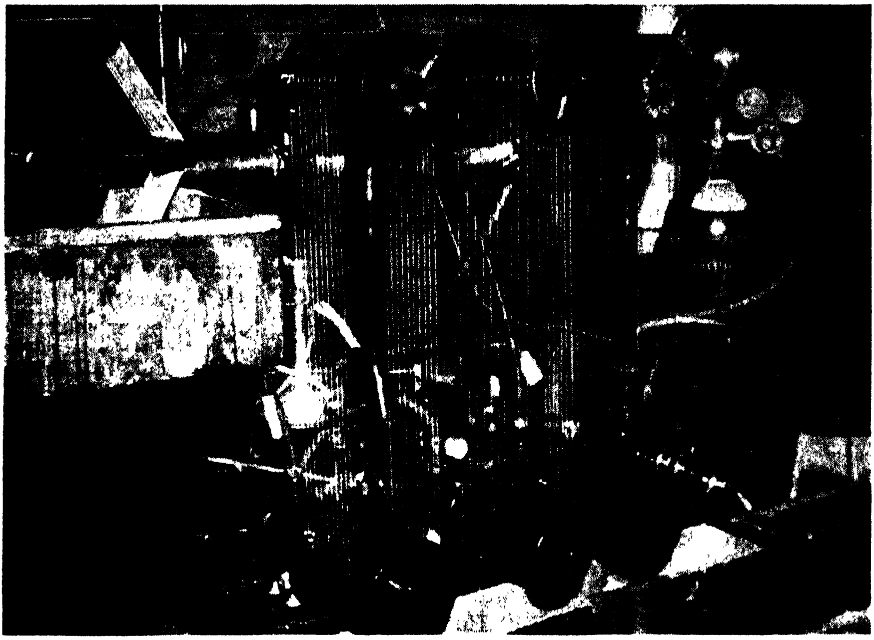


FIG. 8. Spinning Soybean Protein Fiber. (Courtesy Ford Motor Co.)

(See Table 6.) These are employed principally in animal feeding, and as fertilizers, though peanut meal has been used somewhat in plywood adhesives.

Other less promising sources of proteins are to be found in alfalfa and wheat flour.[47] Alfalfa contains 12% of proteins while wheat flour contains on the average of 11% of proteins (gliadin (3.96%), leucosin (0.39%), globulin (0.63%), and glutenin (4.68%)). Isolation of an industrial protein from these sources has not been attempted commercially, and the economic feasibility of doing so remains to be determined.

Corn Protein—Corn is the number one crop of the United States in acreage, yield, and value. Corn contains 10% of proteins[47] and 71.8% of starch. The proteins include the prolamine zein and also albumins, globulins, and glutelins. As the present yearly production of corn starch is nearly one billion pounds, the potential supply of protein from this source can be estimated at one hundred million pounds.[47] In the last few years the prolamine zein, isolated from the

[58] Weidlein, E. R., News Ed., Ind. & Eng. Chem. *18*, No. 7, 291 (1940).

waste liquors of the corn starch industry, has been developed commercially and offered[47] in quantity at a price in the neighborhood of 20¢ per pound.

Zein is unusual by virtue of its solubility in aqueous alcohol. Insoluble in water, or in anhydrous ethyl alcohol (unless auxiliary solvents are contained therein), it is soluble in the range of 60-95% ethyl alcohol (40-5%) water, the most stable solutions being prepared with 90% alcohol. However, the addition of various organic acids, amines, esters, glycols, phenols and other compounds permit its solubility in an anhydrous alcohol medium. Dilute aqueous alkaline solutions will not dissolve it, though it is soluble in solutions having a pH greater than 12.8. Solutions of zein in aqueous alcohols have a tendency to increase in viscosity and eventually form a gel due to the protein being gradually rendered insoluble. Zein, like casein, is compatible with a host of different modifying agents, and the water-resistance of it is improved by treatment with formaldehyde, formamide or hexamethylene tetramine.

Many investigations of the possible applications of zein have been made, and numerous patents on it have been granted. With the development of these applications, future outlets as plastics, adhesives, and coatings and sizings, similar in general to the present uses of casein, are likely. Zein has also received consideration for use in a synthetic (regenerated) fiber. Developments of this abundant vegetable protein having different properties from the other commercially available proteins will be interesting to watch.

PRODUCTION AND USE TRENDS

In certain applications, casein competes with these vegetable proteins, especially soya protein and zein. While isolated soybean protein has recently cost in the neighborhood of 12¢ per pound, casein has fluctuated between 8-23¢ per pound. When the price of casein has been high, it has been replaced in a few uses by soybean protein, though with the return of lower casein prices, soybean protein held but few of its gains. However, casein has not as yet been entirely or permanently replaced in any of its uses. So far, there is not any evidence that any one of these proteins will eliminate any of the others. Present trends indicate that new uses will sufficiently increase the demand for these other proteins to prevent any decreases in their uses. It is likely, however, that the competition of these relatively newly developed proteins will cause certain price adjustments in casein or in the other proteins, in order that they continue to be used in certain fields.

Statistics on the production, imports, consumption and price range of casein are summarized in Table 2.

Over 90% of the total casein imports are supplied by Argentina and France. Of this, France supplied nearly half until 1939. Since then most of it has come from Argentina.[59]

The domestic production of milk in 1937 is given as 105,958,000,000 pounds,[60] while that of skim milk was almost exactly half or 53,000,000,000 pounds. Of this 53,000,000,000 pounds, 26% was utilized commercially for the manufacture of casein, skim milk powder, condensed and chocolate milks, and cheese, the rest

[59] U. S. Tariff Commission, Washington, D. C., Private Communication.
[60] Holm, G. E., News Ed., Ind. & Eng. Chem. *17*, No. 10, pp. 348-9 (1939).

TABLE 2—U. S. PRODUCTION, IMPORTS, CONSUMPTION, AND PRICE OF CASEIN [47, 59]

(Millions of pounds)

Year	*Domestic Production*	*Imports*	*Estimated Consumption*	*Aver. Price * Dollars/lb.*
1919	14.4	8.1	22.5	....
1921	8.1	9.7	17.8	....
1923	14.5	26.5	41.0	....
1925	16.7	18.8	35.5	....
1927	18.0	24.2	42.2	....
1929	30.5	27.6	58.1	....
1931	35.3	3.5	38.8	0.080
1933	24.1	8.3	32.4	0.108
1935	37.7	3.2	40.9	0.131
1937	67.5	5.2	72.7	0.158
1938	48.5	0.4	49.0	0.089 †
1939	...	15.8	...	0.122 †

* Standard domestic grade ground.
† Estimated.

being fed to farm animals or "used inefficiently in some other manner."[60] The 67,500,000 pounds of casein produced in the United States during that year utilized only about 5% of the available skim milk supply, and represents approximately 2.6% of the total milk production for 1937. Actually, there was a potential supply of approximately 1,300,000,000 pounds of casein from the 53,000,000,000 pounds of skim milk produced during 1937.

For many years, it has been estimated that 75 to 80% of casein is used in paper coating, though it is hard to reconcile as high an estimate with consumption claimed in glue, plastics, paint, and insecticides. Because the figures available for consumption in the various industries do not agree with the estimated consumption (domestic production plus imports) it is difficult to obtain reliable statistics on the quantities of casein employed by different industries. Two different estimates for the consumption of casein by different industries are quoted in Table 3, and the original sources of these estimates are given.

TABLE 3—ESTIMATES OF CASEIN CONSUMPTION IN VARIOUS APPLICATIONS IN 1937 AND 1939 [47]

Application	*Consumption*[61] *Pounds* (1937)	*Consumption*[62] *Pounds* (1939)
Paper coating	52,000,000	26,700,000
Plastics	8,000,000	1,800,000
Glue	7,000,000	7,100,000
Paint	3,000,000	8,900,000
Insecticide sprays	1,000,000	....
All other uses	2,000,000	4,500,000
	73,000,000	49,000,000

Notwithstanding the difference in the above estimates, the consumption of casein by the paper industry, as well as in glue, has probably remained relatively the same in the last decade,[61] while casein plastics and casein paints have made

[61] Sutermeister, E. and Browne, F. L., ibid., pp. 402-3.
[62] Data furnished by the United States Tariff Commission.

definite gains during that period. The consumption by "all other uses" is increasing along with improvements in the manufacture of casein leading to greater uniformity of the product, and with the introduction of modified caseins of improved properties. With the recent advent of the more water-resistant phenol- and urea-formaldehyde resin glues and their increasing use in the plywood industry, the consumption of both casein and seedmeals in plywood gluing may decrease.

The production of various animal glues, containing generally greater than 80% protein, are shown in Table 4.

TABLE 4—PRODUCTION OF GLUE [47]

(Millions of pounds)

Year	*Animal*	*Casein*	*Flexible and Fish*	*Total*
1927	112.3	3.2	7.5	123.0
1929	106.4	6.8	10.2	128.5
1931	89.4	4.8	10.2	104.4
1935	90.3	5.9	13.8	110.0
1937	121.1	8.0	15.9	145.0

Estimates of the glues used in the plywood industry in 1939 are shown in Table 5. In addition to those shown, a small amount of animal glue is used by the plywood industry.

TABLE 5—GLUES USED IN PLYWOOD INDUSTRY (1939)

Types of Glue Used	*Million Pounds*
Seedmeal	18
Cassava starch	7
Resin	7
Casein	5
	37

The production and value of the soybean meal, and the other seedmeals referred to in this chapter, for the period 1926-1938, are given in Table 6. The rapid increase in the production of soybean cake and meal during this period is noteworthy. In Table 1, statistics are shown for the production and consumption of soybeans, the meal and the oil for 1939. The 1939 production of isolated soybean protein is estimated at two million pounds.

TABLE 6—PRODUCTION AND PRICES OF SEEDMEALS (MILLIONS OF POUNDS) [63]

Year	*Soybean Cake and Meal*	*Average Price per Ton, 41% Protein, Bagged, Chicago*	*Cotton-Seed Cake and Meal*	*Average Price per Ton, 41% Protein, Bagged Car Lots at Memphis*	*Linseed Cake*	*Peanut Cake and Meal*
1926	16.0	....	286	$30.74	1529.2	15.4
1928	42.4	....	66	41.41	1610.4	24.4
1930	195.4	$32.52	110	26.61	1129.4	30.8
1932	169.4	27.17	230	15.80	753.6	29.2
1934	446.0	34.12	250	32.31	835.2	91.2
1936	984.6	40.61	130	34.34	1231.8	118.8
1938	2107.2	25.98	430	22.16	1012.0	130.8

[63] Feed Statistics, published by U. S. Department of Agriculture, Bureau of Agricultural Economics, Supplement (Feb. 28, 1940).

Improvements in each protein will undoubtedly be made in the future, with increased consumption of each. Improvements in the color and adhesive strength of soybean protein will likely see its use in applications where casein is now used, particularly when prices of casein are high. The already abundant and increasing source of soybean protein should permit maintaining the price of the isolated protein at a low level, while the price of casein will probably continue to be influenced by the demand for milk by-products other than casein such as butter, cheese, powdered milk, and lactose. Of the new uses for these proteins likely in the next few years, the further development of synthetic (regenerated) fiber will probably consume the largest tonnage. Although as indicated previously, casein fiber is now being produced on a commercial scale in this country, while fiber from soya protein has only reached semi-commercial production,—of the two, the fiber from soybean protein appears to be the most significant economically.

READING LIST

CASEIN

Sutermeister, E. and Browne, F. L., "Casein and Its Industrial Applications," second edition, Reinhold Publishing Corp. (1939).

Hadert, H., "Casein and Its Uses," translated by Goldsmith, H., Chemical Publishing Co. (1935).

Tague, E. L., "Casein, Its Preparation, Chemistry, and Technical Utilization," D. Van Nostrand Co. (1926).

Scherer, R., "Casein, Its Preparation and Technical Utilization," third English edition, translated by Stocks, H. B., D. Van Nostrand Co. (1921).

Trimble, C. S. and Bell, R. W., "Methods for Manufacturing Acid-Precipitated Casein from Skim Milk," U. S. Department of Agriculture Circ. No. 279 (1938).

SOYBEAN

Horvath, A. A., "The Soybean Industry," first edition, Chemical Publishing Co. of New York (1938).

Satow, S., Tech. Rep. Tôhoku Imp. Univ. *2*, No. 2 (1921); ibid. *3*, No. 4 (1923).

McBride, G. W., Chem. & Met. Eng. *47*, No. 9 (1940); McBride, G. W., Food Industries *12*, No. 10 (1940).

Boyer, R. A., Ind. & Eng. Chem. *32*, No. 12 (1940).

CHAPTER 45

LEATHER *

EDWIN R. THEIS
Professor of Chemical Engineering, Lehigh University

Leather is made from animal hide or skin so treated by chemical reagents as to make it non-putrescible and thus resistant to decay. Any animal skin may be converted into leather but industrially only certain hides or skins are used for this purpose.

The demand for meat governs the production of leather due to the fact that hides and skins are a by-product of the Packing Industry. Practically all hides and skins removed from meat-producing animals are used in the manufacture of leather, regardless of the demand for leather.

Hides and skins are carefully removed from the animals since any defects such as "cuts" and "holes" affect their commercial usage. The removal of the hide or skin from an animal is known as flaying and in the United States the procedure is somewhat as follows: The animal, after first being stunned, is hung by either one or both of its hind legs, the throat cut and the blood allowed to drain. The animal is moved (Figure 1) by means of an overhead conveyor past a number of men who, each having a particular job to do, strip off the hide or skin. The skin, as soon as it is removed from the animal, is dropped down a chute to the hide cellar, where, after animal heat has been dissipated, it is ready for the "curing" operation.

CURING OF HIDES AND SKINS

The operations of killing and flaying proceed so rapidly that the hide or skin, when it reaches the cellar, still contains the so-called animal heat. This heat must be dissipated previous to curing and for this reason the hide is left to cool for a matter of two hours before curing is begun. Because the skin contains bacteria and autolytic enzymes, the curing operation must not be delayed unnecessarily. After cooling to the cellar temperature, the hide or skin is ready for curing.

The site selected for building a hide pack should have good drainage and should be of rather large area, although there is no hard and fast rule for a

* In all former editions of this Manual, the chapter dealing with Leather was written by the late Doctor Allen E. Rogers of Pratt Institute. It was the great privilege of the present writer to know Allen Rogers, both in a professional way and as a man. Allen Rogers had much to give to the leather industry and to young men and he gave wholeheartedly and abundantly of his time and effort To his memory, this chapter is affectionately dedicated.

pack size. Common practice[1] calls for packs with the width about half the length, namely about 15 by 30 feet. Pack heights should not exceed 4.5 feet for best results.

After the location for building the packs has been selected, No. 2 rock salt should be scattered generously upon the floor in order that the hair side of the bottom layer of skins will be protected with brine. The skins are then

FIG. 1. Removing Hides from Animals.

carefully piled in the packs, a layer of rock salt between each and every skin, and the skins so placed that the brine formed cannot readily run off but must percolate through the pack. The amount of salt used is generally about one pound of salt per pound of hide. The temperature maintained in the curing cellars is about 55° F. After the pack has been completely built, it is usually allowed to remain undisturbed for 30 days in order that complete curing may result.

The object of curing the hides is to prevent decay prior to the processing into leather by the tanner. While salt does not kill bacteria, it retards their activity as it does that of the autolytic enzymes. At the time of the begin-

[1] Price, J., "North American Packer Hides," Pratt Bros., Chicago (1939).

ning of the curing, the hide or skin contains approximately 62 per cent of water: that is, 100 pounds of green hide contain 62 pounds of water and are capable of dissolving some 23 pounds of salt.[2] It is quite natural to ask what role this dissolved salt plays in the actual curing process. Theis has found that the salt is merely dissolved in the free water of the green unsalted skin—surrounding each fibre with a more or less saturated salt solution. The salt in no way combines with the protein of the skin but merely exists as a saline solution upon and within the skin. During the curing, the salt diffuses into the skin, dissolving in the free water of the skin, bringing about a dehydration and causing small rivulets of bloody salt water to run from the pack of skins. This action causes loss in weight and is known as shrinkage. While this shrinkage is in reality no real loss, it is important in computing the price of green salted hides or skins since the shrunken material now contains more leather-making protein. A properly cured hide or skin loses some 35 pounds of its original water and gains some 6 pounds of salt.[3]

It has already been mentioned that curing must not be delayed after the dissipation of body heat, since bacterial and enzymatic action will result. Delay in curing causes the salt to be taken up at a much lessened rate, thus tending still further to favor bacterial activity.[4] This lessened rate is due to certain coagulation of blood and proteins within the skin. It has been found that a delay of only one hour causes the salt to diffuse into the hide only 69 per cent as fast as when curing was started immediately.

After approximately 30 days of curing, the hides or skins are usually "taken up," the excess crystal salt brushed off, the hides bundled and then shipped to the tannery ready for processing.

Argentina has become noted as a large exporter of hides and these hides as a general rule are superior to the domestic brand of large hides, due largely to the method of curing. They are known in the trade as *frigorifico* hides.

Frigorifico hides are treated somewhat differently from domestic hides. The hides, after removal from the animal body, are thoroughly washed in order to remove blood, dung and soluble protein matter. Next, adhering flesh is removed and the hides are soaked for 48 hours in a concentrated brine (NaCl) solution after which they are salted down as in the instance of domestic curing. Brined hides produce more and better leather than merely salted hides.[5]

In the Near and Far East, hides and skins are merely dried. This is a most effective method of preventing putrefaction since bacteria and molds demand water for their activity. The skin must not be dried too quickly, however, because the outer fibres become too hard, while the inside of the skin is too wet, thus preventing proper complete drying. On the other hand, if drying is carried out too slowly, putrefaction may set in, giving rise to hair slippage,

[2] McLaughlin, G. D., and Theis, E. R., J. Amer. Leather Chem. Assoc., *17*, 376, 399 (1922).

[3] McLaughlin, G. D., and Theis, E. R., J. Amer. Leather Chem. Assoc., *17*, 376 (1922).

[4] McLaughlin, G. D., and Theis, E. R., ibid.

[5] McLaughlin, G. D., and Theis, E. R., J. Amer. Leather Chem. Assoc., *17*, 399 (1922).

and eventually, to poor leather. Goat and kid skins are usually received in this country in the dry or *flint* state.

Skins from New Zealand and Australia are now being received that have first been salted down and then kiln dried. These skins are working out satisfactorily.

CLASSIFICATION OF HIDES AND SKINS

Briefly, the classification of hides and skins is as follows—taking as a first premise that a skin is simply a small hide:

In the case of cattle hides—

1. A hide weighing less than 15 pounds in the wet green salted state is called a calf skin. These skins in turn may be further classified as: (a) 4 to 5 pound skin; (b) 5 to 7 pound skin; (c) 7 to 9 pound skin; (d) 9 to 12 pound skin; and (e) 12 to 15 pound skin.
2. If the skin weighs 15 to 25 pounds, it is known as a *kip*.
3. If the skin weighs 25 to 30 pounds, it is called an oversized kip.
4. If the skin weighs over 30 pounds, it is known as a hide.

In the case of cow hides, one weighing less than 53 pounds is known as a light cow, while one weighing over 53 pounds is called a heavy cow. Hides from male animals are classed as bull, steer or stag, according to characteristics of the hide caused by castration. Bull hides are from animals that have not been castrated, and are characterized by very thick heads, necks and shoulders, and by loose flanks. Bull hides are usually poor in quality, heavy in weight, and range from 60 to 120 pounds. Steer hides are from animals castrated as calves. This operation gives a much more satisfactory hide. A steer hide weighing less than 48 pounds is called an ex-light steer; 48 to 58 pounds, a light steer; and 58 pounds and above, a heavy steer.

The leather industry, one of the ancient arts, has a language all its own. A native cow hide is one from an animal which has not been branded, while a Colorado steer hide may never have been near Colorado—the term merely means the hide has been branded on the side or butt area or both. If the hide is compact, narrow and plumb, it is called a Texas steer. Hides that are unusually wide are called *spready,* while plump hides have a dense and uniform structure and have surfaces small in comparison to their weights. Hides are usually designated January hides, June hides, October hides, etc., or perhaps simply as winter or summer take-off. Hides taken off in summer usually give better yields and provide a higher quality of leather. For making fine suède leather, drumheads or parchment, skins of unborn animals are used. Such skins are called slunks. There are other common terms: big-packer hides, small-packer hides, New York City butchers, etc.—all terms applying to the locality of take-off. Hides coming from Argentina, corresponding to the large-packer hides, are known as *frigorifico* hides. Hides from foreign sources may (if cured by drying) be known as dry hides or flint hides; or, if salt is used, dry salted hides.

Goat skins are usually named after the country of origin—Amritsars, Brazilians, Capetowns, Chinas, etc. These skins usually come into this country as flint dry skins. Some kid skins from India arrive which have been treated with a clay known as khari salt. This clay contains sodium sulfate. From

India also come the so-called East India kips and goat skins. These skins have been partially processed and, after arrival in this country, the process is completed.

STRUCTURE OF ANIMAL SKIN

Animal skin is a tissue. It can best be studied by cutting a section and then viewing it under the microscope All skins are divided into three distinct layers: (1) the epithelial tissue, which is a rather thin outer layer and known as the epidermis; (2) the derma or corium, which is a much thicker layer and is in reality the true skin; and (3) the adipose tissue, known to the tanner as *flesh*, which is relatively thin and fatty in character. Figure 2 shows a photomicrograph of a vertical section of a cow hide. The epidermis is shown as a thin dark line covering the upper surface and represents about 1/200th of the thickness of the skin. The adipose tissue can be seen as the dark under-surface and, if stained with a fat dye, would show a great number of fat cells. The thickness of this adipose layer depends principally upon the source of the skin but in general represents about 1/30th of the total thickness of the skin. Between these two layers is the derma or corium. The corium represents the true skin and real leather-making protein. It is divided into two characteristic portions: the thermostat layer, representing about 1/50th of the corium, containing the hair roots, some oil and sweat glands, etc.; and the under-corium, which consists of fibrous bundles making up the strength of the skin. The thermostat layer is known to the tanner as the *grain*. It functions during life as a thermostat controlling body heat.

FIG. 2. Photomicrograph of Section of Raw Cow Hide. 16× (Courtesy John Arthur Wilson)

For the manufacture of leather, the epidermis, hair and adipose layers[6] are more or less completely removed. In the manufacture of furs, the adipose tissue is discarded.

[6] Those readers desiring more information concerning the histology and morphology of animal skin are referred to Wilson's classical works dealing with this subject. (See Reading List at end of Chapter.)

HIDE DAMAGES

Hides and skins are often seriously damaged even while on the animal's back. Therefore, there are two types of hide damage: that occurring during life, and that taking place in the removal of the hide from the animal and in the curing operation.

The damages occurring to the skin of the living animal may be listed as follows: (1) scratches from barbed wire fences; (2) brands, used for identification of cattle; (3) wire damages, coming from the inhuman practice of placing wires in the hides of cattle; (4) grubs or warble flies; (5) lice; (6) ticks, fleas, mange, pox; and (7) ringworm scars.

The other type of hide damage is due to poor flaying or to improper curing. These damages are: (1) butcher cuts; (2) poor pattern; and (3) grain cracks. Curing damages[7] are very important to the tanner; these are: (1) salt stains, formerly believed to be due to salt, but now known to arise from improper curing; and (2) bacterial and degenerative changes, caused by delayed and improper curing.

PRE-TANNAGE PROCESSES

The preceding pages represent processes, treatment and facts concerning hides and skins prior to delivery at the tannery. Immediately upon arrival at the tannery, the skins should be removed to the hide house, the bundles of skins opened, examined for damage, weighed and stamped for identification purposes. The hide house must be cool, and often, for long storage, should be refrigerated. The tanner usually classifies hides or skins as to source in order that the best quality and yields may be obtained. The hides are piled for storage according to weight, kind, substance, damage, etc., so that the same grade of raw stock may be readily available for subsequent treatment.

The hides or skins are removed from the hide cellar as required. They are then trimmed, and the ears, hoofs and tails are removed. For this purpose, the skins are placed over a wooden beam and, by the use of a two handled knife, the parts of the skin having no potentialities for leather making are removed.

The Soaking Process—The first process to which the tanner subjects the skins is the *soaking* process. This operation has two distinct purposes: the first, to remove the salt, dirt, dung and soluble protein matter; and the second, to allow the skin fibres to adsorb water and swell. Essentially, the soaking operation is to allow the skin to come back to as normal a condition as that which existed when upon the live animal. The soaking must be performed in a very careful manner since it is fraught with serious difficulties which will be discussed in the following paragraphs.

The animal skin is made up largely of protein and water. This water exists in two forms, free and bound. The free water is that which is easily removed by pressure, low temperatures or dehydrating agents. The bound water is that which is bound to the protein and is not removed at low temperatures or by pressure. During the curing operation the salt dissolves in the *free* water

[7] McLaughlin, G. D., and Theis, E. R., J. Amer. Leather Chem. Assoc., *17*, 376, 399 (1922). McLaughlin, G. D., and Rockwell, G. E., ibid., *18*, 233 (1923).

but not in the bound water. The dehydration or shrinkage which occurs during curing is at the expense of the free water. Thus one of the purposes of soaking is not only to remove the salt but to put the free water removed during curing back into the skin.

Bacterial Action. As the hide soaks, soluble proteins, occluded blood and lymph diffuse from the skin into the soak water, making an excellent bacteriological media. If soaking is prolonged unduly, bacteria begin to flourish with the subsequent digestion of leather-making protein, or causing hair slippage and other damaging effects. It must be remembered that there is a bacterial life curve composed of four distinct component parts: first, the period of lag; second, the period of logarithmic increase; third, the period of stability in which life and death cycles merely balance; and finally the period of extinction. The first two cycles are those in which we have interest. During the period of lag, the bacteria contained on and within the skin are not acclimated to their surroundings and many die off during the period and thus do not have an opportunity to act upon the skin itself. The time of this lag period is dependent upon temperature, salt content of the skin and rapidity at which the soluble proteins diffuse from the skin. It may be some 24 hours or it may be only a few hours. As soon as the bacteria become acclimated to their surroundings, propagation ensues rapidly and then the cycle of logarithmic increase begins. The skins, if possible, should be removed prior to this second cycle if no bacterial damage is desired.

Effect of pH. During curing, the fibres suffer a change of shape and size and become somewhat shrunken in character, depending upon the rate of drying and other factors. During soaking, the water penetrates the skin and attempts to undo these changes. At the same time the skin hydrates and swells (imbibes water). The amount of swelling is correlated with the pH value of the soak water. Since skin is largely protein, we find that skins swell both in acids and alkalis and much is made of this property as we shall later see when we discuss unhairing and pickling.

Soaking of Calf Skins. Since space herein is limited, only the soaking of green, salted calf skins and dry skins will be outlined in detail. A pack of calf skins is placed in a drum made of cypress wood. The drum usually has a diameter of 8 feet and a width of 5 feet, 4 inches and rotates at a speed of about 14 to 17 revolutions per minute. An abundant stream of water is allowed to flow over the skins as they tumble in the drum. The wash water flows out through the drum door. This operation is usually carried on for some 5 minutes. The skins then are removed from the drum and thrown one by one into a large pit (Figure 3) of clean water maintained if possible at 60° to 65° F. After remaining in this water for 18 to 24 hours, the skins are removed and the adhering flesh removed on a fleshing machine. This machine will be described later. After fleshing, the skins are thrown back into clean cold water and allowed to remain for an additional 24 hours. After thus soaking, the skins are ready for the unhairing bath. In place of the pit, paddle pits may be used. (Figure 4.)

Fleshing. It was noted above that the skins were fleshed between "soakings." This is necessary so that "flesh" is removed, thus allowing the skins to hydrate better and to open out the fibres of the skin, in this manner expediting the soaking and subsequent "liming" action. A fleshing machine consists essentially of two rolls, one of corrugated metal and the other of rubber; the rolls grip the skin with a positive pressure that can be regulated and in this way the flesh side of the skin is drawn across a revolving cylinder set with spiral blades. The revolving bladed cylinder thus passes on the flesh side of the skin, which is backed by the rubber roll, and cuts away the adipose tissue.

FIG. 3. Hides Toggled Together Ready for Soaking.

Some tanners use a 6 to 8 hour soak in a paddle wheel and claim better results for this method. The drum-washed skins, as previously described, are thrown into a vat equipped with a rotating paddle and filled with clean cool water. The skins are paddled 10 minutes out of each hour. After such treatment, the skins are green fleshed and are ready for the unhairing bath.

Soaking Heavy Hides. In the soaking of heavy green salted hides, for example, in the production of sole leather, the hides are usually washed for 5 or 10 minutes in a drum, using running water, and are then placed in still clean-water pits for 24 hours, after which they are green fleshed and ready for the unhairing operation. Domestic large-packer hides [8] should be soaked 24 hours at 65° F., while South American *frigorifico* hides should only be soaked some 16 to 18 hours for the best quality of leather.

[8] McLaughlin, G. D., and Theis, E. R., J. Amer. Leather Chem. Assoc., *18*, 324 (1923).

Soaking Dried Hides. Annually, some 39 million goat skins are received in this country and the great majority of these are in the flint-dried condition. Dried stock, whether heavy hides or light skins, wets back during the soaking operation only with the greatest difficulty. As a consequence, the soaking of such stock becomes important. A dried goat skin should take up 200 per cent of its dried weight in water but in practice this is rarely obtained. Soaking dry

FIG. 4. Row of Paddle Vats Used for Soaking Calf Skins.

hides and skins first in a 10 to 15 per cent solution of salt (NaCl) for 24 to 48 hours materially aids the wetting back of such stock.[8] In practice the stock is soaked in paddles for 48 hours in a salt solution, draining off the salt solution from the paddle vat, and then soaking the salt-treated stock for several days in clean cool water. During this second soaking, the skins may be removed for green fleshing. As a material aid in the salt soaking, a small amount of sodium sulfide may be added. This reagent gives an alkaline reaction and drastically retards any bacterial digestion during the long soak. The same procedure applies, with modification, to heavy dry hides.

Many tanners use certain antiseptics in individual soaking. Liquid chlorine was used by the author (40 parts per million) for many years with excellent results. Certain organic chemicals such as *p*-nitro phenol and β-naphthol are used to retard bacterial activity in the soak waters.

UNHAIRING

In general, regardless of the type of leather, the hides must be unhaired. There are many underlying principles involved in this process and these will be rather fully discussed.

Usually the soaking, liming, unhairing, deliming and bating operations are known as *beamhouse* operations. The object of the unhairing bath is to free the skin from hair, epidermis and from the glands of the thermostat layer. These tissues are made up of a particular protein known as keratin. The remaining part of the skin, freed from these substances, is usually considered to be collagen. For leather manufacture, collagen, a skeletal fibrous protein, is the substance that is of interest and it will be discussed in detail.

Structure of Collagen—According to the latest information, collagen is made up of 288 amino acid groups bound together through peptide linkage as —HOOC—CHNHCO—CHNHCO—$CHNH_2$, by means of the α-amino group of one amino acid with the COOH group of another amino acid. Among these amino acids are those which have strong acidic or basic properties and are known as dibasic or dicarboxylic amino acids. These particular amino acids are only bound in the particular protein chain through the α-amino or α-carboxyl group, thus allowing the residual amino or carboxyl group to be more or less free in the chain. In modern protein chemistry, it is now realized that, in the main, these terminal amino groups of one chain stand more or less opposite terminal carboxyl groups of another chain and thus exert an attraction which tends to hold the chains together. This particular type of attraction is known as a salt linkage and is of real importance in considering the binding of either acids or alkalis. The analysis of collagen is given in Table 1.

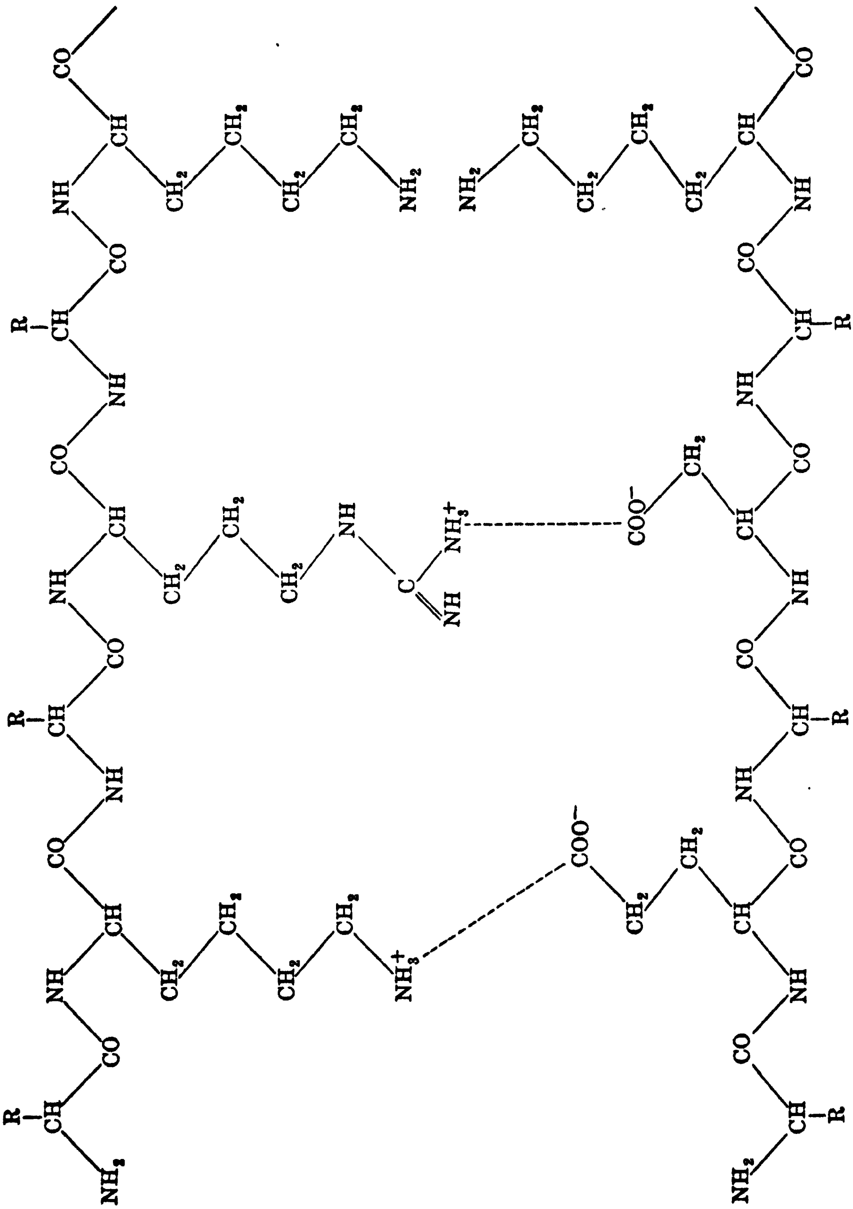
TABLE 1—COMPOSITION OF COLLAGEN *

Amino Acids

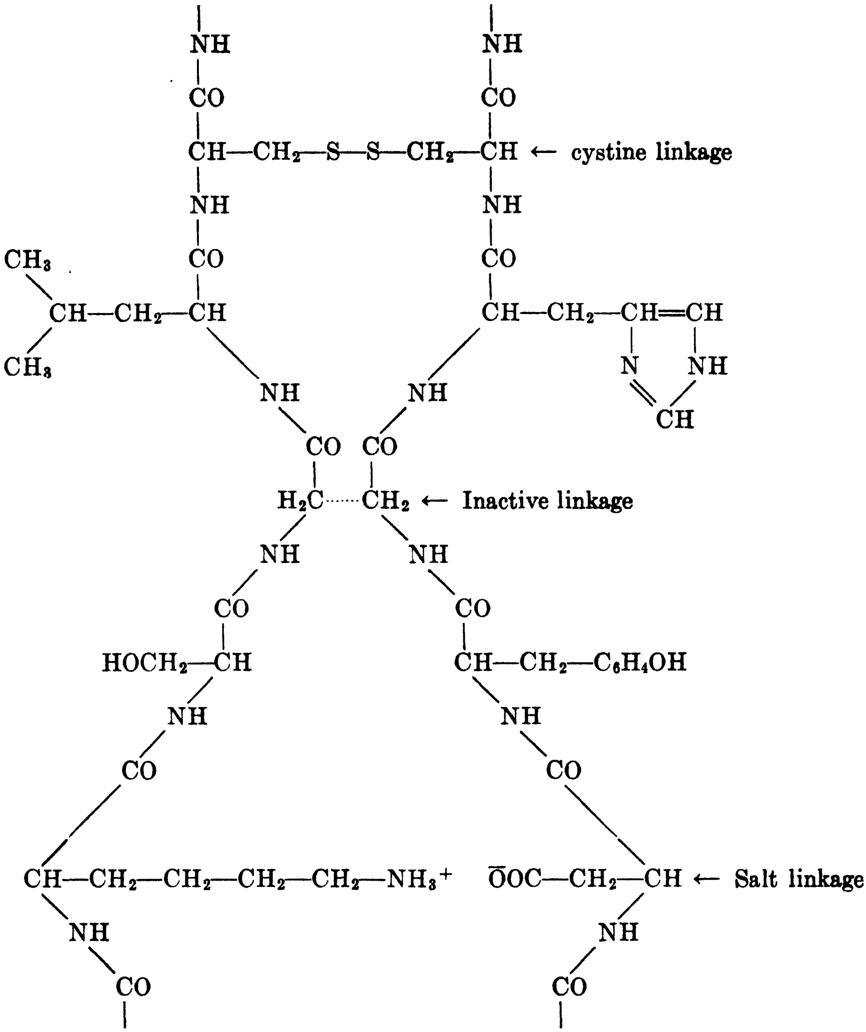
Amino Acid	*Per Cent*
Glycine	24.7
Alanine	8.7
Leucine	7.1
Phenyl alanine	1.4
Tyrosine	1.0
Serine	0.4
Aspartic acid	3.5
Glutamic acid	5.7
Proline	18.9
Oxyproline	10.8
Arginine	8.4
Lysine	4.7
Histidine	0.6

* Taken from "The Chemical Constitution of Collagen," F. Schneider, Collegium, *97*, 839 (1940).

The acids which exert an acidic reaction are aspartic and glutamic acid, and the basic amino acids are arginine, lysine and histidine. The salt linkage mentioned above may be illustrated in the following diagram.



Salt linkages, on the other hand, are not the only linkages between individual protein chains. There are the short linkage, the inactive linkage and the sulfur linkage (only applicable to keratin type proteins). All of these linkages are illustrated in the diagram given below.



Proteins as well as amino acids are considered to exist as zwitter ions and thus the charged amino and carboxyl groups will play a very important role in the liming, pickling and tanning operations. If we express the zwitter ion as follows, using an amino acid as an example—

$$^{+}H_3N\text{—}R\text{—}COOH \underset{}{\overset{HCl}{\leftrightarrows}} {}^{+}H_3N\text{—}R\text{—}COO^{-} \overset{KOH}{\leftrightarrows} H_2N\text{—}R\text{—}COO^{-}K^{+} + H_2O$$

we see that addition of acid represses the ionization of the charged carboxyl group, while the addition of alkali represses the ionization of the charged amino group. Now, if we go one step further and have a charged amino group of one chain stand opposite a charged carboxyl group of another chain, we have

$$\updownarrow\text{—}NH_3^{+} \quad {}^{-}OOC\text{—}\updownarrow \xrightarrow{Ca(OH)_2} \updownarrow\text{—}NH_3 \quad CaOOC\text{—}\updownarrow$$

in which the arrows indicate protein chains. Thus, either the addition of acid or alkali will tend to break this salt linkage. More concerning this linkage will be given under the discussion of the various tannages.

The Lime Method—The oldest method of unhairing is the prolonged contact with skin of a saturated lime solution containing excess solid lime. If this action is studied under the microscope, the first noticeable action is a slow disintegration of the cells of the Malpighian layer of the epidermis. By the end of some five days, such action has proceeded far enough so that hair can be removed by means of a blunt knife. The lime water causes a swelling of the hide, besides bringing about certain hydrolysis of the collagen. Both time and temperature affect the rate of hydrolysis. On the other hand, the keratinous proteins (hair, etc.) hydrolyze more rapidly than collagen and such conditions must be recognized. If the tanner wishes to save the hair (valuable by-product), hydrolysis of the hair must not ensue or it will "mush" and lose strength.

Use of Sulfides. Usually, saturated lime plus solid lime is too slow in causing unhairing and for that reason certain other reagents are added to speed up the reaction. It has long been known that such sulfides as arsenic sulfide or sodium sulfide can cause rapid uphairing. When sodium sulfide is dissolved in the lime, the following reaction takes place—

$$2Na_2S + Ca(OH)_2 + 2H_2O \rightarrow 4NaOH + Ca(HS)_2$$

thus increasing the alkalinity of the lime suspension through the formation of caustic soda. The following table (Column D) shows the increase in pH value of the lime through the addition of various amounts of sodium sulfide.

TABLE 2—EFFECT OF SULFIDES ON pH OF $Ca(OH)_2$ SOLUTIONS

Grams $S^{=}$ Added to 400 Ml. Lime Solution Containing 10 Gms. Solid $Ca(OH)_2$	*As_2S_3 Glass Electrode*	*NaHS* Glass Electrode*	*Na_2S† Glass Electrode*
(A)	(B)	(C)	(D)
0.00	12.47	12.47	12.47
0.25	12.54	12.47	12.50
0.50	12.43	12.47	12.50
0.75	12.43	12.45	12.52
1.00	12.43	12.45	12.53
1.50	12.38	12.45	12.57
2.00	12.35	12.44	12.60
3.00	12.32	12.44	12.68

* NaHS containing 70% NaHS.
† Na_2S flake containing 60 to 62% Na_2S.

This table also shows the effect on pH of sodium sulfhydrate and arsenic sulfide. The reactions of sodium sulfhydrate and arsenic sulfide are

$$2NaHS + Ca(OH)_2 \rightarrow 2NaOH + Ca(HS)_2$$

$$As_2S_3 + 6Ca(OH)_2 \rightarrow 3CaS + Ca_3(AsO_3)_2 + 6H_2O$$

Thus, the reader can readily see that while sodium sulfide in its reaction produces an excess of caustic alkali, the sulfhydrate produces only half as much and in reality does not increase the pH of the unhairing bath whereas the sulfide increases the pH. The use of arsenic sulfide actually decreases the pH value of the unhairing mixture but causes an increase in the dissolved $Ca(OH)_2$. Table 3 shows the effect upon the dissolved calcium ions for the sulfide, sulfhydrate and arsenic sulfide.

TABLE 3—EFFECT OF SULFIDES ON SOLUBILITY OF $Ca(OH)_2$

Grams S Added to Lime Solution	← Grams CaO per Liter →		
	As_2S_3	$NaHS$	Na_2S
0.00	1.320	1.320	1.320
0.25	1.540	....	....
0.50	1.652	1.424	1.222
1.00	1.982	1.454	1.036
2.00	2.650	1.500	0.774
3.00	3.404	1.536	0.646

Until the beginning of the second World War, it was the practice of the American tanner producing the finest calf leather to use arsenic sulfide as an aid in unhairing. It was felt that arsenic sulfide produced a finer grain, more smoothness and better "feel" in the finished leather. Until recently (1940) there was no adequate explanation for this apparent fact other than actual experience, but now it is believed that the effect is due to the actual lowering of the pH value and the consequent decrease in the astringency of the unhairing bath. It is questionable as to whether the calcium arsenite plays any role in the reaction.

There has recently come upon the market a calcium sulfhydrate solution which may have an important bearing in the unhairing bath. This material acts in a similar way to arsenic sulfide, producing a decreased pH value and thus lowering the astringency of the bath. In many ways, it should be the answer to some serious problems in unhairing.

Other Chemical Reagents. Many chemicals have been suggested for the aiding of unhairing. Research work of the Tanners' Council Research Laboratory at the University of Cincinnati suggested the use of dimethylamine. Although this material is an excellent unhairing agent when used in conjunction with lime, it is expensive and therefore not widely used. It is said to produce a very smooth leather. Marriott and Merrill almost simultaneously suggested that any material acting as a reducing agent in an alkaline solution would expedite this unhairing reaction. Such studies of the unhairing activity of such substances as sodium thiosulfate, sodium sulfite and sodium cyanide showed that these sub-

TABLE 4—EFFECT OF ADDITION OF KCN TO 400 ML. LIME LIQUORS CONTAINING 100 GMS. SOLID $Ca(OH)_2$

Grams KCN *	pH Value	Gram Soluble CaO/Liter
0.00		
0.25	12.50	1.424
0.50	12.51	1.424
0.75	12.53	1.410
1.00	12.53	1.406

* Amount of cyanide added corresponds to actual percentage based on green salted skin weight in a liquid-skin ratio of 4 : 1.

stances under proper conditions were ideal unhairing agents when used in conjunction with lime. Tables 4, 5 and 6 show the effect of these reagents upon the final pH and lime solubility of the unhairing bath.

TABLE 5—EFFECT OF ADDITIONS OF Na_2SO_3 TO 400 ML. LIME LIQUOR CONTAINING 10 GRAMS SOLID $Ca(OH_2)$

Grams Na_2SO_3 Added	*pH Value*	*Dissolved Calcium as Grams CaO/Liter*
0	12.50	1.400
.25	12.57	1.251
.50	12.60	1.096
.75	12.62	0.948
1.00	12.60	0.812
2.00	12.76	0.526
3.00	12.86	0.366
4.00	12.95	0.261
5.00	13.01	0.213
6.00	13.07	0.177

TABLE 6—EFFECT OF ADDITION OF $Na_2S_2O_3$ TO 400 ML. LIME SOLUTION CONTAINING 10 GRAMS SOLID $Ca(OH)_2$

Grams $Na_2S_2O_3$ Added	*pH Value*	*CaO Grams per Liter*
0.00	12.53	1.400
0.25	12.53	1.443
0.50	12.53	1.487
0.75	12.53	1.513
1.00	12.53	1.535

All three of these reagents are being used in American tanneries, but for specific results. Sodium sulfite, through its increased pH value, makes very fine suède leather; sodium cyanide marketed by the DuPont Company is being used in the manufacture of kid leather; and thiosulfate in the manfacture of white leathers.

The action of these various reagents upon the hide keratins is a very complex one. Work done in 1941 [9] indicates a breakdown of —S—S— linkages of the keratin with the ultimate formation of thiosulfate as an end product.

$$R{-}S{-}S{-}R + 2NaHS \rightarrow 2RSH + Na_2S_2$$

$$R{-}S{-}S{-}R + 2Na_2S \rightarrow 2RSNa + Na_2S_2$$

$$R{-}S{-}S{-}R + Na_2S_2 \rightarrow 2RSNa + Na_2S_4$$

$$Na_2S_2 + NaOH \rightarrow Na_2S + Na_2SO_3$$

$$Na_2SO_3 \xrightarrow{+\ Na_2S} Na_2S_2O_3 + Na_2S$$

$$Na_2S \xrightarrow{R{-}S{-}S{-}R} Na_2S_2$$

[9] Theis, E. R., and Ricker, M. D., J. Amer. Leather Chem. Assoc., *36*, 62, 201 (1941).

The foregoing pages have given in a brief manner the various theories behind the unhairing reaction. Practice has made use of these theories and the following is a description of the various unhairing baths used in various tanneries.

The Unhairing of Calf Skin—For the unhairing of calf skins, it is usual to employ paddles. However, still pits may be used with reasonable success. The paddle vats are usually constructed so as to hold in the neighborhood of 500 skins or 5000 pounds soak weight. The paddle will accommodate some 2500 gallons of liquid. A paddle similar to that shown in Figure 4 is used. In order

FIG. 5. Unhairing Hides After Liming.

to begin this operation, the paddle is filled with water to two-thirds of its capacity and 300 pounds of hydrated lime together with either 25 pounds of sodium sulfhydrate or 50 pounds arsenic sulfide. The paddle is started and, while running, the 5000 pounds of soaked stock are added. The paddle is run for some ten minutes, then stopped. This paddle is run 5 minutes each hour period for 72 hours, at the end of which time the skins should be ready to unhair. The temperature of the lime should be 70° to 75° F. The operator should be careful not to stir in much air or paddle too often because excess paddling causes the grain to become coarse and the unhairing to be retarded.

As the hair slips easily, the skins should be removed from the paddle and passed to the unhairing machine. Figure 5 shows one type of unhairing machine. Essentially, the unhairing machine is similar to the fleshing machine previously described with the exception that the blades of the rotary cylinder are not sharpened and thus merely rub off the hair in place of cutting as happens in the fleshing machine. After the unhairing operation, the skins are usually subjected to a second fleshing upon fleshing machines. They are then ready for scudding which will be described presently.

In case still vats are used, it is necessary to remove the stock at intervals and either plunge the liquor mechanically or by means of air. This action is necessary in order to lift suspended solid lime and place the skins in a new position. Often a series of such vats are used. The hides are pulled from one pit to another, thus using the liquors over for a period of time. These older lime liquors sometimes offer certain advantages, such as more rapid unhairing and smoother grain surface. On the other hand, since these older liquors contain dissolved protein degradation products, ammonia, amines, etc. (which tend to

FIG. 6. Hand Scudding of Calf Skins. (Courtesy Ohio Leather Co., Girard, O.)

give the old lime less astringency), they are less uniform in character than a sharp lime. Often in order to obtain greater uniformity, half of the old lime is run to the sewer each time and there kept half made-up with fresh lime solution.

As the hides are hauled from the paddles or still pits, they feel rubbery and plump due to the swelling that has occurred during the liming period. The hydrolyzing action of the unhairing bath has extended only to the Malpighian surface of the epidermis. The destruction of this layer allows a complete severance of the outer epidermis from the true skin when subjected to the action of the unhairing machine.

The Scudding Operation. After the calf skins have been unhaired and fleshed, they are usually scudded. This is an action that scrapes and squeezes the remnants of epithelial tissue, hair roots, etc., from the skin surface. This may be a hand or machine operation. The better action is by hand (Figure 6), since if the skin is thrown over a beam and then if the knife stroke is made in the direction of the hair, from root to tip, the dirt, etc., is very easily squeezed out. This operation requires skilled workers and materially adds to the expense of beamhouse operation. For this reason a scudding machine is ordinarily used. This machine consists essentially of a large revolving drum with blades upon its outer surface. A skin thrown over a bolster pushes against the revolving drum and as a consequence of this action, has its surface cleaned in a manner analogous to the hand action explained above.

Cheeking. After scudding, the skins are cheeked in a cheeking machine. The heads and necks are usually much thicker than the rest of the skin, so they are put into this machine which cuts down this thickness any desired amount. After this operation the skins are ready for washing and bating.

Unhairing Goat Skins—The liming of goat skins is a variable operation. Each goat skin tanner has a different procedure. Some tanners lime in a drum while others use paddles. Some operators use a short lime while others may use as long as 14 days for this treatment. A satisfactory method is as follows. The skins are soaked for 3 days and then placed in a paddle (1600 pounds dry weight in a 2500-gallon paddle) together with 400 pounds of hydrated lime and 25 to 35 pounds of sodium sulfhydrate. The lime mixture is heated to 82° F. and kept at about 80° F. throughout the liming period. The unhairing time is usually 3 days. The stock is then unhaired, fleshed and scudded.

Unhairing Heavy Hides—Heavy hides, that is, green salted large-packer hides, can be unhaired similarly to green salted calf skins. For sole or belting leather, a series of vats are employed, usually three. The hides are toggled together (tail to head) and are thus reeled from one pit to the next, each 24-hour period for 3 days. The lime solutions are used over again for a period of 3 to 6 weeks. The unhairing mixture is 8 to 10 per cent lime and 0.25 to 0.50 per cent sodium sulfhydrate (based on green salted weight of skin). Each day the hides are moved to the next vat, the liquor being agitated prior to the entry of the skins. In a matter of 3 to 4 days, the skins are ready for unhairing.

Within the past few years, sole leather hides have been treated in similar way to calf skins. In other words, paddles are used and the hides remain in the same paddle during their entire liming period. In this case, 6 to 10 per cent of hydrated lime together with 0.4 per cent of sodium sulfhydrate (based on hide weight) are used. The lime and sulfhydrate are dissolved in sufficient water to give a ratio of 4 parts solution to 1 part of hide. The liming period is 3 days and the temperature 70° to 80° F.

When the heavy hides are ready for unhairing, they are removed to a warm water pool (90° F.) and kept in this pool for 3 hours. This warm water raises the temperature of the skins, removes some of the excess lime and materially aids unhairing in the unhairing machine.

Special Leathers—In the manufacture of certain side leathers and patent leather, the hair is removed from the hide through what is known as "burning off" the hair. In this process 5000 pounds of hide are placed in a paddle containing 1900 gallons of water, 200 pounds of 60 per cent sodium sulfide and 150 pounds of hydrated lime. The paddle is run for 1 hour and then only 5 minutes each hour for 16 to 18 hours. After this period, the sulfide-lime is drained and the stock subjected to a wash with running water in the same paddle. The skins are removed, fleshed and then returned to the paddle and given a reliming for 24 hours, using 1900 gallons of water and 150 pounds of lime.

During the first sulfide-lime treatment, the hair becomes pulped and largely dissolved. As a result it is not necessary to use an unhairing machine, because the pulped hair is removed during the intermediate washing process. After the reliming, the skins are taken to the fleshing machine for fleshing and in the case of fine side leather, the skins are carefully scudded by machine. After this treatment the hide is ready to be split and bated.

Sheep skins are usually dewooled previous to their arrival at the tannery. The wool is such a valuable commodity that the packer usually treats the skins so that the wool may be obtained, after which the skin is pickled and sent to the tanner as pickled stock. After slaughter, the skins are allowed to cool, are then placed in a paddle and soaked with cool water for a 24-hour period, the paddle being turned at intervals. After thorough draining, each skin is coated with a paste composed of hydrated lime and sodium sulfide. Care is taken that none of the sulfide paste touches the wool. After pasting, the skins are folded down the backbone, flesh to flesh. The pasted skins are hung head down for a 12-to-16-hour period in a room maintained at 80° F. Usually the next morning, the skins are thrown over a beam and the wool pushed off by hand. After dewooling, the skins are placed in a paddle containing a lime suspension and kept at about 80° F. overnight. These skins are then removed from the paddle, scudded, and are then ready for bating and pickling.

There are other methods of unhairing, such as by the use of enzymes or by means of "sweating." "Sweating" is the oldest method and is rarely used today. This method consists essentially of allowing the epidermal cells to decay in a room kept moisture saturated at 100° F. It is a difficult and dangerous procedure to follow.

It has been pointed out that most hides and skins are fleshed and unhaired. The removed hair is very carefully washed and dried and usually there is a ready market for it. The trimmings and fleshings from calf skin are usually sold to the gelatin manufacturer while such offal from heavy hides is sent along for glue stock. Some of the very large sole leather manufacturers render the fatty matter and grease from the fleshings and use the grease obtained in subsequent processing.

BATING

Bating is a process in which the skins are treated with a pancreatic enzymatic material in an ammoniacal solution. The ammonium salts present play a very important role in the action to be described. The proteolytic enzymes used contain proteases which act upon protein substances; lypases, upon fatty materials, and amylases upon carbohydrates. There are some seven important actions[10] during bating. These are: (1) removal of the degradation products of the epidermal system; (2) hydrolysis of elastin fibres; (3) hydrolysis of collagen fibres; (4) falling; (5) regulation of pH value; (6) deliming; and (7) bacterial action. Of these factors, only the first, fourth, fifth and sixth will be discussed in any detail.

Removal of Degradation Products—Degradation of the epidermal system merely means that during liming there has been an action upon the epidermis

[10] Wilson, J. A., "Modern Practice in Leather Manufacture," Reinhold Publishing Corp., New York, 1941.

and glands and that, even after unhairing and scudding, some of this material remains embedded within the surface of the skin. The function of the enzymatic bate is to act upon this "keratose" material, solubilizing and thus removing it. Studies of the action of the enzyme trypsin upon keratose have shown that at pH 7.6, the enzyme completely solubilizes this material. In natural bating, at the same time that tryptic enzymes are acting upon the keratose, the amylases and lipases are acting upon the glandular structures, removing fats and carbohydrates.

Falling is that function of reducing the alkaline swelling or plumping which has taken place during the previous liming. As it enters the bate, the skin is rubbery, hard and highly alkaline in character. During bating, neutralization of both the bound and free lime takes place, and the skin takes on a soft, flaccid appearance and feel. This action is due to the following reaction:

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_4OH + CaCl_2$$

since the bating material contains not only pancreatic enzymes but either ammonium chloride or sulfate. The neutralization of the free lime by the ammonium salt will tend to lower the pH of the bating bath—coming to an equilibrium at about pH 9.0 if no other agent is added. This gradual neutralization of the free lime within the skin causes the alkaline swelling of the skin to disappear. Temperature plays an important part in the falling of the skin.

Regulation of pH—Since we are interested in maximum enzyme activity and neutralization of the free lime of the skin, it is important to regulate the pH of the bating bath. At the time of bating, the skin contains both free lime and calcium ion bound to the protein, as explained in the discussion of unhairing. This bound lime is in form of a calcium salt of the collagen $\updownarrow\!-NH_2CaOOC-\!\updownarrow$. The free lime is to some extent neutralized through the action of the ammonium salts present in the bating material. However, such neutralization does not reduce the pH of the bath sufficiently to give maximum enzyme activity. In order to do this, acids such as sulfuric, sulfamic, hydrochloric or lactic are added previous to the addition of the bate. The acid is added in sufficient quantity to lower the pH of the bate water to 5.0. As lime is neutralized, the pH gradually rises and should be allowed to do so until the value reaches 7.6. At this point the bate should be added. Further acid additions may be necessary to maintain this value throughout the bating period. If acid is added as suggested above, all of the free lime and a portion of the bound lime will be neutralized and at the same time, the alkaline swelling will be completely reduced, and the skin will become very flaccid and smooth. In this way there is an excellent deliming action and a very carefully controlled bath.

For the production of certain types of leather, bating material is not used. In this case the skins are only delimed through the use of such acids as outlined previously. Deliming is not a function of the bating and only occurs if the pH of the bath is maintained lower than 8.4. It should be stressed however that both deliming and good enzymatic action are essential to good leather.

Previous to the present century, bating was a curious and mysterious operation. Each operator kept the process very secret. It consisted in treating the limed skins with a warm water infusion of the dung of dogs and fowl. It was found that such an operation caused the skins to lose their "rubbery" feel and to become smooth and flaccid. It was a disgusting operation but still a well-guarded secret. Due to scientific research in the tanning industry, today no such materials are used but in their place the more efficient, though more or less impure, pancreatic enzymes adsorbed upon wood flour are employed. Probably the most universal bating materials used in the United States are the "Oropons" made by the Röhm and Haas Company of Philadelphia, Pa. They consist of either pancreatic enzymes or bacterial enzymes together with ammonium salts adsorbed upon wood flour. The word "Oropon" is known the world over and rightly so since Dr. Röhm was a real pioneer in this important field of work.

Details of Bating Calf Skins—A practical method of bating calf skins would in general be as follows: The limed, unhaired and washed skins are placed in a paddle filled with water. The type of paddle used is identical to that shown in Figure 10. Enough dilute sulfuric acid is then added to maintain pH of 5.0 for 10 minutes. During this time the paddle is run continuously. Usually the deliming period for calf skins will be in the neighborhood of 30 minutes. The acid water is drained off and fresh water is added. The bath is heated to 92° to 95° F. and 0.8 to 1.0 per cent (based on skin weight) of Oropon added. The pH of the bath should be adjusted to 7.6 by occasional treatment with acid. The paddle is run 5 minutes out of each 15 minutes until bating is finished—usually some 90 minutes. As soon as bating is completed, as noted by the flaccid, smooth and porous condition, the skins should be removed from the paddle and taken to the pickling paddles or drums as the case may be.

Goat skins offer greater difficulty in the bating operation and usually have to be treated a longer period of time. It is usual to add a stronger bating material and the time of bating may be as long as 12 hours. In all other respects the bating of goat skins is essentially the same as that outlined for calf skins.

Degree of Bating—The degree to which a skin is bated depends upon the kind of leather to be manufactured, and care must be taken that the skins are not over-bated. It is usually found that over-bated skins tend to give a firm tinny piece of leather and therefore only a person with experience should judge the bating action in the tannery.

For the bating of heavy leathers such as sole and belting leather, a mild bate is used and a low temperature. For sole leather 0.5 per cent Oropon and a temperature of 80° F. are used. Therefore, in this case, only a surface action takes place and there is practically no deliming.

PICKLING

Pickling is a process wherein bated stock is treated with an acid-salt solution, whereby the stock is brought to a more uniform condition. It is more important as a pre-treatment for mineral tannage than for vegetable tannage and therefore in this treatise, the process will be discussed from the viewpoint of the chrome tanner.

Principles of Pickling—Of recent years, certain basic principles of the process have been outlined.[11] As was shown in our discussion of liming, the skin collagen has the ability to combine with both acids and bases. If bated

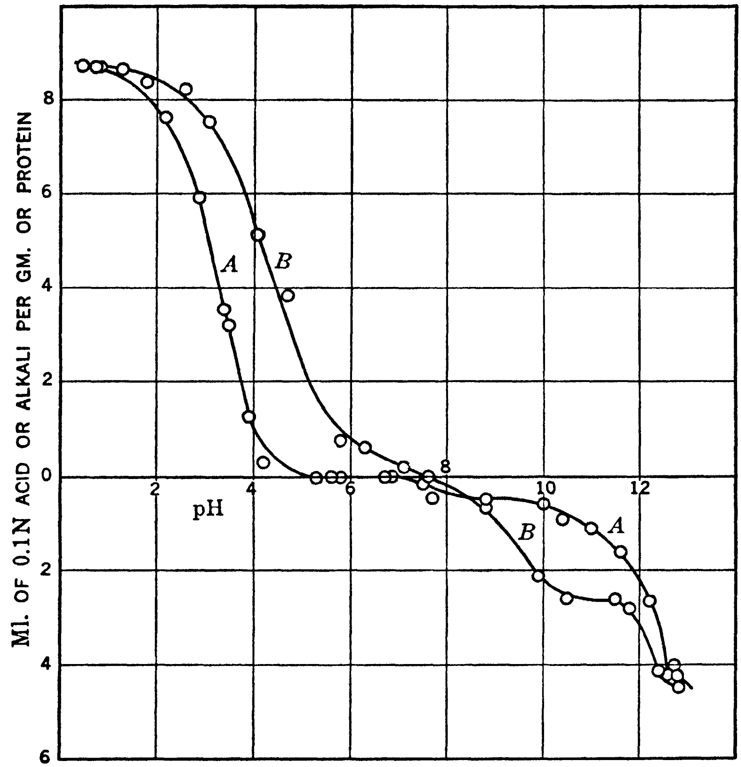


FIG. 7. Showing Acid or Alkali Bound by Collagen. (A) in acid solution only and (B) in acid-salt solution.

skin is treated with acid it swells, reaching a maximum value at about pH 2.8. Though pH 2.8 is the point of maximum swelling, maximum acid combination does not occur until pH 0.8 is reached. Minimum swelling and minimum acid binding occur in the range pH 5 to 7, depending upon the previous history of the skin. The amount of acid bound is an important factor in pickling and in the subsequent chrome tannage. Figure 7 shows the amount of acid or alkali bound by skin collagen over the pH range 0.5 to 13. The curve represents the latest work in this field. From the curve it is possible to determine readily the acid bound to the protein at any given pH of pickling. Acid readily reacts with protein but acid alone tends to swell or plump the

[11] Theis, E. R., et al., J. Amer. Leather Chem. Assoc., *26*, 505 (1931); *27*, 109, 570 (1932); *28*, 193 (1933); *30*, 166 (1935).

skin, which in general is not desired. Therefore an acid-salt solution is used in pickling, usually a sulfuric acid-sodium chloride solution. The usual pickle is 0.1 normal with respect to acid and 1.0 normal with respect to salt. The

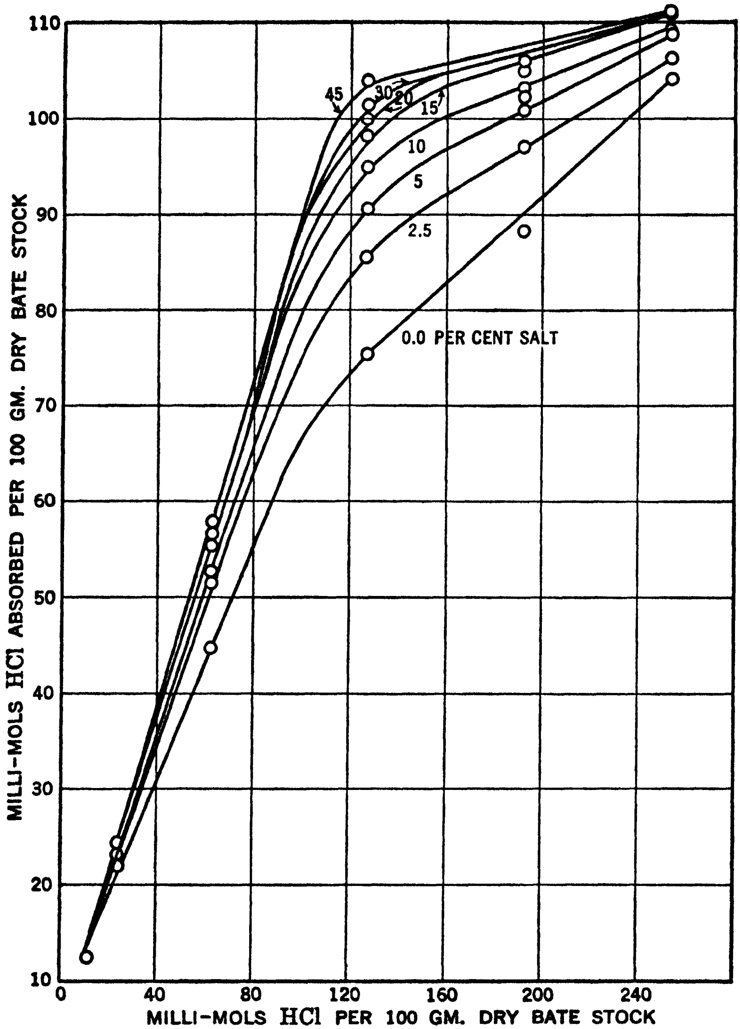


FIG. 8. Showing Acid Absorbed During Pickling, Using Practical Variations in Salt and Acid.

salt used serves a double purpose: (1) represses acid swelling; and (2) causes greater acid binding in the pH range of 2 to 5.

Some eight different important factors in the pickling operation have been formulated: (1) acid concentration; (2) salt concentration; (3) volume of pickle liquor relative to skin; (4) effect of pickle upon grain; (5) hydrolysis of skin; (6) effect upon subsequent tanning; (7) deliming effect; and (8) preserving effect. Most of these factors are self-explanatory and will not be enlarged upon.

It was pointed out under bating that at pH values greater than 8.4, little deliming occurs and that unless considerable quantities of acid are used in

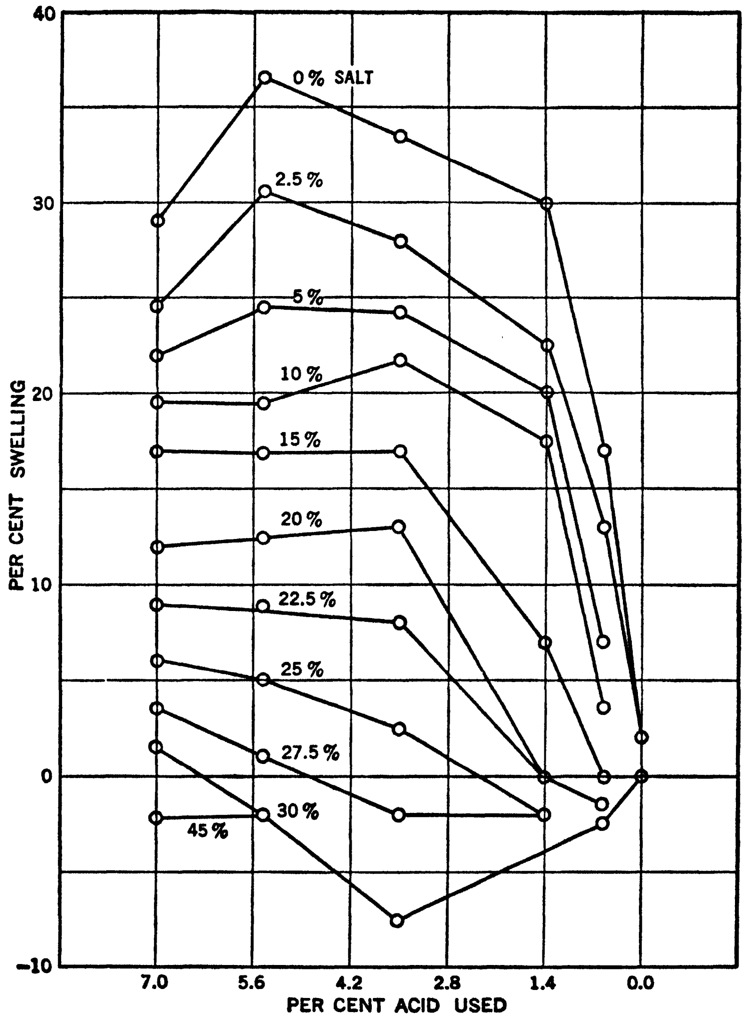


FIG. 9. Showing Swelling During Pickling, Using Various Concentrations of Salt and Acid.

the bating operation, only the free lime is neutralized and none of the bound calcium affected. One of the important functions of pickling is to neutralize completely and liberate both free and combined Ca^{++} ions

$$\updownarrow\!-NH_2 \quad CaOOC\!-\!\updownarrow + H^+ \rightarrow \updownarrow\!-NH_3^+ \quad ^-OOC\!-\!\updownarrow$$

Regarding the preserving effect, it may be said that this is the first time since the hides were started in process that they may be kept "as is" for an indefinite period without harm or damage. Pickled sheep skins are often kept in that state for months at a time.

Data on the degree of swelling and the acid absorption by the skin in various pickles are shown in Figures 8 and 9. Figure 8 indicates the exact salt content for any given acid concentration to produce any reasonable degree of swelling, or in some cases no swelling, of the skin.

Types of Pickling—In practice, two types of pickling are employed: drum pickling, making use of a wooden drum and a short volume pickle; and making use of a paddle vat (Figure 10) and a long volume pickle solution.

FIG. 10. Pickling Paddles. (Courtesy Ohio Leather Co.)

In the first case, the skins are placed in a drum (usually 2000 pounds of bated stock) together with a solution (100 to 120 gallons) made up of the required amount of sulfuric acid (1.0 to 1.5 per cent on weight of stock and salt (5 to 7 per cent). The drum is revolved for some 2 hours during which the pickling action takes place. The tanning solution is then added directly to the skins and pickle liquor.

For the second case, known as an equilibrium pickle, a paddle vat is used, in which 5 to 6 pounds of solution are employed for each pound of bated stock. The pickle liquor is a 5 to 8 per cent salt solution containing sufficient sulfuric acid to give the required degree of acid combination. The acid may vary between 1 and 3 per cent of the bated stock weight and should cause the salt solution to be approximately 0.1 normal with respect to acid. The paddle is revolved for some 2 hours, then allowed to stand overnight and paddled for an additional hour the following morning. Such treatment should completely pickle the skins.

Various acids and salts, such as sulfuric acid, hydrochloric acid, formic acid, sulfamic acid, sodium chloride, sodium sulfate, etc., are used in pickling. However, the standard pickle solution may be said to be sulfuric acid-sodium chloride. Certain antiseptics such as *p*-nitro phenol, β-naphthol, etc., may be added to the pickle to retard mold growth later in the process.

THE TANNING PROCESSES

Archeologists have found many specimens of leather dating back as far as 10,000 B.C. These specimens are mostly in the form of straps, sheaths and trimmings. From examination of such samples, it is known that the art of tanning dates back into the prehistoric ages. In all probability it was found that if a wet skin was allowed to lie in fallen leaves, the skin became stained and that this stained area behaved differently from the unstained portion. Today, we know that the stained portion, formed by infusion of tannins into the skin, was vegetable tanned. Leathers of the ancient Egyptian civilization have been found to be oil tanned, vegetable tanned and alum tanned.

It may be said that tanning is essentially the process whereby animal skin is put into a state that will preserve its desirable properties.

Many of the tannages in use today have been known for centuries and it is by refinement that they have progressed to their present level. It might well be said that the forty years of the present century have seen more progress in the art and science of tanning than all of the rest of time.

The tannages to be discussed in this chapter are, in order of importance: vegetable, mineral, oil, formaldehyde and miscellaneous. Leathers such as sole, belting, harness and upholstery leather are usually vegetable tanned and such leathers represent a large proportion of the industry. Calf, kid, sheep and side upper leathers are in general chrome tanned. This phase of tanning is assuming larger proportions each year.

CHROME TANNING

For this type of tannage, pickled stock is usually used. It is treated with a solution containing basic chromium sulfate. This chemical reacts with the reactive groups of the collagen to form a complex collagen-chromium compound.

In the early days of chrome tanning it was believed that the reaction was simply a chemical combination of chromium with the carboxyl groups of the collagen

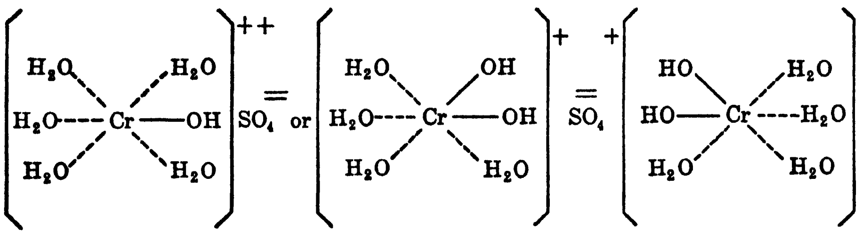
$$3(\text{—R—COOH}) + Cr(OH)_3 \rightarrow (\text{—R—COO})_3Cr$$

It is now known that the reaction is far more complex. Investigators have spent many years studying the reaction of complex chromium molecules with animal skin. This chapter does not allow space to outline all of the theories proposed and therefore only two will be discussed.

The Protein Reactions—Considering protein structure as briefly outlined previously, we find two types of reactive groups of interest in this regard: the one, the free amino groups, derived from the dibasic amino acids in the protein chain; and the other, the free carboxyl groups, derived from the dicarboxylic acids of the protein chain. If we further postulate that in a great number of instances the free amino groups of one chain stand opposite to the free carboxyl groups of another chain then we can express this conclusion in the following manner

$$\updownarrow\!-NH_3^+ \; ^-OOC-\!\updownarrow$$

Basic chromium sulfate is in itself a complex substance and cannot merely be written $Cr(OH)SO_4$. In most of its salts, chromium exists in complex form and the basic sulfate should be written—



33 PER CENT BASIC CHROMIUM SULFATE

66 PER CENT BASIC CHROMIUM SULFATE

In other words, a chromium nucleus exists which can be extremely complex in character. The coordinate groups (in this case water groups) can readily be replaced by other anions, such as sulfate, acetate, oxalate, tartrate, hydroxy or amino groups of the collagen. We can illustrate such replacement somewhat as follows—

I

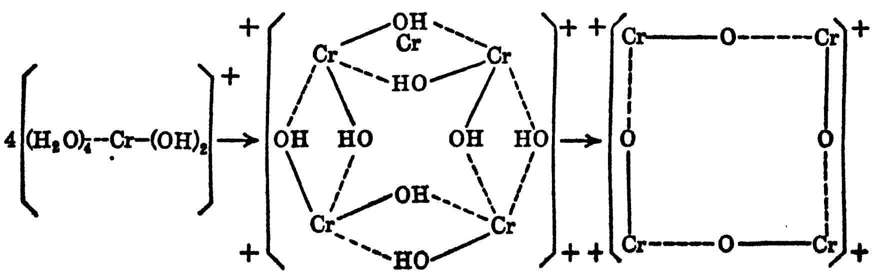
$$[(H_2O)_5\text{---}Cr\text{—}OH]^{++}SO_4^{=} + Na_2SO_4 \rightarrow \left[(H_2O)_3\text{---}\overset{\overset{\displaystyle SO_4}{\|}}{Cr}\text{—}OH\right]^0$$

or II

$$[(H_2O)_5\text{---}Cr\text{—}OH]^{++}SO_4^{=} + 3Na_2C_2O_4 \rightarrow$$

$$[Cr{=}(C_2O_4)_3]^{\equiv}Na_3 + NaOH + Na_2SO_4$$

In case I, "sulfato" groups have entered the coordinate sphere of the chromium and given a neutral complex, while in case II "oxolated" groups have completely replaced all coordinate groups and have given a negative anionic complex. Thus, the chromium may exist as a cationic, neutral, or anionic complex. In addition, the chromium nucleus is much more complicated than just expressed. Usually, several of these complexes react together to give—



OLATED COMPOUND

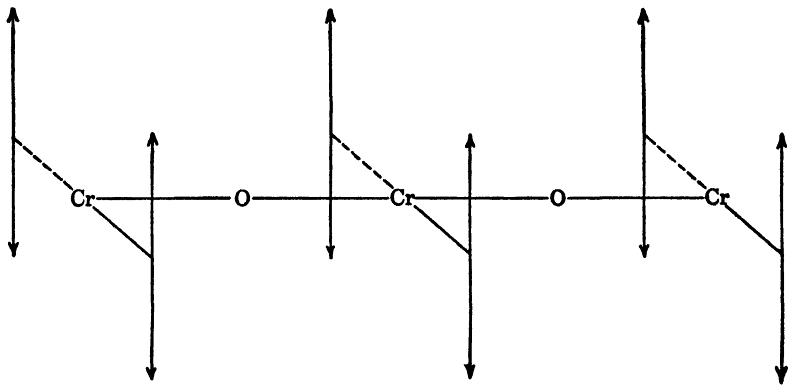
OXOLATED COMPOUND

Theories of Tanning—From a theoretical viewpoint, the chromium salts, as shown above, react with collagen, the free amino group of one chain displacing one coordinate group utilizing coordinate valence, while the carboxyl group utilizes a primary valency bond—

$$|\!-\!NH_3^+ \quad {}^-OOC\!-\!| + [Cr\!-\!O\!-\!Cr] \rightarrow \updownarrow\!-\!NH_2\cdots Cr\!-\!OOC\!-\!\updownarrow$$

In this way a strong bridge link between two protein chains is formed.

Since many chromium atoms are grouped together in the form of a more or less colloidal aggregate, the probable bridging between a number of protein chains is—



In the above diagram the arrow lines represent individual protein chains and these chains are tied together by means of—Cr—O—Cr—bridges.[12] A great deal might be said regarding this theory but it is sufficient to indicate that it fits in with our present-day knowledge of protein structure and the structure of the chromium complex.

In a well-known adsorption theory, it is postulated that during tanning a two-thirds basic chromium sulfate compound is deposited upon the collagen fibres. In other words, during tanning, acid is withdrawn from the basic chromium sulfate aggregate until a two-thirds basic compound obtains. In reality there is no real conflict between these two theories. The theory used by Küntzel and Theis makes use of a two-thirds basic compound but claims chemical combination, while McLaughlin et al. postulate adsorption of the two-thirds basic compound upon the fibre.

Methods of Chrome Tanning—In general, there are two methods used for the chrome tanning of animal skins, namely, the two-bath and the one-bath method. Essentially, the principle is the same—the fixing of a basic chromium salt upon the animal fibre.

The two-bath method is generally used for the tanning of goat, kid, horse and sometimes sheep skins. This method of tanning does not allow the scientific control that obtains in the one-bath process. The general method is as follows: The bated stock is placed in a paddle, using a volume ratio of 1 pound of skin to 5 pounds of solution. The solution contains 5 to 6 per cent of sodium dichromate and 2.5 to 3 per cent of 33 per cent hydrochloric acid

[12] Küntzel, A., Collegium, 1930-1940.

based on bated skin weight. The skin absorbs the chromic acid formed in 2 to 5 hours, the skin becoming a uniform yellow color. The skins are then removed and aged or "horsed up" overnight in order to allow the chrome to set and fix upon the fibre. The superfluous liquor is then removed either by setting out by hand or by machine. The chromed skins are again placed in a paddle together with a solution containing 12 to 20 per cent sodium thiosulfate and 6 to 10 per cent of 33 per cent hydrochloric acid based upon the bated stock weight. The skins are run in this bath until all of the yellow chrome is completely reduced in the thickest parts of the skin. Usually the hydrochloric acid is added slowly and at intervals.

The skins are then removed from the paddle, aged for 24 to 48 hours in order to complete the tannage. They are then set out, shaved and sorted and are ready for neutralization.

The reactions taking place may be shown by the following equation—

$$Na_2Cr_2O_7 + 3H_2SO_4 + 3Na_2S_2O_3 \rightarrow 4Na_2SO_4 + 2Cr(OH)SO_4 + 3S + 2H_2O$$

The basic chromium sulfate, $Cr(OH)SO_4$, which is formed causes the tannage of the skin.

For the one-bath method, a basic chromium sulfate solution is used. In the majority of cases, the skins are pickled previous to the tannage. One-bath methods may make use of either paddles or drums. For drum tannage (Figure 11), the following procedure prevails. Hides and skins are placed in a drum to which basic chromium sulfate is added. The amount of added chromium salt will vary between 1.5 and 3.0 per cent Cr_2O_3, based on the weight of the pickled stock. The volume of solution is generally 8 to 12 gallons per 100 pounds of pickled stock. The drum revolves 8 to 17 revolutions per minute. The time of tannage may vary from a few hours to 24 hours. After complete penetration of the chrome liquor, a dilute neutralizing solution is added ($NaHCO_3$, NH_4HCO_3, Na_3PO_4 or borax) in order to set the chrome salt upon the fibre. After such neutralization, the stock is removed from the drum, horsed up for 48 hours and is then ready for shaving, coloring and finishing.

Chrome tanning was discovered by Knapp in 1858 but was first put into practice by Schultz in 1884. Martin Dennis, in 1893, made a careful study of the use of chromium salts and through the study developed a successful one-bath process. The discovery of chrome tannage so revolutionized leather manufacture that the great bulk of upper leather is now made by means of it.

Preparation of the Chromium Salts—The chemistry of the chromium salts has been extensively studied during the past twenty years with the result that the tanner and leather chemist now has fairly exact knowledge regarding their preparation. In order to prepare a one-bath chrome liquor, it is essential to know the various reactions taking place when dichromate is reduced in acid solution by sugar.

Theoretically, there are three methods of making a chrome liquor: (1) adding sugar to acid-dichromate; (2) adding acid to sugar-dichromate; and (3) adding dichromate to acid-sugar. The first two methods are the only ones used in the commercial preparation of basic chromium sulfate. The following theoretical equation does not obtain—

$$4Na_2Cr_2O_7 + 12H_2SO_4 + C_6H_{12}O_6 \rightarrow 4Na_2SO_4 + 8Cr(OH)SO_4 + 14H_2O + 6CO_2$$

Fortunately the sugar is not oxidized completely to CO_2 and H_2O, but gives rise to certain sugar degradation products such as oxalic acid, formic acid, levulinic acid, formaldehyde, etc. These degradation products play an important part in the tanning action—giving complex chromium salts which in-

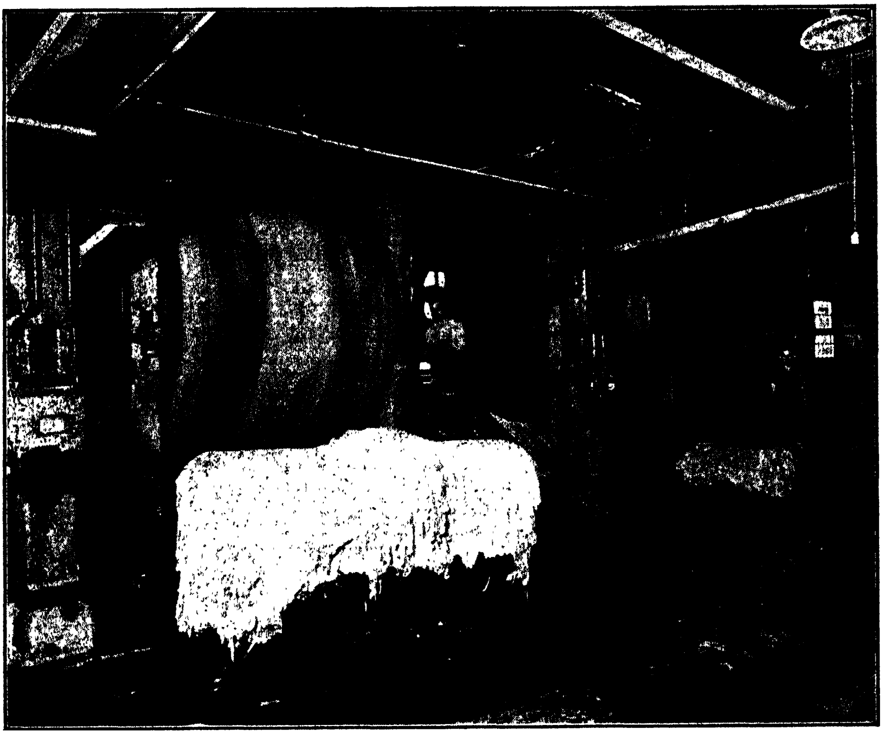


FIG. 11. The Tanning Operation, Carried Out in Drums.

fluence the tightness, fullness, and feel of the finished leather. In other words, the chrome tanning liquor contains Glauber's salt, basic chromium sulfate and in addition certain chromium compounds of these various other organic acids.

Making One-bath Chrome Liquor. Most tanners make their own one-bath chrome liquor. For 1000 gallons of finished chrome liquor, 1000 pounds of sodium dichromate is dissolved in about 500 gallons of water. To this is added 900 pounds of 66° Bé. sulfuric acid. To the hot acid-dichromate solution 300 pounds of glucose are added slowly and with constant agitation. The solution is boiled for 1 hour after all sugar has been added, is allowed to cool over night and then made up to volume (1000 gallons) with water.

There are other methods of making one-bath chrome liquors such as through the use of: (1) sodium bisulfite, (2) sulfur dioxide, (3) cane sugar,

(4) blackstrap molasses, etc. However, the writer believes the one shown above will give the best all around results.

In modern chrome tanning, the leather manufacturer is making use of such organic salts as sodium formate or sodium oxalate. These salts added to a regular one-bath chrome liquor profoundly influence the physical properties of the leather.

After the tanned leather, either from one- or two-bath tannage, has been horsed up for 48 hours, it is set out and shaved by machine. The shaving

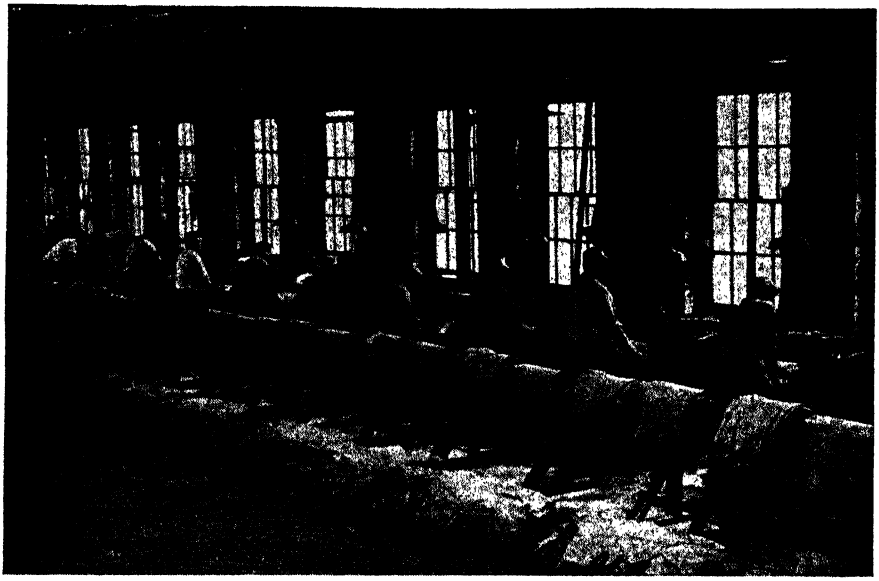


FIG. 12. Battery of Shaving Machines. (Courtesy Ohio Leather Co.)

machine (Figure 12) rapidly cuts away the flesh surface of the skin, giving an even thickness to the skin. After shaving, the skins are ready for neutralization and coloring.

VEGETABLE TANNING [18]

Formerly, all types of hides and skins were vegetable tanned but today this method of treatment is only used for certain kinds of leather. These might be enumerated as: sole leather, calf leather for Russia calf; skivers, upholstery leather, belting and harness leather. Since sole leather is by far the most important of these, the sole leather tannage will be described in detail. It must be borne in mind that there are many different methods of sole leather tannage, but in principle all tend to give the desired result.

Sole Leather—The most common method of producing sole leather consists in the use of a combination of hemlock and chestnut extracts. However,

[18] Portions of the work dealing with Vegetable Tanning were taken from the Fifth Edition written by the late Allen E. Rogers, since little or no important change of procedure has taken place in this field since 1931.

the combinations used are as numerous as the tanneries themselves. In most tanneries the combination is made entirely with extracts, although some plants still hold to the old leach system. Strictly speaking, union tannage is a combination of hemlock and chestnut, but most tanners add other extracts, such as quebracho, mangrove and myrabolans, etc. The liquors are prepared in large mixing tanks, a set of separate tanks being used for each unit of the yard. When completely dissolved, the liquors are run into coolers and are then ready for the head pits of the particular system. As a rule union leather is cropped; that is, the bellies and shanks are cut off during the early stage of tanning, leaving what is known to the trade as "bends." The leather, known as "union crop," has a better cutting value than sides and brings a higher price. The bellies and shanks are tanned in the same pits as the bends, but do not receive as much care as the more valuable material. They are used mostly for innersoling where less wearing quality is required.

Union sole leather is generally made from green salted hides, those from South America known as *frigorificos* being the most highly prized. As they enter the process, the hides are milled for about half an hour in cold running water, which opens up the stock and removes the excess of salt and dirt. They are then spread in piles and, after being toggled together, are placed in the soak for 24 hours. From the soak pits they are reeled into the lime. The system giving the best results consists of a press method in which sodium sulfide is added to the tail lime liquor. The hides are passed forward each day, meeting stronger and fresher limes, until at the end of from 5 to 7 days they enter new lime liquor. After remaining in the fresh lime for 1 day the stock is placed in a warm pool for half an hour to soften the stock somewhat before unhairing. The depilated hides are now dehaired on the machine and then fleshed. In order to be sure that all fine hairs have been eliminated, the hides are worked by hand over a beam and are then placed over sticks in the cold pool where they remain overnight. In some tanneries lactic or acetic acid is added to the water in the cold pool, but this is not the most common practice.

The Rocker System. From the cold pool the hides enter the rocker system (Figure 13), the pits of which are arranged in such a manner that the liquor from one may be pressed to the next in series. The fresh stock, usually as full hides, is placed in the tail pit, which is free of liquor. The rocker frames work on a cam. From the extract house fresh liquor is pumped into the head pit, which contains the hides that have been in the liquor for the longest time. As this strong liquor enters the head pit, the liquor already in overflows into the next in series, passing from the top of one pit to the bottom of the next, and so on down the line until the tail pit, containing the fresh hides, is full.

The next day, in order to secure an empty pit, the most advanced pack is removed and passed to the layer. The liquor in this pit, which is the head pit of the system, is pumped to the next in series and in so doing causes a change of all the liquors throughout the rockers. The overflow from the tail pit may be thrown to waste, or may be pumped back to the extract house as desired. The usual procedure is to pump back for two days and reject on the third. The pit which was the head pit of the system after pumping it free from liquor, receives the fresh stock and so becomes the tail pit of the rocker unit. The same operation is repeated, as just described, from day to day, and as a result uniform treatment is maintained.

The Layer Pits. When the hides are removed from the rockers, they are fairly well struck through and any subsequent absorption must of necessity be rather slow. They go then into the first layer liquor. The layer pits (Figure 14) are not connected with an overflow, as has been mentioned for the rockers and press layers, but are individual pits in which the liquor is

FIG. 13. Hides Entering the Rockers in a Sole Leather Tannery.

not changed for the period (usually 7 days) that the hides remain in them. No bark is dusted on the hides in the first layer, and no change of the hides takes place. The strength of the liquor should stand at about 42° Bé., and the tanning content should be about 4.5 per cent. No free acid is required in the first or subsequent layers, as the stock at this stage of tanning should have reached its full degree of plumpness.

In the second layer, the hides are placed in a liquor of 46° Bk., which has a tannin content of 5 per cent. Here they remain for 12 days without moving, in a combination identical to that used in the first layer liquor.

As the hides are drawn from this second layer, they are cropped. The backs are placed flat in the third layer liquor, and the bellies thrown in on top. This procedure makes certain that the best portion of the hide shall be in contact with the insoluble portion of "reds" that settle from the strong liquor. The third layer liquor consists of a straight quebracho solution, the density of which should be about 55° Bé., and the temperature at the start

Fig. 14. Sole Leather Yard, Showing Cropped Hides Going to Layers.

Fig. 15. Hides Being Removed for Extract Wheel.

115° F. In the third layer, the hides remain undisturbed for 35 days, by which time they should be thoroughly tanned.

Extracting the Hides. As the trade calls for a full, plump leather with good cutting value, it is common practice to extract the hides as they come from the third layer. This is done by first placing the stock in a pit containing water at 100° F. Here they remain for 1 hour, after which they are passed through the Quirin press to remove excess of water and clean off the

FIG. 16. Bleaching Sole Leather.

grain. The well pressed and fairly dry backs are then placed in the drum together with 500 pounds of 100° Bk. quebracho at a temperature of 150° F. for each 100 backs. The drum is then set in motion and run for 1.5 hours, by the end of which time practically all of the extract has been absorbed (Figure 15). In order to retain the extract in the stock, the backs are next placed in the tempering pits for 4 days, where they are allowed to remain in contact with a 45° Bk. quebracho extract at a temperature of 80° F.

Bleaching. As the backs are removed from the tempering pits they are suspended on sticks. These sticks are placed in the frames of the bleaching equipment (Figure 16) and hung for 7 minutes in fresh water at a temperature of 125° F. The bleaching frames are so arranged that they may be lowered or lifted at will and by proper mechanism the frames carrying the stock can be made to move forward. Thus, after the backs have been in the fresh water for 7 minutes, the frame is lifted and passed forward in order to bring the stock over the second pit. In this pit there is a 0.3 per cent solution of sodium carbonate, standing also at 125° F. The backs are lowered into this solution and remain there for 7 minutes. From the alkali bath the backs pass to the first acid dip which is 1.5 per cent of sulfuric acid solution also at a temperature of 125° F. The backs next go to a 1 per cent sulfuric acid solution for another 7 minutes. To eliminate as much of the sulfuric acid as possible, the backs are placed in running water for 7 minutes, and are then considered to be bleached.

Having been bleached, the backs are passed through the Quirin wringer and in the partly dried condition are ready for the loading.

The bellies, as they come from the third layer, are washed in warm water and bleached at once without extracting or tempering, and are then finished the same as the backs.

As the backs come from the wringer they are placed in the loading drum and, for each 100 backs, 50 pounds of crystal magnesium sulfate is added. The door is placed in position, the mill started, and a mixture at 150° F., composed of 175 pounds of glucose, 6 gallons of sole leather oil, and 1 gallon of cod oil, added through the trunnion. The time required to absorb this material is about half an hour, after which the backs are set out on the Quirin press and taken to the dry loft.

Drying. As the hides enter the dry loft they are placed over sticks, and for the first two days the light is excluded and the room kept as cool as possible. Care should be taken, however, to provide adequate ventilation, as imperfect circulation is very apt to result in mold formation and bad color on the grain. As the hides start to dry, the temperature is slowly raised and light is admitted to the loft.

When thoroughly dry, the leather is taken down and dipped in warm water containing a small quantity of glucose and then placed in piles to sammie or temper. The uniform dampening of the hides in this manner takes from 1 to 2 days. The grain is then brushed over with warm water, followed with a coat of cod oil. While still in a damp and oily condition, the leather is set out and rolled (Figure 17). It is then again taken to the dry loft and this time suspended from the end. After drying the second time, the hides are again rolled. This finishes the operation as carried out in most plants, but some tanners apply a final season and run the stock through a brushing machine.

Belting Leather—In the production of belting leather a much different product is desired than when the same class of hides goes into sole leather. In sole leather we require body and stiffness with little thought of its pliability and strength. Belting leather, on the other hand, must be sufficiently stiff to prevent curling at the edges when shifted on a pulley, but, of more importance still, it must be pliable so that the belt may hug the pulley, and it must be strong enough to carry a heavy load without breaking.

Belting leather should not stretch, but at the same time it should have sufficient elasticity to take up and release the load as it travels over the pulley.

The majority of belt manufacturers purchase their raw material in a tanned condition in the form known as rough belting butts, although some manufacturers are also tanners.

In the production of belting leather the best hides possible should be secured. They are usually green salted packer hides or the best grade of South American hides. They should be free from brands, have no flesh cuts, and be clear of scratches and grub holes. All such imperfections would not only mar the appearance of the leather, but would result in a weakened condition when such leather is put into service. For belting, the hide should be full and plump, spready or flat hide not being suitable for this purpose.

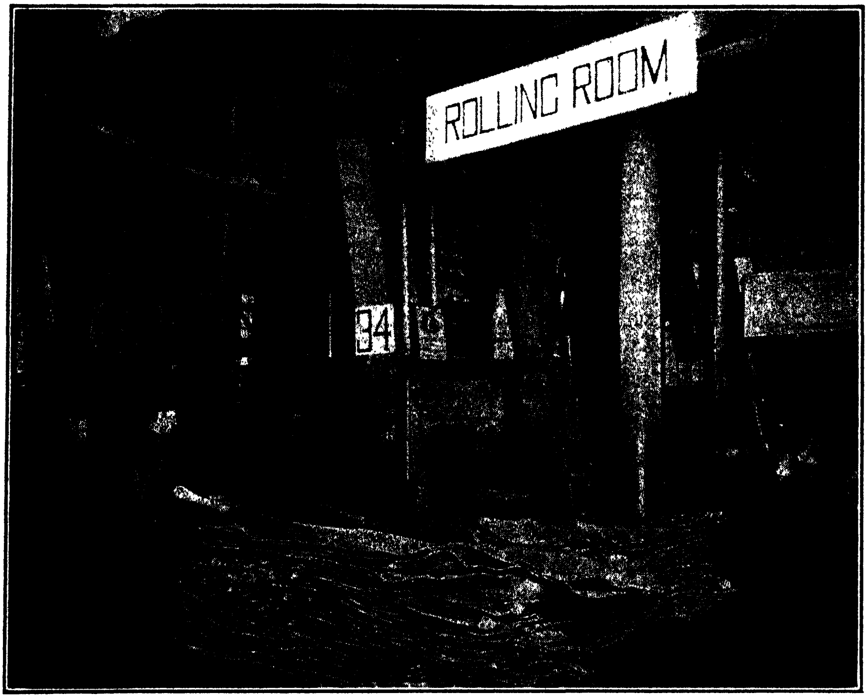


FIG. 17. Rolling Sole Leather.

In this country it is the most common practice to put the stock through the beamhouse in full hides, and usually they are also carried through the early stages of tanning in the same condition. In England, where a considerable amount of belting leather is produced, the hide is cut into a belting butt or bend, or in other words, the hide is "rounded" in the beamhouse. The belting butt or bend represents the most valuable part of the hide.

The principles of belting leather manufacture are essentially those of sole leather manufacture. For this reason, no description of soaking, liming, bating and tanning of this type of leather will be given. However, the description of the finishing processes used in making belting leather follows.

Currying of Belting Leather. Although most belt manufacturers do not themselves tan the leather they use, they do curry it, almost without exception. Currying may be defined as a process of introducing grease into leather and giving it a finish which will best adapt it to the special purpose for which it is to be employed. It is claimed that the process is a sort of a supplementary tannage, the oil or grease combining with the fibres which have been separated by the vegetable tanning materials.

The first step in the currying of leather is to dampen the stock and, if it has already been scoured, to cut it into three pieces—a center and two sides—the cuts being made parallel to the backbone and equi-distant from it on either side. If the belting butts have not been scoured, they are treated as previously described before currying can be undertaken. To insure a uniform thickness of the leather and to provide a clean flesh side, the pieces are passed through a belt knife splitting machine, the process being known as *skiving*.

The leather now being in a clean condition and of uniform thickness, it is next subjected to the stuffing process. There are three methods in use for stuffing leather, namely: hand stuffing, wheel stuffing and hot stuffing. Regardless of the method to be employed, the leather is dampened back and piled down to sammie, that is, to even up the moisture content. This is absolutely necessary, as the leather must be in a uniform condition of dampness before any grease is applied.

Hand Stuffing. After tempering, the leather is set out by hand or on a Vaughn machine. If setting is done by hand, the leather is spread on the table and worked out by a slicker until it lies perfectly smooth. The same result must also be obtained if the machine is used, although it sometimes requires several rollings to get the desired flat condition. When the leather has been set out it is given a coat of the grease or stuffing on the flesh side and a coat of cod oil on the grain side. The stuffing compound, also called dubbing, is composed of a mixture of about 1 part cod oil and 4 parts of tallow. The tallow is melted and the oil stirred in, stirring being continued until the mass is cold and of a salve-like consistency. The dubbing is applied with a brush, the amount depending upon the quantity which the currier feels will be absorbed by the leather. The oil is the only portion of the dubbing which will be absorbed, the stearine of the tallow remaining on the surface after drying. The leather, having been given its dubbing on the flesh and the oil on the grain, is hung up in a moderately warm room with a good circulation of air and allowed to dry. When the leather is dry it should show no oiliness and should have only a white scale on the flesh side. It should then be taken down, wet back again, and piled down to temper, after which it is ready to stretch.

Wheel Stuffing. The leather to be stuffed in this manner is skived as for hand stuffing, but is not cut into strips until after stuffing. The wetting-back operation is more important in this method than in hand stuffing. The leather in this case should not be wet uniformly, but the softer and spongier parts should be distinctly wetter than the firmer parts, otherwise these parts will absorb more oil and then show black and greasy spots in the finished leather. The leather, after having been dampened, is placed in covered piles, where it is allowed to remain until well tempered and until a certain amount of heat is developed by fermentation. The warm stock is then placed in the drum and the hot stuffing grease added. The door is now closed and the mill begins to rotate. The temperature inside the drum is maintained at about 120° F. by means of hot air forced in through the trunnion. In drum stuffing, a much harder compound is used than in hand dubbing, the ratio between cod oil and tallow being about 1 to 9. The amount of grease used on the sammied stock should be about 12 per cent and the time required to force it into the leather is about 1 hour. During the last part of the drumming the door of the mill is removed in order to cool the leather somewhat and to set the grease. As the stock is removed from the drum, it is piled down overnight and turned several times to prevent overheating. The leather is now set out by hand or on the machine until the baggy condition is entirely overcome and the stock is perfectly flat. After having been well set out, the butt is cut into a center and sides, worked on the Vaughn machine, and oiled on the grain. It is then ready for stretching.

Hot Stuffing. If damp leather is treated with a very hot grease it will immediately burn the leather, making it weak and brittle. If, on the other hand, a very hot grease is added to an absolutely dry piece of leather no harmful effect will result. Advantage is taken of this fact in what is known as hot stuffing. This consists of placing the belting butts on benches in a dry room where they are heated until all of the moisture is removed. They are then either placed on a table and hot grease poured over the flesh and grain, or they can be dipped in a tank of the melted grease. In either case the temperature of the grease may be 200° F. or over. The leather which has been filled on the table is at once dipped in cold water to set the grease, while the leather filled in the tank is placed in the hot room to allow the surface grease to drip off, after which the leather is dipped in cold water to set the grease. The grease added to leather in this manner simply acts as a filler. To secure a more intimate contact, the leather is wet through by milling in the drum and then set out either by hand or on the machine. To improve the leather it is also necessary to employ some form of bleach to clear up the grain. It is then cut into center and backs, worked on the Vaughn machine, and is ready for stretching.

Stretching. The processes of finishing are the same whether hand, wheel, or hot stuffed. The stretching process is simple and consists in fastening the ends of the leather in clamps, one of which is tight, while the other can be moved. When all of the stretch has been taken up, the frames holding the clamped leather are set aside to dry. When dry, the leather is removed from the frames, rolled on the flesh side to remove stiffness, and then either brushed or glazed, as the trade demands.

Vegetable Tanned Calf Skins—The bulk of the calf skins available is converted into a chrome-tanned leather for the shoe leather trade. A certain quantity, however, is given a vegetable tanning for the production of shoe uppers, while a comparatively small quantity is utilized for fancy leather purposes. The most commonly employed vegetable tannage for this purpose is quebracho, although other single tanning as well as combinations of tanning materials are also used. The process is somewhat similar to that used for sole leather and will not be described in detail.

The tannage should be started in a weak liquor, usually not over 10° Bk., otherwise a drawn condition of the grain will result. Where pickled skins are being tanned, salt should be added to the tan liquor to prevent an over-plumping of the stock. As the tanning proceeds, the strength of the liquor is slowly increased until it reaches 20° to 25° Bk. The time required to accomplish the tanning depends, of course, upon the thickness of the skins and upon the strength of the liquor. The slower the tannage, the smoother will be the grain. The period necessary for average weight skins is from 7 to 14 days.

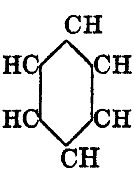
When the skins have become thoroughly tanned they are removed from the pits, washed, fat-liquored with a sulfonated oil, set out, and hung up to dry.

VEGETABLE TANNING MATERIALS

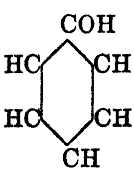
The word "tannin" is a generic name for a great group of substances distributed in the higher plants. Tannins are found in leaves, in wood and stems, in the bark and in the fruit of such plants. Tannins[14] may be characterized by the following properties:

1. They are usually amorphous.
2. They are astringent.
3. They give colors with ferric salts.
4. They are precipitated by potassium dichromate and by alkaloids.
5. They precipitate gelatine (leather-making property).
6. Their sols develop a red color on the addition of potassium ferricyanide.
7. They are soluble in hot water to form colloidal sols.
8. They all contain polyhydroxyphenols or derivatives. Some may contain a sugar residue which plays no part in the tanning reaction.

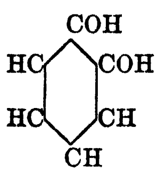
Types of Tannin—The tannins are divided into two classes: one is known as the pyrogallol tannins; the other is called catechol tannins. Although two substances may contain the same kind of tannin, the leathers produced from them may differ widely from each other in their general appearance and characteristics. Often the insoluble matter present plays an important part in producing certain desirable conditions, such as the firmness noticed in sole leathers. These insoluble tannins are known as "reds." The tanning materials which give a bloom to leather are usually of the pyrogallol group, while those giving no bloom are of the catechol group. The pyrogallol tannins, when decomposed, yield pyrogallol, whereas the catechol tannins yield catechol, hence the names. These bodies are all phenols, derived from benzene, C_6H_6, in which one or more of the hydrogen atoms are replaced by the hydroxyl group (OH). The following graphic formulas represent the structure of the phenolic bodies:



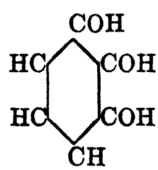
Benzene



Phenol



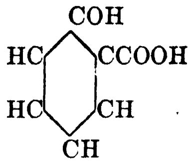
Catechol



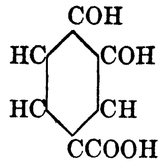
Pyrogallol

[14] Gortner, A. R., "Outlines of Biochemistry," 2nd Ed., John Wiley and Sons, New York (1938).

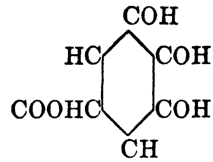
When a further hydrogen atom is replaced in the ring by the carboxyl group (COOH), a phenolic acid is the result. The following graphic formulas illustrate such acids.



Salicylic Acid

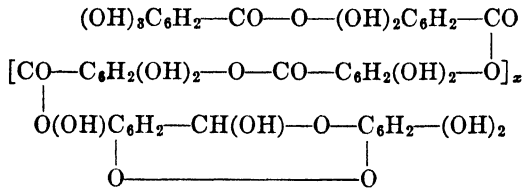


Protocatechinic Acid



Gallic Acid

These bodies are linked together to produce the tannins, but still there is some uncertainty as to the exact manner, except in the case of gallo-tannin, which is now fairly well established. Though there is some difference of opinion, the graphic formula of this substance may be illustrated as follows:



Gallo-tannin

Sources of Tannins—The principal source of tannins is the wood or bark of various trees. The method of obtaining the tannins is essentially the operation of extraction which will be briefly described later.

Chestnut Wood. This tree belongs to the oak family and is distinguished by its narrow, pointed, serrated leaves, its fragrant flowers, and its fruit.

The air-dried wood contains an average of 8 per cent of tannin, but in some cases, may run as high as 14 per cent. The soluble matter obtained in the manufacture of chestnut extract usually contains about 60 to 65 per cent of tannin and 35 to 40 per cent of non-tannin substance. The tannin is of the pyrogallol group. The non-tannin substances consist of sugar, gallic acid, pectose compounds, resin, and mineral matter. The sugars are valuable in the tannery because of the acid they produce. As a tanning material, chestnut extract has been confined chiefly to the production of sole, belting, and other heavy leathers and has become a staple article in the production of such stock.

The importance of chestnut as a source of tannin has greatly decreased because a blight has practically made the tree extinct on the eastern seaboard.

Oakwood. The wood from all oaks yields tannin in varying quantities, ranging from 3 to 5 per cent. No oakwood extract is made in this country and our only supply comes from southern Europe. Only the waste material is utilized for extraction, as the lumber is of more value than the tannin that could be obtained from it. This extract gives a leather which differs but slightly from that made with American chestnut.

Quebracho. From the standpoint of production and consumption, quebracho wood tannin is as important as that obtained from chestnut. The quebracho tree grows in many of the South American countries, but is most abundant in Argentina and Paraguay. The common trade name quebracho is said to be derived from the Spanish word, "quebra," to break, and "hacho," axe, or break-axe, this nomenclature no doubt being due to the great hardness of the wood.

The quebracho is an evergreen tree, which grows to considerable height and has a spreading or umbrella-like top. On account of the extremely slow growth, taking from 400 to 600 years to attain a girth of 6 to 8 feet, its disappearance is only a matter of time, for it is being cut much faster than it grows.

Quebracho wood contains about 18 per cent of tannin and yields from 22 to 25 per cent of extractive matter, of which 80 per cent is estimated as tannin and 20 per cent as non-tannin. The tannin belongs to the catechol group. The extracts, which are of a deep red-brown color, are soluble with great difficulty in water, and in order to obtain satisfactory results it is necessary to clarify them either by sedimentation or chemically rendering them soluble, the most common method being to treat the extract with sodium bisulfite.

As a tanning agent quebracho is employed for all classes of leather, being especially adapted to the production of light leather. In conjunction with hemlock and chestnut it is used in the manufacture of bag, case, patent and automobile leather. For sole, belting, and harness leather it is always used with other materials, as it does not contain the necessary sugars required for this kind of stock.

Barks—Formerly the tanners depended upon the native barks near at hand for tanning material. The hemlock bark in the early nineteenth century was supposed to be inexhaustible in the Northern States, while oak bark was equally abundant in the Southern States. With the areas badly depleted, the tanner has been forced almost to abandon bark tannage, although, in the form of extracts, these valuable tanning agents are still available.

Chestnut Oak Bark. Prime chestnut oak bark contains about 10 per cent of tannin, and yields from 18 to 20 per cent of extractive matter which is rich in acid-forming sugars. Because of this it is considered one of the most valuable of all tanning materials. Its tannins are of the catechol group.

On the Pacific Coast there is a variety of oak which grows abundantly in California and Oregon. The bark from this tree is the richest in tannins of any of the oaks, frequently containing from 17 to 20 per cent of tannin and yielding as much as 30 per cent of soluble extractive matter.

Hemlock Bark. Next in importance to oak and chestnut woods and barks comes hemlock bark.

In the Eastern States and Canada the supply is fast approaching the vanishing point, and of the thousands of square miles once covered with practically unbroken hemlock forests comparatively little remains, and it doubtless would have entirely disappeared had it not been for the introduction of other tanning materials.

The bark of the hemlock contains varying quantities of tannin. As a rule, it yields about 10 per cent of the weight of the air-dried bark, with about 16 to 18 per cent of soluble extractive matter. The tannins are of the catechol group, and the soluble non-tans are rich in acid-forming sugars. The liquors are of a bright red color and are soluble with difficulty.

As far as North America is concerned, it has been the tanning material par excellence, and the only one with which it is possibie to produce good leather of all kinds. It is well adapted for making light and fancy leather, on the one hand, and is equally satisfactory in producing heavy sole.

Mangrove Bark. Mangrove bark is a tanning material derived from the tree which is widely distributed in practically all tropical island districts. There are over twenty different species ranging in tannin content from 8 to 30 per cent. The most largely used variety is that known as *Rhizophora mucronata.* The mangrove tree requires considerable moisture and is, therefore, found in swampy or marshy land, and along muddy seacoasts.

The difficulty of securing this bark has had much to do with the limitations of its use. However, there are thousands of acres of this material that are available, and there is no question but that eventually it will become an important raw material in the manufacture of leather.

Wattle Bark. Wattle bark is obtained from various species of Australian acacia and, on account of its exceptionally high content of tannins, bids fair to become an important factor in the production of leather. Much work has been carried out with this material in recent years, and the results obtained look very promising. Some samples of the bark contain as high as 50 per cent of tannin.

Mimosa Bark. Mimosa bark is from the *Acacia arabica* and is used quite extensively in India for the tanning of kips. It contains from 12 to 30 per cent of tannin.

Leaves and Fruit—*Sumac* is a much-prized tanning material. The best grade is obtained from Palermo, Sicily. The leaves of the mature bush are picked by hand and are dried out in the fields or on rocks, after which they are separated from the stems by beating. The leaves are finally ground to a fine powder under edge rollers[15] and shipped as such in bags.

Good sumac contains from 25 to 27 per cent of tannin, and sometimes may run much higher. The tannin is mostly gallo-tannic acid. Sumac is the best tanning material known for light-colored and soft leather and finds extensive application in the production of sheep skin and skivers. It is also used to a large extent for improving the color of leather that has already been produced with darker tannages.

Second in importance to Sicilian sumac is the product known as "Staghorn," which is a variety of sumac found in Virginia. It contains from 10 to 18 per cent of tannic acid, and the color which it produces is nearly equal to that obtained with Sicilian sumac.

Gambier is a tanning material derived from the climbing shrub *Uncaria gambier,* found in the Dutch East Indies. It is also raised by the Chinese and is converted by very crude methods into the product used by the tanner. The tannin content of good cube gambier is from 50 to 65 per cent and is a catecholphloro-glucol derivative. Gambier produces a soft tannage and is largely used in the production of glove leather.

[15] See Chapter 2.

Myrabolans is a tanning material obtained from the unripe fruit of the *Terminolia chebula,* a tree growing in India and reaching a height of from 40 to 50 feet. The content of tannin varies from 30 to 40 per cent, depending upon the maturity of the fruit. The product, known in the trade as "Bombays," meaning its point of shipment, is the least unripe, the latter producing a color very closely resembling sumac. The tannin present in myrabolans is of the gallo-tannic and the ellagitannic acid types. The nuts should be hard in character, and not of a waxy or soft appearance; otherwise difficulty in grinding is encountered.

Valonia is a tanning material obtained from the acorn cup of the Turkish oak, which grows in Asia Minor. As it is shipped from Smyrna, it goes under the trade name of "Smyrna Valonia." The tannin content of this grade of valonia is about 40 per cent. From the Grecian Archipelago an inferior grade is obtained containing from 20 to 30 per cent of tannin, this variety being known as "Greek Valonia." The tannin in valonia is of the pyrogallol type.

Divi-divi is a tanning material obtained from the dried pods of the *Caesalpinia coriaria,* a tree growing in Central America. The pods contain from 40 to 50 per cent of tannin of the pyrogallic and ellagitannic variety. When used in strong liquors, it produces a heavy and firm product which is very desirable in the manufacture of sole leather. When used in the drum or paddle in dilute liquors, it produces a very good color on light leather.

COMMERCIAL PREPARATION OF TANNING EXTRACTS

In the production of commercial tanning solutions the bark, leaves, twigs, or wood from a great variety of vegetable substances are used. The material containing the tannic acid is first reduced to a fine state of division either by grinding or chipping and is then extracted or leached with water.

Grinding of Bark—To extract the tannin, a material must first be reduced to a fine state of division, the degree of fineness of course depending entirely upon the nature of the material. The method of grinding varies also with the material and is influenced somewhat by the kind of extraction process employed. For the grinding of bark the cone mill[16] is almost exclusively used.

Extraction—Having been reduced to the required degree of fineness the material is next treated with hot water to dissolve or extract the soluble portion. The most common method of extraction, and the one that is simplest in operation is the press leach. This consists of a number of tanks, arranged in what is known as a battery, usually six in number. The liquor from one tank flows by gravity into the next in order and so on through the series.

The coolers are large wooden tanks where the liquor is held until cool enough for the yards. When concentration is to be carried out, no coolers are necessary except as storage space. The temperature during leaching should be moderate, as excessive heat will darken the extract due to oxidation, which extract in turn will produce a dark leather. For very light-colored stock, leaching is often carried out in the cold.

[16] See Chapter 2.

Where extracts are manufactured on a large scale it is quite common practice to employ the autoclave system in which the material to be extracted is treated under pressure. A pressure diffusion unit, as it is called, consists of a series of 6 or 8 cylindrical copper vessels or cells of about 200 cu. ft. capacity, and capable of working under a pressure of from 15 to 50 lbs. per sq. in. These diffusion units may be operated either on the decoction or continuous diffusion basis, the final results in either case being about the same.[17] Each unit has a battery fitted with steam, water, and air connection by means of which it may be operated in the same manner as an open leach. In the case of the autoclave method, however, the extraction is done under a pressure of from 15 to 30 lbs. per sq. in. The time of treatment in the autoclave varies with the kind of wood and degree of fineness and, of course, is much shorter than in the open leach. Extracts made in the autoclave contain much more sugar than when lixiviation is carried out in the open leach, the reason no doubt being due to a partial decomposition of the glucosides present. As is the case with open leaching, the liquors either go to the coolers, clarification tanks, or direct to the evaporators.

Clarification—The liquor containing the tanning material is next clarified or decolorized. In the case of a simple bark extraction, where it is only necessary to remove the dust and fine particles of wood which have passed the strainers, filtering only is required. This filtration may be carried out in several ways, but ordinary bag filters are the ones most commonly employed. In plants where the liquor is to be used at once for tanning, no filtration is necessary, but when the liquor is to be concentrated, an absolutely clear solution should be obtained before evaporation is started.

In order that the temperature of the liquor may be maintained it is essential that the filtration should be made as rapidly as possible and care taken to provide adequate insulation to prevent loss by radiation. Large settling tanks are often used to aid clarification in which insoluble matter settles to the bottom, thus allowing the clear liquor to be drawn from the top. By this means of settling and filtration a fairly clear extract may be obtained. It is not, however, absolutely clear and so, for some purposes, further clarification and decolorization are resorted to in order to get the desired results. Decolorization may be brought about by chemical means, and may be either by precipitation or direct chemical action. Most of the chemicals used in decolorizing an extract combine with the coloring material at the expense of the tannic acid, forming a more or less insoluble substance which settles out in the form of a mud. Such materials as aluminum sulfate, lead acetate and barium chloride act in this manner. The best clarification substance is blood albumin. The mode of procedure is to cool the liquor to 90° F. and, while stirring, spray the solution of blood albumin into it. When well mixed, the temperature is raised to 125° F., which causes the albumin to coagulate, which, in settling out, carries down other insoluble matter with it. The clear liquor is then drawn off for concentration, while the precipitate taken from the bottom of the tank is filter-pressed to recover as much of the liquor as

[17] For a discussion of a similar diffusion operation in the beet sugar industry see Chapter 35.

possible. Although this method produces an excellent product, it is somewhat expensive, and so some of the cheaper substances are often used. In addition to the chemicals mentioned above, such substances as casein and glue are sometimes substituted.

A method frequently employed to brighten extracts consists in treating them with sulfurous acid. This is accomplished by allowing the sulfur dioxide gas to bubble through the liquor. Certain tanning materials, such as hemlock and quebracho, contain more or less insoluble tannins which may be rendered soluble with alkalis or alkaline sulfites. Several brands of clarified extracts containing sodium bisulfite are, therefore, on the market. The insoluble tannins may be rendered soluble by means of an alkali, and then brought back to neutralization by means of an organic acid.

Concentration—In order that tanning extracts may be transported economically it is necessary to eliminate the excess of water employed for lixiviation. The removal of water is brought about by concentrating the liquor at a low temperature in some form of vacuum apparatus. The apparatus usually employed is a multiple-effect evaporator.[18]

After concentration, the extract is allowed to cool and settle and is then pumped into tanks, cans, or barrels, ready for shipment.

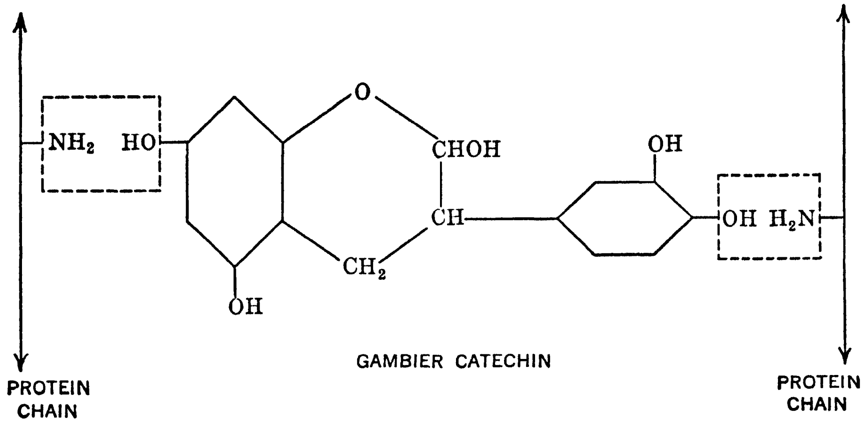
Powdered Extracts—In recent years a demand has sprung up for powdered extracts. These are produced by means of the rotary drum drier,[19] or film drier, which consists of an internally steam-heated drum inclosed in an airtight casing. While the drum revolves, it comes in contact with a trough of extract, and, picking up a film, carries it along the greater part of its revolution (during which time it is thoroughly dried), until it comes in contact with a scraper set against this drum, which removes and drops it into a suitable receiver. During this process the vapor is removed by a vacuum pump.

A recent innovation in producing solid extracts consists in spray drying,[20] where the material to be evaporated is forced hot through small openings into a high vacuum chamber. The fine spray readily gives up the moisture content, the solid material falling to the bottom of the chamber.

MISCELLANEOUS TANNAGES

In the discussion of the chrome-tanning theory it was shown that the chromic salt bound together several chains of the collagen protein, thus bringing about greater stability, strength and increased "leathering" action. Chromic salts utilized both the free amino and free carboxyl groups of the protein. In the case of vegetable tanning, it is believed that only the free amino groups of the protein are utilized in the reaction—the tannin material bridging two or more protein chains through reaction with the free amino groups. Since the vegetable tanning materials contain a large number of hydroxy groups such a reaction can be easily visualized—

[18] For a discussion of multiple effect evaporation see Chapter 2.
[19] See Chapter 2.
[20] See Chapter 2.



Such a reaction between the tannin molecule and the various protein chains would bring about an increased stability and impart characteristic changes in the protein structure.

In all probability some 90 per cent of all leather is either tanned by means of vegetable extracts or by basic chromium sulfate. However, certain other leathers are tanned by means of other agents in order to give specific types of leathers definite characteristics. Therefore it is necessary to discuss briefly, in passing, such tannages as alum, formaldehyde, tungsten, zirconium and calgon.

Alum Tanning—The use of aluminum salts in tanning dates back centuries. Aluminum salts act in a somewhat similar manner to chromium salts, although aluminum does not combine as readily or form as stable a complex upon the link fibre as does chromium. It is believed that the basic aluminum salt forms a bridge-like structure between the protein chains, utilizing the amino group of one chain and the carboxyl group of another chain. This bridge or link does not have the great stability of the chromium link.

The usual procedure of alum tannage is to place the pickled stock in a drum together with a solution of aluminum sulfate (or alum) and salt. After 1 to 3 hours revolving in the drum, soda is added and the drum again revolved for an hour. The stock is allowed to remain in the drum overnight. The following morning sufficient soda is added to bring stock and solution to pH 4.2. The leather is then removed from the drum. After being set out and shaved, the stock can now be fat-liquored and finished.

Leather made in such a manner is somewhat hard and "tinny" and additional tanning is usually necessary. Previous to fat-liquoring, the alum-treated stock may be treated with a so-called Syn-tan or with formaldehyde. In order to accomplish this, the stock is again removed to a drum, treated with a solution of Leukanol (Syn-tan) and drummed for 4 hours, then washed and sent on for fat-liquoring. In place of the Leukanol, formaldehyde may be used or as often happens both of these reagents are used. This last condition obtains in the manufacture of some white leathers. The Röhm and Haas Company of Philadelphia has developed a splendid process utilizing basic aluminum salts, formaldehyde and a special Syn-tan.

Today, use is being made of such salts as basic aluminum formate, acetate and citrate. The use of such salts allows a greater pH value of tanning to obtain without precipitation of the aluminum hydroxide.

Formaldehyde Tannage—The use of formaldehyde as a fixing agent for proteins dates back a great number of years. However, as a tanning agent,

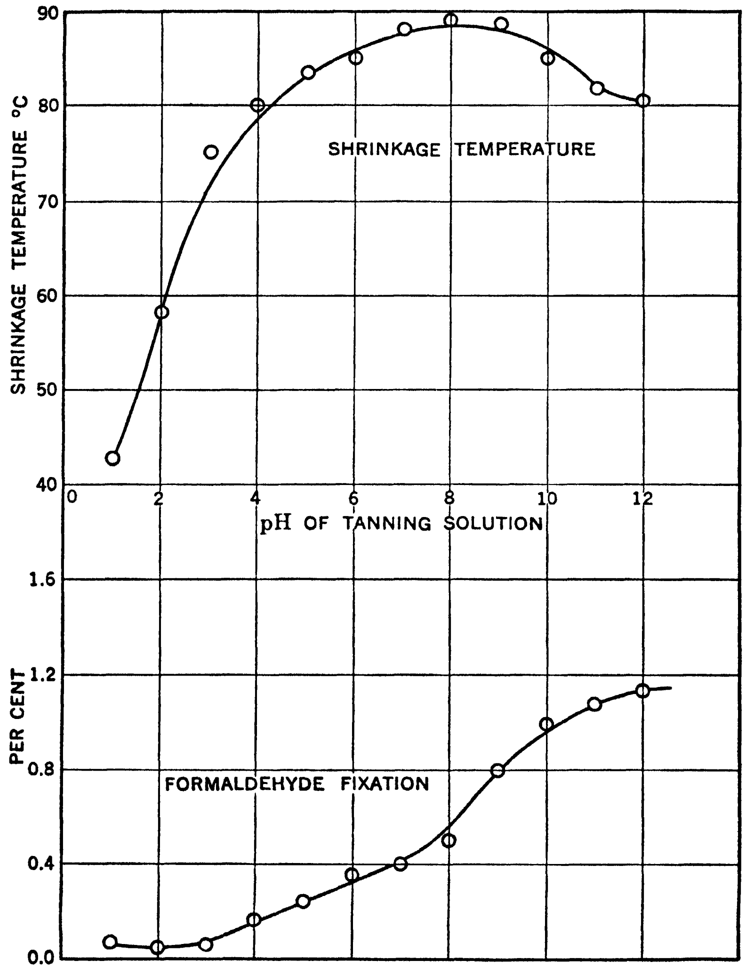


FIG. 18. Showing Formaldehyde Fixation and Corresponding Shrinkage Temperature of the Leather over the pH Range. Shrinkage temperature is a measure of the degree of "leathering" taking place.

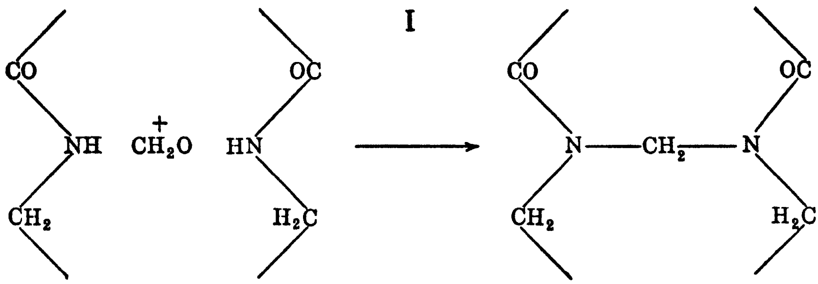
this material has only been used efficiently during the past fifteen years. The combination of formaldehyde with protein is a function of the hydrogen ion concentration and of the inorganic salt content of the tanning solution. Formaldehyde does not combine readily at pH values less than 5 and, if salt is not present, at pH values less than 7. The extent of formaldehyde fixation is shown in Figure 18.

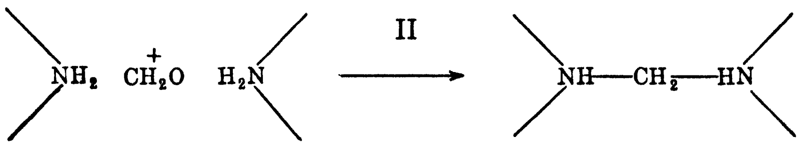
Formaldehyde is supposed to combine through the free amino groups of the protein in a manner similar to the reaction with an amine—

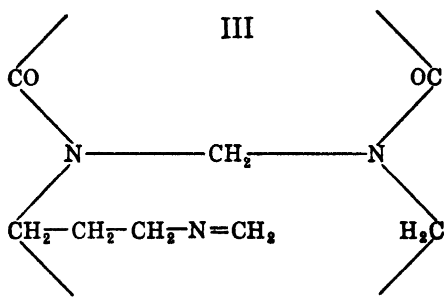
$$—NH_2 + CH_2O \rightarrow —N{=}CH_2$$

$$—NH_2 + 2CH_2O \rightarrow —N\begin{matrix} \diagup CH_2OH \\ \diagdown CH_2OH \end{matrix}$$

However, such reactions do not satisfy the conditions usually obtaining in aldehyde tannage. Research work of the past five years has shown in rather conclusive fashion that the aldehyde combines both through imino and amino groups of the protein forming a bridge or link between protein molecules—







In all probability all three combinations are utilized in aldehyde tannage.

The use of formaldehyde at pH values of 5 to 8 gives an excellent leather for certain purposes. Salt (NaCl) is necessary both for aiding aldehyde combination and for preventing grain damage.

The usual procedure for formaldehyde tannage is as follows. The bated stock is placed in a drum with a solution containing 8 per cent formalin (40 per cent CH_2O) and 3 per cent salt based on bated stock weight. The pH of the solution is adjusted to 7 with sodium bicarbonate and precipitated chalk. Tannage is usually allowed to proceed for 3 to 6 hours. The tanned stock is then removed from the drum, allowed to drain overnight and is then ready for setting out, shaving, and fat-liquoring.

If formaldehyde is used in conjunction with other tanning agents, it may either precede or follow such tannages. Formaldehyde tannage is excellent for the production of white suède leather.

Oil Tannage—Certain oils have been used as tanning agents since prehistoric times. In all probability, oil tannage preceded all other known tannages. Today sheep skins are the raw materials used for manufacturing chamois. The actual reaction taking place in the chamois process is not known. Some research workers believe that it is a reaction with hydroxy groups of the oil while others believe that aldehyde and ketone groups, formed during the oxidation of the oil, are responsible for the tannage. It has been found that such oils as linseed and cod liver oil are excellent tanning oils while olive oil has no appreciable effect. Fatty acids of linseed or cod liver oil gave a faster tannage than the corresponding oils but also gave a harsh leather. These workers found that cod liver oil increased by some 20° F. the resistance of the finished leather to temperature. Since linseed and cod liver oil both contain highly unsaturated fatty acids, we can expect the oxidation of such oils (produced through the "kicking" and heating occurring during processing) to yield hydroxy and oxy fatty acids and we can further expect the formation of acrolein and other bodies of this type. Any or all of such products in all probability have some tanning action.

Usually the sheep skins, for chamoising, are received in the pickled condition. The skins are placed in a drum and de-pickled by washing in running water for some 20 minutes. They are then removed from the drum and pressed in a hydraulic press at 200 tons pressure. This pressing removes excess acid, water and grease. The grease is sold to the soap manufacturer. The skins are dry milled in order to open them, and are then placed in water to allow a certain amount of swelling. The stock is then split on a machine, which separates the grain from the flesh layer. The grain layer is known as a skiver while the flesh layer is used for chamois manufacture.

The flesh layers are placed in a drum and treated with cod oil (fish oil). The drum is revolved for about 4 hours, during which time the oil distributes itself and to some extent penetrates the skin. The stock is then piled down in order to allow oxidation and heating to occur. Such action may require hours, after which the stock is hung in a damp humid room in order to finish tanning. It is during the "pile down" that fermentation and oxidation proceed and that various aldehydes, ketones, fatty acids, etc., are formed.

After 2 or 3 days hanging, the skins are returned to the drum and again treated with cod oil. The drum is run until all of the oil is absorbed. The stock is then returned to the humidity room and hung for 3 to 4 days in order to complete the reaction.

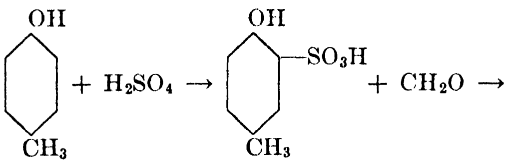
In some cases, instead of using drums, the stocks are "kicked" in machines with the oil. It is claimed that the skins are softened by such a process. The pummeling is stopped from time to time in order to allow the stock to cool. The stock is removed from the machines, re-oiled and returned to the "kickers." Several changes of oil are made in this manner, the stock usually allowed to remain piled down overnight between "kickings."

After tanning, the leather is washed with warm water (110° F.) to which some soda has been added. After washing, the leather is pressed to remove the free oil. This pressed oil is sold as moellon *degras.* After further washing, the skins are wrung out, buffed and dried.

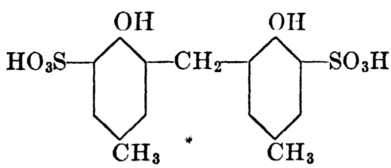
Tungsten Tannage—Pickled stock is de-pickled by washing with a 5 per cent salt solution. To the de-pickled stock is added a solution of sodium tungstate and acetic acid to a pH of 7. After 3 to 4 hours running in a drum, aluminum sulfate and sodium chloride are added. The wheel is run for 3 hours with the alum solution. After washing, the stock is ready for fat-liquoring. This tannage is not in general use.

It might be said that leather can be made using salts of iron, sodium silicate and acid, basic zirconium sulfate and calgon. While leather has been made using the above materials, the writer knows of no American tannery employing them. For details of such tannages the reader is referred to Wilson in "Modern Practice in Leather Manufacture."

Syn-tan Tannage—In 1912 Stiasny developed a new class of tanning materials—the synthetic tanning substances. These materials were made by the sulfonation of phenol, cresol, etc., and then the condensation of the sulfonated aromatic with formaldehyde—

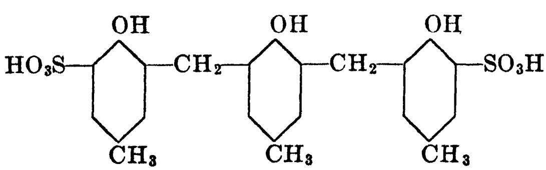


I

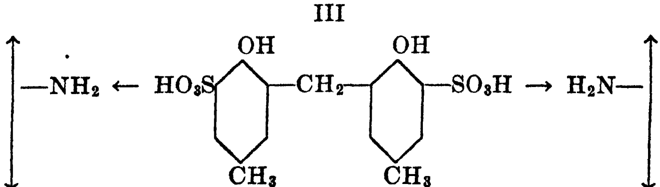


II

or



III



IV

These products are water soluble, precipitate gelatine from the solution and thus exhibit marked tanning action. The materials II and III are known commercially as Syn-tans and are marketed under such trade names as the "Leukanols," "Tamol" or "Tanak." Material IV is the probable protein-syn-tan combination.

While these syn-tans may be used as a complete tanning agent and produce pure white soft leathers, the leather so produced is empty, and low yields are obtained. However, one of the "Leukanols," namely, "R," is said to produce a full leather.

The syn-tans are ordinarily used in conjunction with other tanning agents such as chrome, vegetable or alum. The syn-tan penetrates through the skin rapidly and causes more rapid penetration of vegetable or chrome during subsequent retannage with such agents.

The syn-tans are often used as a retannage or "bleach" after chrome tannage in the production of the so-called "white" chrome leather. After shaving, the chromed stock is treated with 10 per cent of Leukanol for 1 hour at 140° F. The Leukanol has a particular action upon the chromium complex fixed upon the hide fibre, turning it a very light blue and thus adapting it to the production of white leathers.

FINISHING PROCESSES

After the leather has been tanned by a given procedure, it is then set out on a machine which presses the excess water from it. After setting out,

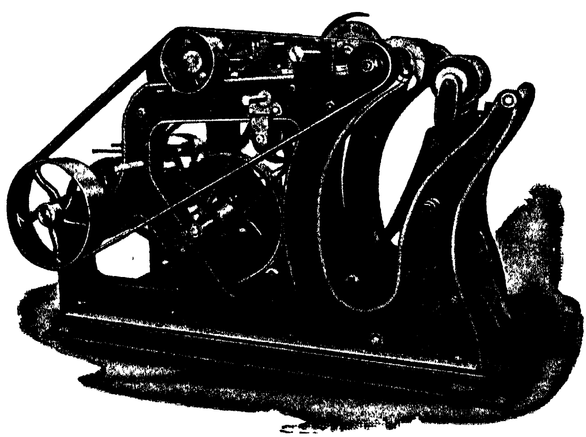


FIG. 19. Shaving Machine.

the skins may be split into layers. For light leathers, however, the leather is shaved on a shaving machine (Figure 19). This machine is fitted with a spiral knife blade of steel. The knife blades revolve at a high rate of speed and are constantly sharpened. If the leather is split, a band-knife machine is used (Figure 20). This machine consists of an endless double-beveled knife. The leather is pushed toward the knife by two feed rollers, the grain split passing over and the flesh split under the knife. The thickness of the knife can be varied at will.

Coloring—After shaving, dressing leather is ready for the coloring operation. If the leather in question has been vegetable tanned (calf, side upper, upholstering, etc.), it is placed in a drum and treated with a dilute solution of formic acid. After 15 minutes, the acid solution is removed, a dilute solution of tartar emetic introduced, which after 15 minutes is also drawn off from the stock. From 0.5 to 2.0 per cent of a basic dye is now added, the drum

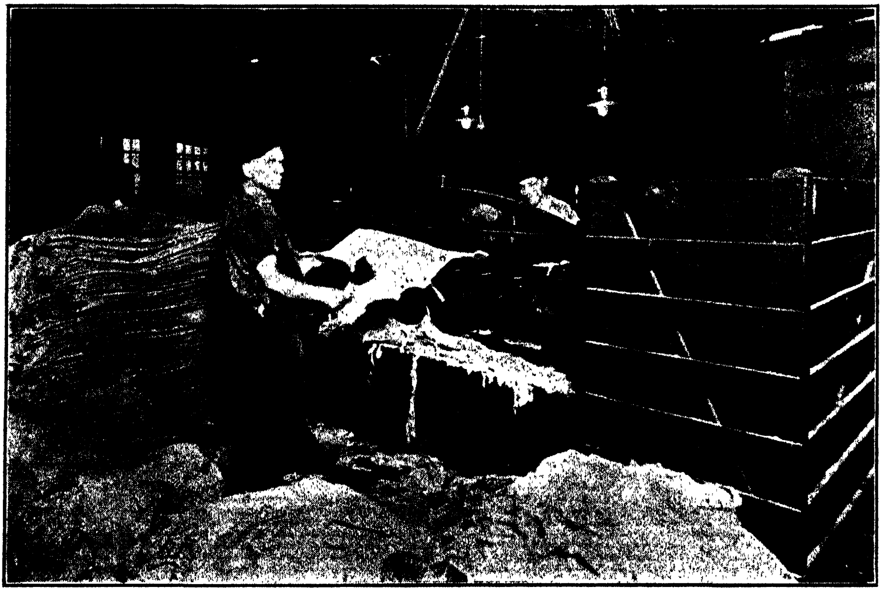


Fig. 20. Splitting Machine in Operation.

revolved for 15 minutes, after which a little formic acid is added to exhaust the dye. The excess dye solution is drawn off and an oil solution added. This oil solution may consist of sulfonated neatsfoot oil or soap and raw neatsfoot oil. This operation is known as fat-liquoring.

In a work limited to so few pages, it is impossible to give formulas for coloring all types of chrome leather—black and colored suède, glove, bag, etc. For this reason only a coloring formula for black chrome-tanned shoe uppers will be given.

Coloring Chrome-tanned Stock. After shaving, the chrome-tanned stock is placed in a drum, washed, neutralized, using a solution containing a small amount of ammonium bicarbonate, and again washed. Then to the stock is added water at 120° F., direct black dye, and the drum is allowed to run for 15 to 20 minutes. A small amount of hematine and ammonia is then added to the drum. After the drum has revolved for an additional 15 minutes, the dye liquor is drained off and a fat-liquoring oil (sulfonated neatsfoot-egg yolk mixture or sulfonated oil-raw neatsfoot oil mixture) is added, using about

6 gallons of solution at 120° F. for each 100 pounds of shaved stock. After 30 minutes running, the leather is washed, removed from the drum and then

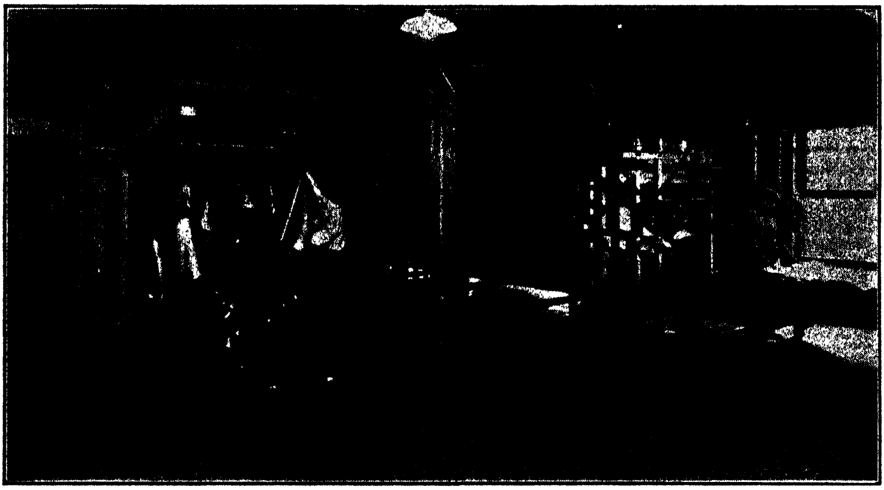


FIG. 21. Drying Tunnel in Calf Skin Tannery.

FIG. 22. Staking Machines.

horsed up overnight. The following morning, the stock is set out by machine and sent forward to dry. Drying is usually accomplished in a tunnel dryer (Figure 21). After drying, the skins are carefully wet back (dusting) by being placed in damp wood dust until they attain an approximate moisture content

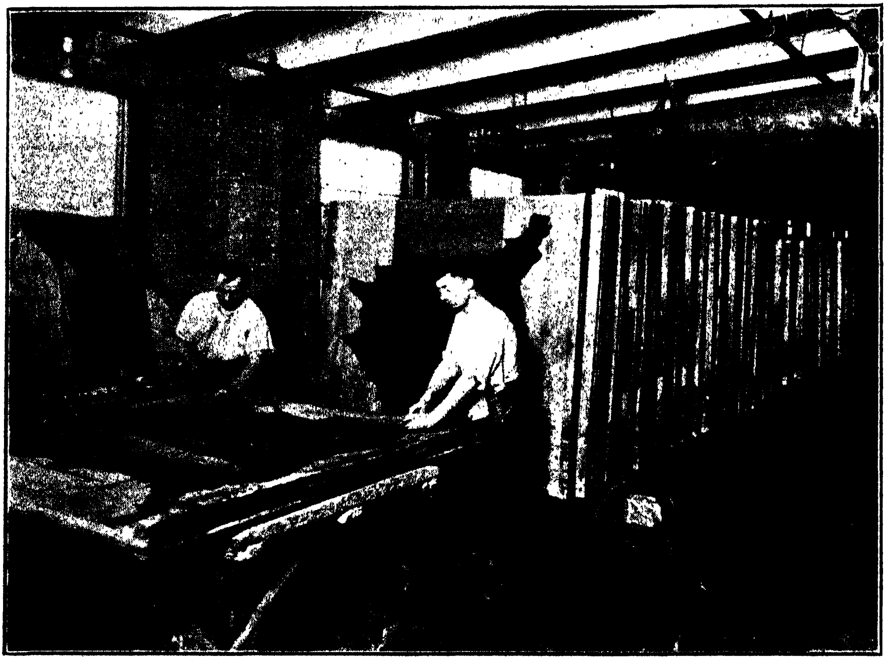


FIG. 23. Tacking Room in Calf Skin Tannery.

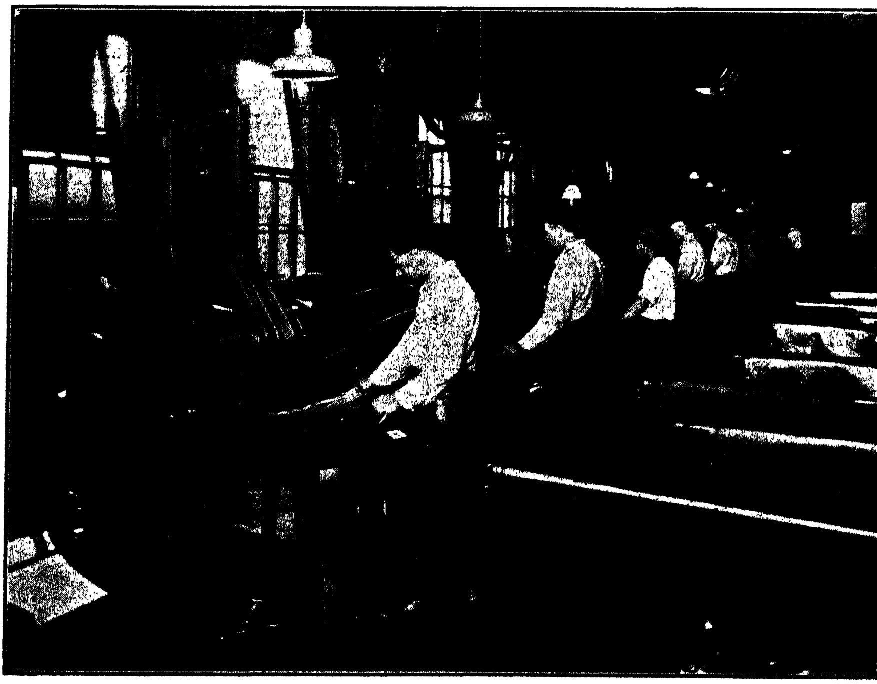


FIG. 24. Line of Glazing Jacks in Calf Skin Tannery.

of 30 to 25 per cent. The skins are then staked (Figure 22) because, when dry, they are in a firm state and must be softened. The staking machine softens the skin with a kneading motion and at the same time stretches and pulls the skin. After staking, the skin is either toggled or tacked. Figure 23 clearly shows the tacking operation. The skins are stretched and tacked in a tight state to the boards and allowed to dry.

After this second drying, the skins may be again lightly staked and are then ready for "finish." They are placed on a table and swabbed with a solution made from such raw materials as shellac, casein, flaxseed mucilage, ammonia, wax and dye and pigment. They are dried, again treated with the finish solution, dried, staked and then finally rolled with a glazing jack (Figure 24). The glazing roll is a glass cylinder which creates heat through friction and thus causes the skins to take on a "gloss." This finishing operation is extremely important, for the finished appearance of the skin may depend upon the careful and intelligent effort used. Usually it is found that each individual tanner has his own pet formula for finishing and the particular shoe or bag leather may depend greatly upon such formulation.

Patent Leather Finish—When three coats of properly prepared finishes are applied to leather to give a rich high gloss varnish surface "Japanned," "Enameled" or "Patent" leather is produced. The three coats are known as the daub coat, which is applied directly to the leather; the brush coat or first varnish, and the top coat or second varnish. Patent leather varnishes differ from other varnishes in that they must have extreme elasticity as well as good elongation, tensile strength, and waterproof qualities. These properties are essential because of treatment of the leather by shoemakers. The necessity of wetting the leather, together with severe mechanical treatment in lasting, subjects the patent leather to unusual conditions in the production of shoes.

The desirable properties in patent leather finish are realized by the production of a leather compatible with the finish used, the careful selection of raw materials for the varnishes, the control in the production and application of the varnishes, and the constant check on the physical and chemical properties of the varnishes.

The Base Finish. When finishing patent leather, as is the case with all protective coatings, the base finish is probably the most important coat. The daub must adhere well to the leather without excessive penetration. It must also adhere to the brush coat and yet be hard enough to withstand pummying. In preparing a daub, linseed oil which has been blown to a definite specific gravity or oxygen content [21] is heated with litharge and umber at a temperature of about 550° F., usually with ladling, and passes through several visible stages of polymerization. The first indication of approaching a finish is the appearance of "roping" or the formation of long rope-like strings from the ladle. In a short time, the oil reaches the "leafing" phase when the daub drips from the ladle in leaves. Shortly thereafter the daub is tested for "necking," at which stage the daub oil forms a web between the ladle and the ladle handle. The batch is forked and the kettle cooled externally with water, after which naphtha in the ratio of two volumes of naphtha to one of daub oil

[21] See Chapter 41.

is added. Stirring is continued until a homogeneous and non-sticky plastic mass is produced. The daub is allowed to stand in containers for a day after which it is placed in a mixer and Prussian blue and additional naphtha are added. After filtering and cutting with naphtha to desired viscosity, the daub is applied to the hide by hand, using either "slickers" or sponges. The skins are then dried in low temperature ovens or heated rooms.

A combination of linseed oil and soluble cotton is used by some manufacturers in the finishing of fine grain leather such as calf skin and kid. This daub is made from cellulose acetate solution, bodied linseed oil, amyl acetate and a suitable thinner.

The Brush Coat. In the production of the brush coat or first varnish, it must be realized that this coat is placed between a daub coat with molecular weight of about 1800 and a top coat of molecular weight 1550. Furthermore, the daub is largely a gel product with some viscous oil in the liquid phase and the second varnish is a relatively low viscosity material in the liquid phase. Thus, to reduce to a minimum the diffusional potential between the layers, the brush coat should be cooked to a viscous oil without gel formation.

This type of brush coat is prepared by heating to 250° F. a linseed oil, sufficiently low in break to prevent excessive foaming. Driers consisting of umber and litharge are incorporated and the temperature raised to and held at about 560° F. The final product is determined by matching viscosities with a standard to obtain the desired string and molecular weight. Some japanners use a thinned daub for the second coat.

Top Coat. Top or second varnish is usually prepared from completely or partially refined linseed oil. The oil is heated to 250° to 300° F. and about 3 per cent by weight of Chinese lump blue added. The temperature is then gradually raised to 550° to 600° F., and either held at a given temperature or cooked in "heats" until the desired molecular weight of 1550 to 1600 is obtained. The varnish is then cooled to 300° F. and thinned with naphtha. After storing for ten days to two weeks to allow any insoluble matter to settle, the decanted varnish is further thinned to the desired gravity.

The varnish is applied in a room at a temperature of 100° F. to insure free flow of the finish. Large brushes with long bristles are used to obtain rapid application and an even coating without streaks. The frames of leather are placed horizontally in an oven overnight at about 160° F. Care must be taken to have no dust or lint particles reach the wet surface during application or drying. The dried surface should be brilliant without being glassy, and slightly tacky. The final drying or polymerization of the varnish film is by "sunning" in direct sunlight from one-half to two days, depending upon the weather. After this treatment, two varnished surfaces will not stick when placed face to face. This careful method is essential to the production of a film which is not brittle, yet dry enough not to be sticky. The sunning of patent leather introduces a real problem to the japanner since total capacity is largely measured by the balance between storage capacity and continued inclement weather.

Developments in the production and use of ultra-violet lights have resulted in their limited use in this field, in place of sunning.

The major problem in the production of patent leather finishes is the control of raw materials such as linseed oil, colors and driers and the duplicability of batches in oil processing. Linseed oil composition and effectiveness vary from seasonal effects and geographic location. The driers, which in many cases are earths, must be analyzed to differentiate between inert pigments and available reactive driers in their compositions. Varnishes must be examined in test films to determine their life history with respect to tensile strength, elasticity and elongation. The varnish maker is limited to time and temperature specifications of production together with experienced observation of definite endpoints since no automatic devices are available.

COMMERCIAL ASPECTS OF THE LEATHER INDUSTRY

In considering the commercial aspects of the leather industry, it is best to refer to the data collected from the records of the Tanners Council of America. These records show that the number of hides and skins consumed in the United States for the year 1940 were distributed as follows:

Cattle hides	21,147,000
Calf skins	11,502,000
Kip skins	2,289,000
Goat and kid skins	34,819,000
Sheep and lamb skins	37,489,000
Cabrettas	2,800,000
Deer and elk skins	900,000
Kangaroo skins	920,000
Horse hides	870,000

The United States is not self-sufficient in the matter of hides and skins and the following tabulation shows this dependency:

	Imports	*Exports*	
Cattle hides	4,582,978	364,018	pieces
Calf and kid skins	2,280,017	274,425	"
Goat and kid skins	40,152,954	......	"
Sheep and lamb skins	19,131,717	1,137,210	"
Wooled skins	5,293,689	......	"
Kangaroo	928,681	......	"
Horse and colt skins	15,131,065	......	pounds
Deer and elk	928,866	......	pieces

It is often remarked that the consumption of leather is decreasing and that other commodities are replacing it. However, data regarding leather production for the years 1922, 1930 and 1940 do not substantiate such contentions for all categories as is shown in the following summary:

	1940	*1930*	*1922*
Sole leather produced (sides)	14,065,000	15,514,000	18,393,000
Belting leather produced (sides)	1,369,000	1,434,000	1,676,000
Side upper leather produced (sides)	21,155,000	11,114,000	13,788,000
Calf leather produced (skins)	11,387,000	14,171,000	10,874,000
Goat and kid leather produced (skins)	37,697,000	55,445,000	48,904,000
Sheep and lamb leather produced (skins)	37,920,000	30,393,000	23,015,000

It is true that from literally thousands of very small tanneries, the industry has consolidated to a matter of hundreds of much larger establishments. The United States Leather Company controlled at one time a great many small tanneries located in the state of Pennsylvania but today operates only a few very large ones. The need of careful chemical control and supervision necessitated consolidation and in so far as possible the centralization of the whole tannery operation under one roof.

THE FUR INDUSTRY

There are many common problems in the manufacture of leather and furs. In fact, the fur industry needs nearly all the leather man's knowledge plus that necessary to treat hair and fur. The leather tanner, for the most part, wishes to remove the hair completely while the fur tanner wishes to preserve it. The common plane is the actual leather in both instances.

The pelts of animals used for the manufacture of furs are of entirely different type and nature from skins used in leather manufacture. For instance, many millions of rabbit pelts are dressed per year—these to go into fabrication of coats. The pelts are so treated as to simulate many types of furs, such as "Lapin," "Coney," "Sealing" or "Near-Seal." Muskrat, native to North America, is dressed and dyed and becomes "Hudson Seal." The lamb family comprise quite a number of items—Persian or Caracul. The Alaska seal is one of the really valuable furs. The Alaska seal pelts are tanned in the United States only in St. Louis and are controlled by the U. S. Government.

Fur pelts may be dressed by means of sulfuric acid and salt (very old type of dressing); by means of alum and salt; by means of oil in a manner similar to oil tanning of chamois; or by a combination of alum, salt and oil. As an example, the millions of rabbit skins dressed each year are usually treated as follows: The pelts are soaked for 24 hours in a dilute salt solution, hand fleshed, treated for 2 to 3 hours in dilute formaldehyde solution and then placed in an alum-salt solution for 18 to 24 hours. After such treatment the pelts are wrung out and given an oil treatment by swabbing oil on the flesh side of the pelt. The pelts are then dried, staked and dry drummed with sawdust in order to clean them. They are then ready for dyeing. The methods of dyeing all furs are mostly secret and each fur dyer has his own formula and process. As has already been mentioned, rabbit pelts can be so carefully processed as actually to simulate to a high degree pelts of other and more expensive types.[22]

RESEARCH IN THE LEATHER INDUSTRY

The art of leather manufacture began to change to a science with the beginning of the twentieth century. Procter in England began his classical work in the early part of this century and is rightly called the Father of Leather Chemistry. With the collaboration of Wilson, Procter gave to the world the first real definition of "swelling" as applied to proteins. In the past

[22] See Reading List at end of chapter.

thirty years, such workers as Stiasny, McCandlish, Atkin, Wilson, McLaughlin, O'Flaherty, Highberger, Frey and Theis have been active in furthering the science of leather technology and have indeed added materially to the literature of the field. Most of their work can be found published in the Journal of the American Leather Chemists Association, Journal of the International Society of Leather Trades Chemists or Collegium.

In the United States, leather research is today being actively carried on in the Tanners Council of America Leather Research Laboratory at the University of Cincinnati under Doctor Fred O'Flaherty; in the Leather Research Laboratories of Lehigh University under the direction of the author; in the B. D. Eisendrath Memorial Laboratory, Racine, Wisconsin, under the very able supervision of Doctor G. D. McLaughlin; in the Leather Laboratories of the Department of Agriculture and Bureau of Standards of the U. S. Government. All of these laboratories work actively together in harmony both in spirit and effect.

READING LIST

LEATHER MANUFACTURE

Procter, H. R., "The Principles of Leather Manufacture," London (1922).
Wilson, J. A., "The Chemistry of Leather Manufacture," Vol. I and II. Reinhold Publishing Corp., New York (1928-1929).
Stiasny, E., "Gerbereichemie," Steinkopff (1931).
Wilson, J. A., "Modern Practice in Leather Manufacture," Reinhold Publishing Corp., New York (1941).
Price, J., Jr., "North American Packer Hides," Pratt Bros., Chicago (1939).
Mudd, J. S., "Leather Finishes," Chemical Publishing Co., New York (1939).
Burton, D., and Robertshaw, G. F., "Sulfated Oils and Allied Products," Harvey, London (1939).
Merry, E. W., "The Chrome Tanning Process," Harvey, London (1936).
McLaughlin, G. D., J. Amer. Leather Chem. Assoc., 1921-1941.
Theis, E. R., et al., ibid.
Rockwell, G. D., ibid.
Küntzel, A., Collegium, 1930-1940.

FUR INDUSTRY

Austin, W. E., "Fur Dressing and Fur Dyeing," New York (1922).
Bachrach, M., "Fur," Prentice-Hall, New York (1930).

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