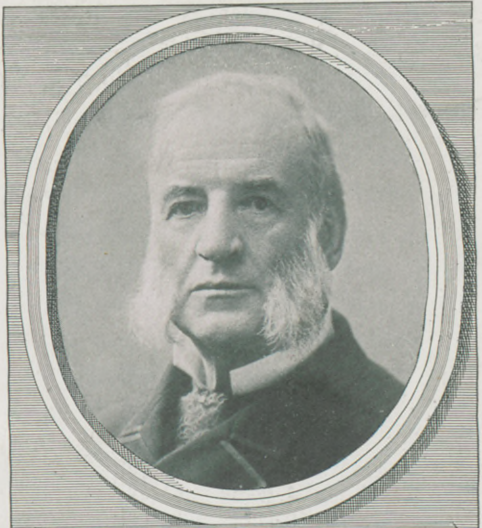

AMERICAN CHEMISTRY

A RECORD OF ACHIEVEMENT
THE BASIS FOR FUTURE PROGRESS

BY

HARRISON HALE, Ph.D.
Head of Department of Chemistry, University of Arkansas

63 ILLUSTRATIONS

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TO

EDGAR FAHS SMITH
AMERICAN CHEMIST
WHOSE LOVE OF COUNTRY AND DEVOTION TO
CHEMISTRY HAVE LONG BEEN AN INSPIRATION

PREFACE

Chemistry is constantly becoming of greater importance in the life of the American people. The realization of its value has been deepened by recent events. This situation calls for a simple and clear statement of the more outstanding facts of American Chemistry, which is the purpose of this book.

It seeks to be of service both to the general reader and to the reader still in school. For the student it is intended for use either as collateral reading along with a course in General Chemistry, or as a short separate course. For both courses the author has used this material satisfactorily in his classes.

Two objects have been sought: to call the attention of the reader to the fundamental importance of chemistry to America as well as to the wonderful chemical possibilities in America; second, to encourage in him the habit of reading articles in current literature with a bearing on chemistry, to which frequent references are given. It is surprising how many such articles are being printed in the newspapers and non-technical magazines.

That the record of the American chemist is one of achievement, and furnishes a very real basis for future progress is the firm conviction of the writer. In these facts there is an inspiring source of patriotism.

HARRISON HALE.

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CHAPTER I

INTRODUCTION

American Chemistry.—In discussing what we have chosen to call American Chemistry two outstanding facts constantly force themselves upon our attention: the absolutely fundamental and increasing value of chemistry in the development of the world to-day, and the real importance of the United States in modern chemistry. We shall hope to see not only the very creditable part America has had in the past, and the work now being done, but also to obtain some idea of the great possibilities of the future. In other words, we wish to know *what chemistry is doing for America and what America is doing for chemistry.*

Very Early History.—Though no great attention was paid to the achievements of American chemical industries until they proved themselves one of the most powerful factors in bringing the World War to a successful conclusion, yet it is interesting to note that the first industries of the earliest American colony at Jamestown were those which are now considered chemical industries. The following report is given by Mr. C. A. Browne in the Journal of Industrial and Engineering Chemistry, January 1919 (Volume 11, page 16):

"The London Company, the year after they founded the Jamestown Settlement, sent eight

Poles and Germans to the new colony to make pitch, tar, glass, and soap-ashes. No sooner were these workmen landed than they began operations. . . . From this small beginning in 1608 we must date the commencement of chemical industries in America. The glass-house used for these trials stood in some woods about a mile from Jamestown."

Expansion of chemical industry was even then in evidence for in 1620, 150 men were sent out to set up three iron works. Salt works to supply the Atlantic Coast fisheries were started and lead smelting was begun. But " all industrial efforts were paralyzed by the Indian massacre of 1622." " Chemical industries in the New England colonies were destined to run very much the same course as in Virginia."

Chemical Industry.—From these early beginnings chemical industry has grown to its present proportions, not by a steady development, but hindered or stimulated by harmful or helpful economic or industrial conditions. By far the greatest advance has been made within the last twenty-five years, much of it in the last ten. This has been due to the recognition of the fact that almost all industries are in basic principle chemical, and to the employment of chemists in the control and direction of these industries. By the labors of the American chemist aluminum and numerous other metals have been extracted from their ores, cotton seed has given up its oil to form a number of valuable food products, water supplies have been safeguarded and purified, petroleum has by refining given its numerous products now considered necessities. These and many, many other industries owe their present commanding and helpful position to the efforts and the skill of the chemist (1).*

It must be clearly kept in mind that the field of the chemist is far broader than that of the so-called chemical industries. The iron and steel industry, as well as that of all the metals, while not a chemical industry, so-called, must be carried on under rigid chemical control. In fact but a very small fraction of the twenty-six billions of dollars of manufactures reported in the last (1914) U. S. census is not either directly or indirectly dependent upon the work of the American chemist (2).

Chemical Societies.—This splendid development of our industries is due in very large measure to the interest and the knowledge fostered by the association of chemists and persons of kindred ideals in chemical societies. The first society of this kind in the world was the Chemical Society of Philadelphia founded by James Woodhouse in 1792 (3). Though active only some seventeen years, it had a decided influence upon American chemical thought of its day and has left us some interesting papers. In an address before this society delivered April 11, 1798, Thomas P. Smith makes suggestions which are as vital and timely to-day as they were a century ago. In Smith's " Chemistry in America " page 36, he says:

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* This number refers to references given at the end of the chapter.

" The only true basis on which the *independence* of our country can rest are *agriculture* and *manufactures.* To the promotion of these nothing tends in a higher degree than chemistry. . . . It is to a general diffusion of a knowledge of this science, next to the *virtue* of our countrymen, that we are to look for the firm establishment of our *independence.*"

Joseph Priestley came to make his home in Pennsylvania in 1794. His discovery of oxygen twenty years earlier and its interpretation by Lavoisier is frequently considered as marking the beginning of Modern Chemistry. On August 1, 1874 a group of American chemists gathered at Priestley's grave to celebrate the centennial of the discovery of oxygen and to thus pay a tribute of respect and appreciation. There the organization of a chemical society was suggested by one of the ladies present (4). As a result there met in New York City, April 6, 1876 a group of thirty-five chemists for the purpose of founding the American Chemical Society. To-day this society with its 16,000 members is by far the largest chemical society in the world, and exerts an influence which cannot be measured. Its three publications have been of great value, and its plans for the future give promise of still greater usefulness.

The American Electrochemical Society, the American Institute of Chemical Engineers, the Association of Official Agricultural Chemists and a number of other organizations have done much for the development of American Chemistry. The American Chemical Journal, fifty volumes of which were published by Ira Remsen, before its consolidation with the Journal of the American Chemical Society, the Journal of Physical Chemistry, the Chemical Age, Chemical and Metallurgical Engineering and similar publications have been influential and valuable.

Colleges and Universities.—Not the least of the influences at work in moulding and directing chemical thought has been that of the chemical departments of the American colleges and universities. Priestley was offered the professorship of chemistry at the University of Pennsylvania and even at that date a noteworthy group of men were engaged in such work (5). With the growth in numbers and material equipment of the universities this influence increased and for years it has not been necessary to leave the United States to secure the best training in chemistry and chemical engineering (6).

Co-operation.—As chemical industries developed rapidly and educational institutions increased in number and in facilities for research, it became increasingly evident that, to obtain the best results, there should be some closer connection between the two: to give to industry the spirit of research dominant in the university, and to the university something of the efficiency and energy of industry. This feeling has shown itself in several ways. The founding of industrial fellowships at the University of Kansas under the direction of Robert Kennedy Duncan was followed later by the dedication on February 26, 1915 of Mellon Institute at Pittsburgh

Mellon Institute of Industrial Research. A Splendid Example of Co-operation due to his influence (7). The trade courses of the University of Cincinnati and the Master's Course in Chemical Engineering at the Massachusetts Institute of Technology (8) are praiseworthy efforts to combine practical experience with university training (9).

Not only is there need for closer co-operation between industry and education but the aid of the Federal Government in the solution of industrial engineering problems, many of which are chemical, is vitally necessary and is at present rightly receiving much attention.

The organization of the Chemical Foundation, Inc. to purchase from the Alien Property Custodian for the benefit of American industry 4500 patents (mainly German) applying to chemistry promises much for American chemical independence and "for the advancement of chemical and allied science and industry in the United States (10)."

As a result of all of these efforts and of the spirit of co-operation which is beginning to dominate them we may expect even greater triumphs for Chemistry in the United States in the near future than those already won, and it is to this record and to this promise we wish now to turn our attention.

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CHAPTER II

RECENT RAPID GROWTH—WAR CHEMISTRY

Explosives. Gas. Chemical Warfare Service. Permanent Gain

Industrial chemistry, already expanding at a rapid rate, received a tremendous impetus from the demand of the nations at war in 1915, and even the increased production thus resulting was far exceeded when the United States had actively entered the war. Says an American writer in summarizing the year 1918 (1):

" Reactions which in the laboratory proceed in test tubes, have been put upon a commercial basis of quantity of production that would astound the chemist of a generation ago."

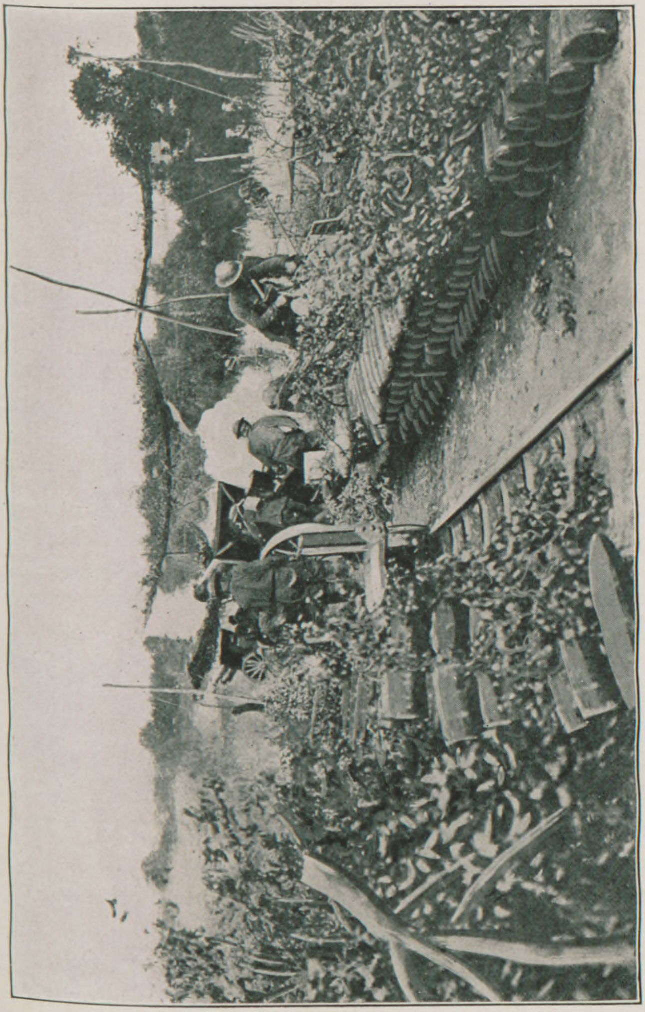
This increased production was by no means confined to munitions and other necessities of war, though, of course, most noticeable there. Fortunately much of the equipment and machinery can be turned to the manufacture of articles as useful in peaceful pursuits as in war, so that there was a real permanent gain in the midst of the economic loss which war necessarily brings. We shall first consider Explosives and Gases and the American Chemical Warfare Service in their relation to the War and also on the basis of possible permanent gain, and in later chapters other industries not so directly related, but which in a large measure felt the stimulus which the War brought.

Explosives

In the midst of the resounding din of the present day battle one is hardly likely to think of the primitive bowman of long ago. And yet the idea of effectiveness at a distance is the same, only to-day man uses the energy of chemical action instead of muscular force and the range is increased from yards to miles. Moreover by chemical force he may not only send his projectile to a desired point but he may cause its explosion there, increasing its effectiveness.

An explosion is due to a sudden increase in volume and may be initiated either by a mechanical shock or by an increase in temperature. The element used almost universally in military explosives is the same element which, uncombined, is used as a diluent for the more active oxygen of the air. Though compounds of nitrogen are often used for the destruction of life in warfare, other compounds of the same element are absolutely essential for any form of animal or plant life. Hence compounds of this element must be present in our food and in the soil in which our food grows, and yet many of our most violent poisons are compounds of this same element.

Compounds of nitrogen are comparatively rare and expensive, though over each square mile of the earth and the sea as well, it is estimated there are approximately 25,000,000 tons of the free element. Only recently has it become practically possible to combine even a small amount of this



Firing 155 Millimeter Howitzer During Argonne Fight

atmospheric nitrogen into compounds of value, and it is asserted on high authority (2) that Germany waited before putting her plan of world conquest into action until the methods of fixing atmospheric nitrogen had been perfected! (See Fertilizers, page 53.)

Classes of Explosives.—Very many substances of an explosive nature are known, but not all can be sufficiently controlled to be of practical value. Those now in common use may be placed in three groups:

1. Black powder, which has been in continuous use for military purposes since the fourteenth century, though its use for industrial work is confined to the last two hundred years. The standard black powder of the United States Army contains the following by weight:

	Chemical Symbol	Per Cent.
Potassium nitrate (saltpetre)	KNO_3	75
Carbon (as charcoal)	C	15
Sulfur	S	10
		100

Compared with explosives of more recent discovery gunpowder is open to three objections: (a) it is a mechanical mixture, not a chemical compound and the generation of gas is relatively slow. It has been calculated (3) that while the explosion of a kilogram (2.2 pounds) of dynamite occupies 1/50000 of a second, the same weight of ordinary black powder requires 1/100 of a second, or five hundred times as long. (b) More than half of the products of the combustion of black gunpowder are solids, causing large amounts of smoke. (c) In a gunpowder explosion the volume of the gas produced is less and the temperature is less, thereby giving a much less energetic explosion.

2. Smokeless powder and similar products, are explosive chemical compounds or mixtures of such compounds. These are made by treating various organic materials with a mixture of nitric and sulfuric acids, great care being necessary both in the selection and purification of materials, as well as in the processes of manufacture. These explosives may be divided into two classes of which nitro-glycerin and tri-nitro-toluol, commonly called TNT are the best known representatives.

Nitro-glycerin, discovered by Sobrero, an Italian chemist, in 1847, is prepared by spraying glycerin into a mixture of nitric and sulfuric acids, which must be kept cold. The nitro-glycerin is a heavy, pale yellow oil, very poisonous and very easily exploded by a shock. Because of these properties this glyceryl trinitrate, the really correct name for this explosive, was put to little or no practical use, until Sir Alfred Nobel,* a Swede, in 1866 prepared dynamite by the absorption of nitro-glycerin in sawdust, infusorial earth, or some similar substance. In this form it can be handled with much greater safety.

Nitro-cellulose is formed by treating carefully prepared cellulose with a mixture of nitric and sulfuric acids. This cellulose is generally obtained from cotton of short fibre, purified by special

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* Founder of the Nobel Peace Prize.

processes, though wood cellulose can also be used. The material thus obtained, cellulose nitrate, occurs in a number of varieties depending upon the chemical composition and the conditions of manufacture. Cellulose nitrate for explosive purposes must be made from materials of a high degree of purity and by processes, demanding time and extreme care. Under the name of guncotton this material finds extensive use and is considered one of the safest of modern explosives.

Certain coal tar products when treated with nitric and sulfuric acids under proper conditions yield powerful and satisfactory explosive compounds, some of which are often used. They differ to some extent in their chemical composition from the compounds just described and contain the benzene ring found in practically all coal tar products. Picric acid and TNT are the most important.

3. Primers and detonators, which are used to produce the requisite shock for the explosion of the main charge. Mercury fulminate made from mercuric nitrate, nitric acid and alcohol is generally used. (Latin: fulmen, fulminis, thunder.)

America's distinction lies in the tremendous output of such explosives in very recent years.

Permanent Gain.—While the very word, explosive, is coupled in our minds with the idea of disaster and of death, yet on further thought we readily recognize that the power wrapped up in an explosive can be used for constructive as well as for destructive purposes. Clearly the explosive is

Road Built with Aid of Explosives, Colorado entitled to rank along with steam and electricity in the aid it has given to man in his conquest of nature. In the manufacture of explosives to be used in the building of roads and waterways, railways and tunnels, the equipment America has

Removing Stumps by Explosives—Tamping the Charge

recently acquired will be of decided value. New uses for explosives are possible, most noticeable among these being in shattering ground for the planting of fruit trees and in other forms of agricultural work.

Again, the fixation of atmospheric nitrogen, carried out in our recently constructed plants upon a scale never before dreamed of, can be of the greatest practical value in the manufacture of fertilizers. In practically all large explosive plants sulfuric acid has been manufactured. This acid has countless industrial uses. Greatly to be desired sources of supply for our newly established dyeing industry have already been found in the saving of certain crudes in coal tar previously used in making explosives. (See Sulfuric Acid Manufacture, p. 183; also Dyes, p. 88.)

> " All surplus TNT and other explosives owned by the War Department, which can be used in clearing land, building roads, general construction work . . . have been turned over to the Department of Interior. . . . This material, which at one time was considered practically worthless, now has an estimated value of $15,000,000."(4)

War Gases

A description of the use of poisonous gases in warfare in a book on American Chemistry would have been impossible a few years ago. Such use had been distinctly forbidden at the Hague with the concurrence of many of the leading nations of the world, including Germany. While the United States did not ratify this agreement, American army men and chemists had no plans for this use of gases and no attention whatever had been given to them. But when the suffocating waves of greenish-yellow chlorine were sent by the Germans over the Ypres salient, April 22, 1915, a new phase of most hideous warfare was added by Germany's utter disregard of all agreements and her effort to terrorize her foes (5).

Forms of Gas Attack.—This first attack and those following it for months were gas clouds, or drift gas, and depended for their successful use upon weather conditions. Cylinders weighing about ninety pounds each, containing forty pounds of liquefied chlorine were placed along the trench at intervals of about a yard and opened when there was a moderate wind of four to eight miles velocity blowing in the right direction. A few months later phosgene, carbonyl chloride ($COCl_2$), was used because of its after effect, frequently causing death hours after the actual time of gassing, when the victim had gone out of the danger zone.

The use of the hand grenade, containing bromine, chlorosulphonic acid, or other corrosive or poisonous substance, was a second form of attack found exceedingly useful in the clearing out of trenches and dugouts, and not dependent upon the direction of the wind.

While not so spectacular, the third and most effective form of gas attack was by the use of the gas shell. Its use came not many months after the first use of drift gas, but its great value was shown in the German offensive in the spring of 1918, for it proved to be one of the most decisive factors in making possible that advance. It is claimed that in some localities as many as 200,000 shells per day, each containing five pounds of gas, were fired for four successive days. Thus large areas could be covered and the strain on the soldiers under attack from the long wearing of masks was terrific, even when there were few casualties.

This was called the neutralization of the infantry. The gas shell allowed also the use of a wide variety of substances, many of which were in reality not gases, but heavy corrosive liquids or solids with some high explosive as TNT to cause their proper dispersion.

Classification of " War Gases."—According to their effects the so-called gases may be classified as death-producing or lethal, tear-producing or lacrymatory, sneeze-producing or sternutatory, corroding or blistering. These classes are not mutually exclusive, the same gas falling in several classes, depending in part upon the concentration. Some individuals were found much more susceptible to a certain gas than others. The Germans distinguished some of these shells by marking them with a colored cross, thus, blue, green, yellow, and even red. This red cross shell contained a mixture of both tear-producing and deadly gases, so by its use, as by the use of others, Baskerville claims the Germans intended that the " soldiers were to weep at their own funerals! " (6)

American War Gases.—In November 1917 it was decided by the Ordnance Department of the Army to establish a small shell-filling plant at Gunpowder Neck, Maryland (7), and the next month it was decided to erect there such chemical plants as would be needed to furnish the materials for filling the shell. In January 1918 Colonel Wm. H. Walker, then Chief of the Chemical Service Section (in times of peace, in charge of the School of Chemical Engineering Practice at the Massachusetts Institute of Technology—see p. 7) was placed in charge and it is in large measure due to his energy and efficiency that so splendid a record of American achievement was made. This plant with others where " gas " materials were manufactured passed under the care of the Chemical Warfare Service when that was organized.

At this plant were manufactured four " gases " which may be regarded as typical of a very large number of substances that were used in gas warfare. These were either shipped abroad in bulk or used to fill hand grenades or gas shells.

Chlorine, the basis of the other " gases " prepared here was manufactured by the electrolysis of sodium chloride, or common salt. After drying a part was used to make sulfur chloride and phosgene and most of the remainder liquefied for shipment overseas. (8), Phosgene, or carbonyl chloride, a highly poisonous gas, was made by passing carbon monoxide and chlorine over a carbon catalyzer. It, too, was used either in filling shells or shipped in drums.

Chlorpicrin, a strong lacrymator as well as a poison, is a liquid made by the reaction of calcium picrate with bleaching powder. Mustard gas, which is really not a gas at all, but a liquid with a vapor five times as heavy as air, is BB-dichlordiethylsulfide. It affects the eyes, causing temporary blindness, may produce inflammation of the lungs, and also make burns like those of phosphorus, very painful and difficult to heal. This " gas " is produced by passing ethylene into sulfur chloride and the reaction must be carefully controlled (9).

Lewisite, a gas whose composition is still kept secret, is claimed to be seventy-two times more deadly than any war gas actually used. Its discovery and production in America came too late for it to be used on the battle front (9).

Gas Defense—The Mask.—It is stated that the Allies had been warned that the Germans were preparing for a gas attack but were unable to give such a report credence. Whether this be true or not, it is certain that there was absolutely no defence for the gas waves at Ypres. Within a week after this attack, thanks to the help of English women, hundreds of thousands of gas masks were provided for their soldiers. These first masks were mainly a heavy cloth saturated with soda and sodium thiosulfate to neutralize the acid and the oxidizing effect of the chlorine.

As time went on and other gases were used the masks were perfected, the object being mainly to neutralize the effect of the gas. Later the idea of absorption became the dominant one, and this caused an unprecedented demand for carbon, or charcoal, made from cocoanut shells and the seed of peaches, apricots and other fruits, which pure research several years before the war had shown best suited for this purpose. This charcoal mixed with selected chemicals was placed in canisters, and could be renewed.

The importance of such defence is seen from the statement of Colonel Raymond F. Bacon, Chief of the Technical Division (in peace times Director of Mellon Institute—see p. 5), who says: (10)

" In proportion to the amount of gas shell used the casualties produced thereby have been far in excess of those caused by any other form of ammunition." Thirty per cent of all casualties among American troops were due to gas (11).

The extremely toxic effect of the gases used is seen in the haste necessary in donning the mask, or, as put by a British officer, " In gas warfare there are but two classes, ' the quick and the dead ' "(12).

Every effort was made to keep the trenches free from poisonous gases, these being removed by creating air currents, either by fanning or the building of fires, or by the neutralization of the gas by some form of chemical spray.

Permanent Gain.—The chlorine so widely used either alone or in the manufacture of other gases has also a wide use in times of peace in the sterilization of water supplies, in sanitation, in medicine, and in the preparation of a large number of chemicals including dyeing materials.

The use of masks in certain industries has already resulted and will doubtless find a wider application. The use of their masks by returned soldiers, serving as members of city fire departments, was reported in a number of instances shortly after their return. The knowledge gained as to the toxic effect of numerous substances and the best method of counteracting them has been a valuable gain to the physician (13).

The record of the American chemist in beating the German in twenty months at his own game, in which he claimed all the homage due to the superman and for which he had been preparing for forty years, is in reality a permanent gain of no small value. For at the close of the war the American soldier was better protected from gas attacks and the gas offense of the American, though finding slight use on account of the steadiness of the enemy's retreat was far more deadly than anything the German had devised after his decades of preparation. This is not a cause for undue pride, and credit in large measure is due to the knowledge gained from our allies, but it is a source of added confidence as we face the future of American Chemistry.

Chemical Warfare Service

Those who were fortunate enough to be present at the closing banquet of the meeting of the American Chemical Society in Champaign, Ill., in April 1916 could not but be impressed with the words of President Herty, when he said, in substance:

> " Let us, as we go to our homes, remember the responsibilities that rest upon us as American chemists, ready to serve if our country needs us in the momentous days that may lie ahead."

Altogether consistent with this attitude was the action of his successor, President Stieglitz, early in February 1917 in offering without reservation to President Wilson the services of the members of the Society in any emergency which might arise (14). This action was unanimously reaffirmed at the spring meeting in Kansas City a few days after a state of war had been declared. By June 1917 a committee of the Society had presented a report on "War Service of Chemists."

Chemical Service Section.—In the early days of the war little attention was paid to a man's qualifications as a chemist and so a number of graduate chemists were found serving in the army in a non-chemical capacity. The first recognition came in the formation of the Chemical Service Section, National Army, and largely through its influence an order was issued May 28, 1918, stating (15),

> "Owing to the needs of the military service for a great many men trained in chemistry, it is considered most important that all enlisted men who are graduate chemists should be assigned to duty where their special knowledge and training can be fully utilized. . . .
>
> "Enlisted men who are graduate chemists will not be sent overseas, unless they are to be employed on chemical duties."

Under this order hundreds of men were actually placed in chemical work. As the insignia of this Section crossed alembics, or retorts, surmounted by the benzene ring were chosen, and for a hat cord, the colors of the American Chemical Society, cobalt-blue and gold.

Census of Chemists.—In February 1917, two months before the declaration of a state of war, the Bureau of Mines through its Director, Dr. Manning, and the American Chemical Society through its Secretary, Dr. Parsons, had at the request of the Director of the Council of National Defense undertaken a census of the chemists of

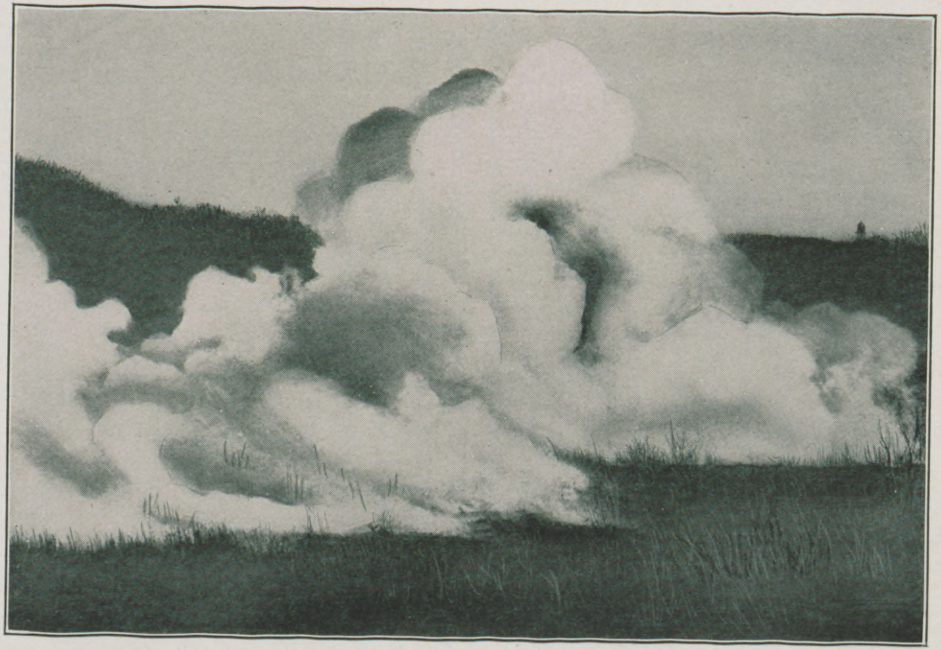
America, which was kept up and revised till the close of the War. This list contained some 17,000 names, classified as to their particular line of work, and proved invaluable in the assigning of men.

Chemical Warfare Service.—The first call for chemists came for work on Gas Defense, which at the beginning was placed in the hands of the Bureau of Mines, for with them was the little knowledge then available in regard to gases and the protection from them. Almost at the same time chemists began active work for the ordnance department, the sanitary corps of the medical department, and in countless other fields of chemical manufacture and investigation stimulated by the war. Naturally there was considerable confusion and duplication of work. With the idea of remedying this President Wilson in an order dated June 28, 1918, directed

> " the gas service of the Army to be organized into a Chemical Warfare Service, National Army, to include: (a) The Chemical Service Section, National Army, (b) All officers and enlisted men of the Ordnance Department and Sanitary Corps of the Medical Department (9)."

Major General William L. Sibert was appointed Director, Chemical Warfare Service, and it is significant that the sentence setting forth his varied and wide reaching duties is one of the longest sentences on record, containing 574 words (15).

How successfully the American Chemical Warfare Service both at home and overseas carried out their part of the world program is now a matter



How Shells Produce Smoke or Gas Clouds—Two 8-inch Smoke Bombs Twelve Seconds After Bursting. Note the Effective Way in which the Vision is Shut off.

of history. In an equally splendid manner chemists connected with the essential industries gave of their energy and their devotion, and to them equal credit is due. The measure of their success is clearly stated in a sentence from an editorial published in January 1919:(16):

> " Through the conservation of trained men, resulting from their sacrifice of personal inclination, this country was enabled to assemble and utilize efficiently the greatest corps of chemists in any of the allied countries, as is abundantly attested by foreign official representatives whose timely warnings, however, were of the greatest aid in effecting this conservation of trained men."

And this is to say that thus was assembled the greatest corps of chemists in the history of the world. Shall we be able to maintain such a position in times of peace?

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CHAPTER III

WATER AND SEWAGE. SANITATION AND MEDICINE

The remains of the old Roman aqueducts, several of which were built before the birth of Christ, show the importance of the public water supply in the minds of the ancients. That this supply must be pure is emphasized by Hippocrates writing four hundred years B.C. and advising the boiling and filtering of a polluted water before drinking (1). The recognition of the necessity of purity in a city supply was slow in crystallizing into a demand in America. This has been offset in some degree by the rapidity with which efficient methods of purification have been adopted by American cities within the last twenty years.

Testing the Purity of a Water Supply.—In the early days of this republic when the land was thinly populated, Nature furnished an abundant supply of pure water. As population multiplied and pollution increased, new difficulties arose, not the least of which was to get the public to adapt themselves to the changed condition. Again and again the writer has been told while taking a sample of water, later tests of which showed frightful contamination, that " we have been using this well for thirty years and know it is pure and alright." Perhaps it was pure thirty years ago, but not in the crowded conditions now often prevalent.

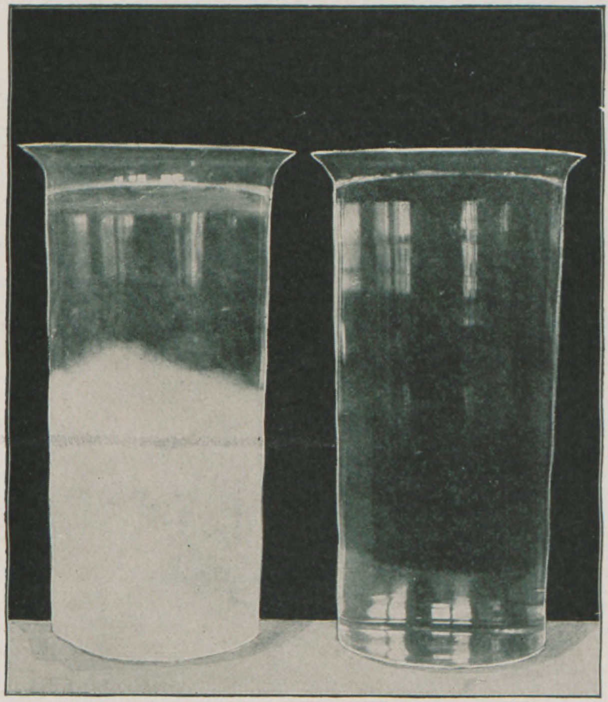
The three diseases usually considered as water borne are typhoid, Asiatic cholera and some forms of dysentery. Typhoid has caused by far the chief trouble in this country, and is transmitted through water by discharges from a typhoid patient, or carrier, contaminating the supply.

The sanitary survey, bacteriological tests and chemical analysis are the three general methods in use for the determination of the safety of a drinking water. In the sanitary survey notice is taken of the source of supply, possible causes of contamination and their admission into the water. By its use the water expert can frequently determine in large degree the suitability of a supply. Wherever practicable, however, this should be accompanied by bacteriological and chemical tests. The bacteriological examination generally includes a count of the total number of bacteria of all kinds that are present and a test for the Bacillus coli communis. As this bacillus occurs in the intestines of man and the warm blooded animals its presence in large quantities is usually considered as indicative of pollution, and a presumptive test for the typhoid bacillus. The presence of coli, however, does not necessarily indicate typhoid, and it is now established that there are strains of non-fecal origin.

In the chemical analysis the amounts of chlorine, of nitrogen as ammonia, as nitrate, as nitrite, of oxygen consumed, and of various other substances are determined to give to the experienced analyst an idea of conditions indicative of sewage contamination and favorable to the growth of disease-producing bacteria. Unfortunately there is no simple test, either bacteriological or chemical, which alone can fully determine the purity of water for drinking purposes. Chemical tests for hardness and for various metals are also made, as those substances may affect the suitability of the supply for general use.

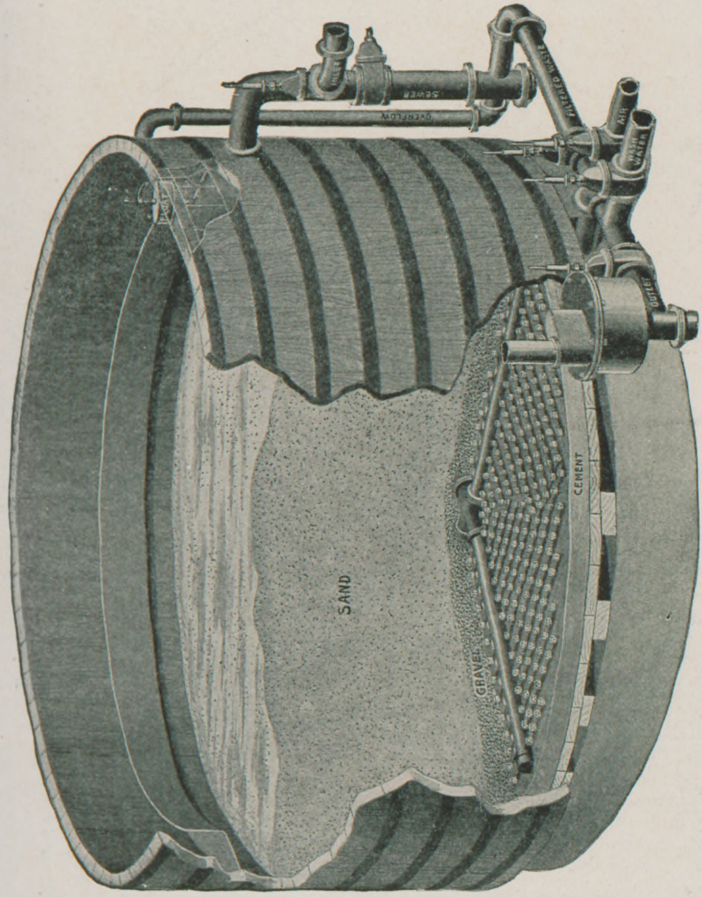
Purification.—To obtain supplies of water as occurring in nature in sufficient amount to meet the requirements of a city is generally difficult and sometimes impossible, if any reasonable standards as to purity are maintained, Hence it is usually customary to secure the purest available source and then safeguard this by purification. This is accomplished by filtration, usually through sand filters, or by the use of a germicide, more frequently by a combination of the two methods. In fact, the time has already come when a city without a method of safeguarding its water supply is an exception and the same standard is rapidly being extended to any town large enough to have a public supply.

Filtration.—Originally the English filter-bed system, or slow sand filtration, was in general use in which the water filters through some five or six feet of fine sand, coarse sand and gravel, arranged in layers. There has now been largely substituted for this the American, or rapid, system of mechanical filtration. In such filters the sand and gravel layer is not nearly so thick and a coagulant, generally aluminum sulfate, is used. This forms with the lime, either already in solution in the water, or added to it, a thin coating of aluminum hydroxide upon the sand, which greatly increases the efficiency of the filter. These filters may be made of wood or of iron, but on the large scale are always of concrete, and the water is forced through them by pressure or drawn through by suction. A sedimentation basin is always provided where usually much more than half of the sediment is deposited before the water passes onto the filter. After

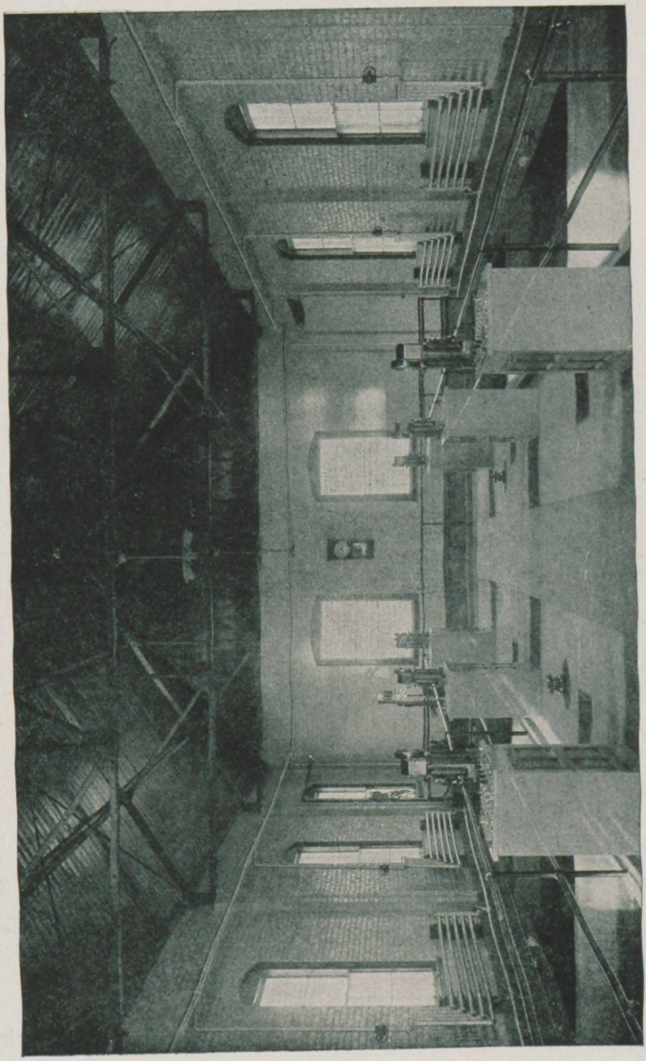


Beginning to Clear Muddy Water

Clarifying Water by Coagulation with Alum



Wooden Gravity Filter—Showing sand, gravel and perforated bottom for washing



Interior Filtration Plant Using American System—Penobscot River Water, Bangor, Maine—Filter beds on each side; operating floor in center.

filtration the water goes to the clear water reservoir and is then ready for delivery to consumers either by gravity or by pumping.

The advantages of the American system, now in very general use in this country, are lower construction cost, greatly lessened requirement of land for the buildings and the ease of washing the filter, which is generally carried out daily by the use of compressed air followed by filtered wash water forced up from below and allowed to run to waste.

Sterilization.—The generally accepted use of chlorine in some form as a germicidal agent to reduce the bacteria in a water supply dates from the successful treatment of the Bubbly Creek supply at the Chicago stock yards by G. A. Johnson in 1908 (2) and in the same year the purification of the Boonton supply of Jersey City, N. J. by Johnson and Leal (3). Here chloride of lime, or " bleach," was used. Very rapidly this method increased in favorable use, till in 1918 more than 1000 cities and towns in North America were using this process, chlorinating more than 3,000 million gallons daily. In recent years liquid chlorine in steel cylinders has, on account of the easy control in adding it to the water, largely replaced " bleach " (4).

In this work of sterilization America has easily been the leader, and the method is being adopted all over the world. Chlorine in some form, generally as chloride of lime was used by all the great nations in safeguarding the water supplies at the front, and in most of the cantonments and camps in America.

Other forms of chlorine, especially chloramine, have been used to a limited extent, but their general use has not as yet been clearly established. The same may be said in regard to ozone and ultraviolet light, which, while efficient as germicides under certain conditions, have on account of expense and other causes been unable to replace the more widely used chlorine.

Consumption of Water.—The daily per capita consumption of water as given by Mason (1) is:

American cities, Unmetered,	average	161	gallons
American cities, Metered,	“	73	“
English cities	“	33	“
German cities	“	28	“

Did this mean a proportionate cleanliness for Americans it would be a credit, but this cannot be claimed. It rather shows a wastefulness which is not to our credit, which is further emphasized when the metered and unmetered consumption is compared.

Sewage Disposal.—Sewage may be defined as the used water supply of a community contaminated by household wastes, and frequently containing street washings or industrial wastes (5). In the earlier days the disposal of sewage demanded little attention and received less. As the amount of sewage increased and the germ theory of the transmission of certain diseases became established, some care as to the disposal of sewage became imperative. This was especially true in the case of cities discharging their sewage into rivers from which other cities drew their water supply, or its discharge into the ocean with the possible contamination of shell fish.

For much of the early work we are indebted to the Massachusetts State Board of Health, which, shortly after its organization in 1886, established the experiment station at Lawrence, and has since that time made tests of great value in a practical and educational way. Largely as a result of such work the average annual death rate of 46 per 100,000 from typhoid in Massachusetts during the years 1886–1890 became in the five year period twenty years later only 14 (6). Similar investigations were begun and are still being carried on in a number of other communities with results of great value.

Results Sought.—The disposal of a city's sewage is a separate problem in each case, the several factors being

(1) the nature and amount of the sewage, which is largely affected by trade wastes,
(2) the degree of purity necessary, which is to some degree determined by conditions below the point of discharge,
(3) the volume of the stream, or other body of water, into which discharge is made.

In general it is sought to have an effluent which, when mixed with the volume of water into which it is discharged, will be free from objectional odor, will not deposit sludge banks, and will not be too highly contaminated with organic sewage matter and disease germs. The changing of sewage into a sterile effluent is generally unnecessary as well as impractical.

Treatment of Sewage.—The general methods employed in sewage treatment, all of which may or may not be used in any given case are

(a) screening, in which the sewage is passed between metal bars or screens to remove the larger floating materials which might clog pumps or be objectionable later,

(b) septic tank treatment, in which by the action of anaerobic (living without air) bacteria, much of the sewage is changed into an unobjectionable sludge,

(c) Filtration, frequently in trickling filters, made out of stones about the size of an egg, upon which the sewage is sprayed or allowed to run in fine streams at intervals, the object being to obtain an abundance of air so that organic matter may be destroyed by the action of aerobic (living in air) bacteria.

(d) sedimentation to increase the clearness of the effluent,

(e) sterilization by some form of chlorine or other germicide to decrease the number of bacteria in the effluent.

The mixing of sewage which has already been subjected to bacterial action, so-called " activated sludge " with fresh sewage, especially with further aeration, has given very satisfactory results in sewage purification (7).

Home Sewage Disposal.—Excellent methods for the disposal of sewage about the home, where there is no public sewerage system, have been devised and are carried out with comparatively small expense and reasonable efficiency. These depend upon the same general principles as those used in city disposal. Where there is no water supply available, the waste material from barns and other outhouses should be carefully screened and either buried or better sterilized by suitable antiseptics. This is fully described in excellent agricultural bulletins (8).

Medicine and Sanitation

War brings blessings, because it brings us face to face with problems which must be met and mastered. The frightful and inexcusable destruction of life is in some degree offset by the increased efficiency of medical and sanitary knowledge.

Epidemics.—Formerly epidemics were thought to be a necessary accompaniment of war. Our own sad experience in our war with Spain in which many more died from disease than from wounds made a deep impression upon the American mind. The brilliant and gratifying work of the army medical men in learning successfully to combat and to master yellow fever, which for generations had held the southern part of our nation in a state of constant fear, is one result of the war with Spain. It marks in a way the beginning of a period of efficiency on the part of the Medical Corps of the U. S. Army which may well be a source of pride and inspiration to every American. The further effects of this work were soon seen in the unparalleled sanitary record made at Panama during the construction of the canal. More recently in the trouble with Mexico, both at Vera Cruz and on the border, this record was maintained.

With such ideals and such a record the relatively few medical men in the service early in 1917 were ready to co-operate enthusiastically with thousands of their fellows who volunteered from civil life in the carrying out of careful and well made plans.

In the Franco-German War in 1871 there were 73,000 cases of typhoid in the German army. In the Boer War the British had over 50,000 cases. In the short Spanish-American War the United States had 20,000 cases. So efficient had become the work of the army doctors by sanitation and by using inoculation first practiced by the British in 1898, that there were almost no cases in the American army during the World War. In fact, it was the proud boast of the Army Medical Camp for instruction at Camp Greenleaf, Georgia, that no lectures on the treatment of typhoid were given, because " We do not treat typhoid; we prevent it " (9).

Prevention.—In recent work the emphasis in the treatment of disease has been upon prevention, or in other words to use an Irish expression, to stop it before it was started. Wholesome food, fresh air, sunlight and cleanliness of body and of surroundings have been the simple and yet effective measures chiefly employed.

As a by-product of this cleanliness of surroundings the collection and sale of garbage, manure, tin cans, paper, bottles, etc. at the cantonments of the National Army yielded decidedly satisfactory financial returns. Are there not many towns and cities in America where a similar plan might be used to advantage (10)? The annual value of by-products from existing garbage reduction plants in the United States has been estimated at more than $10,000,000 (11).

In the preparation of antiseptics and disinfectants it has been the privilege of the chemist (12) and bacteriologist to work with the physician, as seen, for example, in the treatment of water supplies and of sewage. The recent use by Dr. Alexis Carrel, a Frenchman by birth and an American by adoption, of a solution of sodium hypochlorite of definite strength for the flushing of wounds, thereby returning the patient to the active duties of life in days instead of weeks, is typical both of the remarkable work of the surgeon (13) and the efficient help of the chemist.

Other Work of the Chemist.—The chemist has aided the physician, also, in the standardization of his remedies and the furnishing of medicines of known and unvarying strength. Chemical tests have become absolutely necessary for correct diagnosis. In the preparation of anesthetics, his work has been the means of saving untold hours of agony.

By the continued co-operation of the physician, bacteriologist and chemist, together with an enlightened public, we may hope for a world in a still larger measure released from sickness and suffering.

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CHAPTER IV

FOOD. FERTILIZERS

Very few of America's millions have ever known the pangs of extreme hunger. Prior to 1914 this generation was said to be the best fed in the world's history, and the Americans fared far better than the people of nearly any other country. Hence we were not in a position to realize the great value of food. The possibility of want due to war and the absolute necessity of conserving food have been brought home to us in the last few years, as never before.

Foundations for Conservation.—Prior to our entrance into the War much work had been done as to the nature of various foods, the amount needed, and the functions the different foods performed; and the experience of Herbert Hoover in the Belgian relief work had shown that he was able to control the supplies of food on hand that they might do the most good.

The Scientific Basis.—A very large amount of interesting and valuable work on foods had been done by Lusk (1), Chittenden (2), Sherman (3), McCollum (4) and others in America on foods as related to the body processes. In its simplest terms it had been shown that food was needed for a threefold purpose:

(1) To supply the body with heat and energy.

(2) To rebuild waste tissue.

(3) To regulate body processes.

Comparing the body with a steam engine, and the comparison is not a bad or unusual one, the food has to take the place of the coal used to furnish heat and energy, but it is also necessary for food to go further and furnish the materials necessary to repair the human engine, and in the case of the young to provide for constant growth. In addition to this certain substances, not all of which are clearly understood, are necessary to control and regulate body processes. That the body under usual conditions finds these in ordinary food is a clear evidence of the wise provision of Nature for man's needs.

Classification.—In the main the organic matter of food consists of carbohydrates, fats and proteins; these with the mineral matter and water are the usual basis of classifying the daily ration. Sugar, cellulose and the starch found in wheat, corn and other grains are carbohydrates; butter, oils and other animal and vegetable fats make up the second class; while the proteins are the substances containing nitrogen and are found in meats and other animal foods, especially milk, as well as in the legumes, such as peas and beans. Vegetables and fruits are rich in needed mineral salts. These classes are by no means mutually exclusive, in that one food may be rich in several, thus good milk though very high in water, contains considerable fat, protein, carbohydrates and mineral matter as well as certain regulative substances, such as the hormones and vitamines.

Needs.—Food experts are generally agreed that the average man requires each day food equal in heat value to approximately 3000 Calories, which expressed as mechanical energy would be sufficient to lift one ton nearly a mile high (5). This amount will be more or less depending upon the degree of activity and kind of work done by any individual. Further, this number of Calories must be furnished by a properly balanced ration, the most important item of which is that of protein, due care being taken to keep in excess those elements which are basic rather than those which are acid (6). The American soldier was furnished with a ration of 4600–5000 Calories, though on an average he could consume only about 3900 (7). To prevent waste and to insure sufficient satisfactory food the United States had food inspection parties made up of food experts who constantly checked up this matter, visiting camp after camp.

In the light of all this knowledge it was easily possible to suggest the foods which could be most advantageously shipped and those which could be best substituted. How clearly has been impressed upon the minds of every one the urgent request of the Food Administrator to

SAVE Meats!
Wheat!
Fats!
Sugar!

The Practical Administration.—The splendid response of the people as a whole to the request of the Food Administrator made possible a hitherto undreamed of record in the shipping of food supplies. This in no small measure turned the tide of victory. But this would not have been possible without a man of vision and of practical experience to apply with wisdom and efficiency the scientific facts which we have been discussing. This splendid combination was found in Administrator Hoover. His ready grasp of the bigness of the situation and the tactful manner in which his decisions were made effective supplied the needs of ourselves and of the allied world. His statement that

> " Real conservation lies in the equitable distribution of the least necessary amount, and in this country we can only hope to obtain it as a voluntary service, voluntary self-denial, and voluntary reduction of waste, by each and every man, woman and child according to his own abilities."

and his challenge that

> " There is a possibility of demonstrating that democracy can organize itself without the necessity of autocratic direction and control."

met a ready and practically unanimous response (8).

With these principles in view the campaign was carried out along three general lines: reduction of consumption, stimulation of production, control of prices. The results were highly satisfactory in securing the needed foodstuffs in the required amounts without general trouble or inconvenience, and the educational campaign carried out will continue to bear fruit for years to come. Even in 1917 its effect was evident when returns from sixty

American cities showed an average decrease of fifteen per cent in garbage collected, and a reduction of fifteen per cent of grease per ton of this garbage.

Permanent Gain.—We have learned as a nation:

First, The real value of food; the folly, if not the sin, of wastefulness; and the economic balancing of the family ration. A summary of the latter is given in the advice of Sherman (9) to spend for the family food an equal amount for milk (10), for meat, and for fruit and vegetables.

Second, The possibility and in some cases the advantage of substitutes. The widely increased use of corn meal in several forms wlll continue to give variety to our food. The various forms of war bread have shown the possibilities of flours other than that from wheat. The use of cotton seed oil under a number of trade names, both as an oil and as a solid fat, is due to American industry in obtaining a valuable food product from the seed, a by-product all but useless before (11). This use was necessarily increased by the War, though the process fortunately had previously been in successful operation. More recently by treating cotton seed oil with hydrogen in the presence of a catalyzer, the melting point is raised due to an increase in the molecular weight of certain constituents, and so a larger amount of solid fat can be obtained.

Third, New methods of preserving foods, and the wider use of the methods already known. Perhaps the most interesting of these is the dehydration process of preservation, in which it is claimed that with many foods there can be a saving of 90 per cent. by weight and 80 per cent. by volume. It is stated that eggs bought at six cents per dozen in China can be canned rapidly, 51 yolks making one pound, and that they will make a far safer omelet than can be obtained from cold storage eggs! Time will settle the full justice of this claim, and of the additional claim that this War may cause the general use of dehydration for preserving foods as our Civil War brought in the use of canned foods (12).

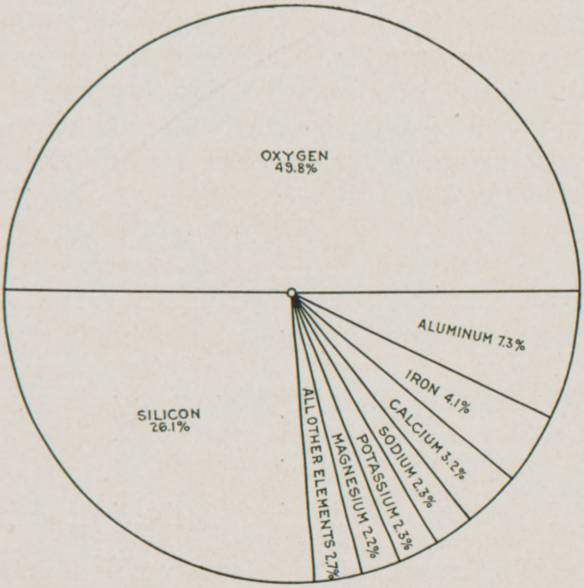
Certainly the American people caught the spirit of these lines in which there is probably fully as much truth as poetry:

> " Can the Kaiser,
> Brine the Brute,
> Pickle the Prussian,
> Tin the Teut!"

Fertilizers

According to the figures of Dr. F. W. Clarke, Chemist of the United States Geological Survey, more than 97 per cent. of the earth's surface, or crust, including the ocean and the atmosphere, is made up of eight elements; the remaining elements, though about 80 in number, containing less than 3 per cent. This is nicely shown in the diagram from Kiett (13) at top of next page.

Though the elements do not occur in like amounts and are not equally distributed, yet in spite of this there is so vast a store of most elements contained in the soil, in water, or in the air, that their removal



Percentage of Elements in Earth's Surface, including the Ocean and the Atmosphere after Keitt.

by crops need cause us but slight concern. Of three elements, however, vitally important in the life process of plants, the soil does not furnish a complete supply, nor may they be obtained except by the addition of substances rich in them. These are nitrogen, phosphorus and potassium. The percentage of nitrogen and phosphorus present in the soil is very small, phosphorus being about 1/10 of 1 per cent. on the average and nitrogen not so high in most cases, but exceeding this figure in soils of unusual richness.

Large amounts of these elements are found in growing crops and are removed with them. With the exception of nitrogen these three elements are entirely taken from the soil, which has been formed almost wholly by the weathering and decomposition of rocks. The amounts removed from only one acre are shown in the following slightly modified table of Van Slyke (14):

Crop	Yield	Nitrogen	Phosphorus Pentoxide	Potassium Oxide
Corn	50 bu.	78.4 lbs.	27.6 lbs.	55.2 lbs.
Wheat	25	42.5	16.6	21.0
Oats	75	72.0	27.0	61.2
Cabbage	10 tons	60.	20.	80.
Beans	25 bu.	88.	24.	57.5
Turnips	10 tons	50.	20.	90.
Apples (30 trees per acre)	300 bu.	16.5	4.7	18.8
Peaches (100 trees per acre)	400 bu.	78.5	21.	90.

The immense value of our farm crops, which have contributed so largely to the wealth and happiness of the United States, depends directly upon a sufficient supply of these elements for the growing crops. Indeed, the American farmer has in many cases been accused of being only a miner, who draws his wealth from the soil leaving it poorer and of less value after each successive crop. The boasted greatness of our crops, it is claimed, has been due, not to any credit of our own, but to the fertility of the soil upon which we find ourselves. There is some truth in this statement, and a continuous yield of rich harvests without a corresponding robbing of the soil cannot be had except by building up the soil either by proper crop rotation or by the addition of fertilizers containing these elements.

The Agricultural Triad.—One can almost fancy Nature to have been in a facetious mood when the three elements so essential for the growth of plants were chosen. This agricultural triad is made up of

Nitrogen, a gas so inert under ordinary conditions that one of its uses in the air is to dilute the more active oxygen,

Phosphorus, an element which takes fire spontaneously when exposed to the air, and so poisonous that its use in one form in matches is prohibited,

Potassium, which when dropped on water causes the evolution of a gas which bursts into flame.

But it is not in the form of elements that these three are important for plant growth but in their compounds, so that in speaking of soils we usually think of nitrogen as in ammonia or in nitrates, of phosphorus as in the pentoxide or in phosphates, and of potassium as in the oxide, potassa, or in the carbonate, potash. Calcium in the form of lime is frequently added to soils with advantage, but it is not distinguished by membership in the triad because in most cases soils contain sufficient calcium for plant growth. The value of lime added to soils lies in its correction of acidity, if acid be present, and under proper conditions in the increase in the supply of available nitrogen or potassium.

Nitrogen.—There are four sources of nitrogen for fertilizers: (1) animal matter, (2) gas works, (3) earth deposits, (4) atmosphere. The use of manure which contains considerable amounts of all three members of the agricultural triad has been practiced for centuries, but in no age has its importance been more clearly emphasized and its value more fully understood than at the present. Other refuse animal matter, such as dried blood, fish scraps, products of garbage reduction and sewage disposal plants, are used. Ammonium salts obtained as a by-product in heating coal to manufacture gas and coke make an excellent but expensive fertilizer.

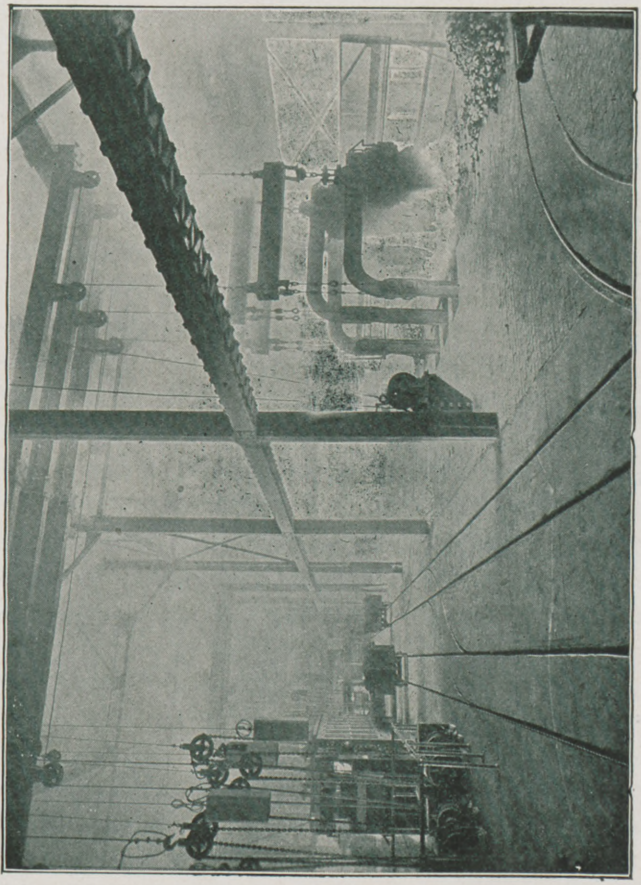
Quite generally in soils of very dry regions there are found deposits of sodium nitrate, but usually not in sufficient quantity to make their extraction and purification profitable. However, on the western coast of South America, chiefly in Chile, are deposits of great extent (13). Formerly it was thought this supply would be exhausted during the first half of this century, but the discovery of more extensive beds has greatly increased the amount known to be available. These beds are now known to extend along the coast for more than 200 miles and in some places are two miles in breadth. They are supposed to have been formed in recent geological time, being due to the nitrification of marine vegetation.

The atmosphere seems to have been the source of practically all of our nitrogen. Only about two ten thousandths of 1 per cent. of the nitrogen in the world is serving actively either in animal or vegetable life (15). That now present in the soil has probably been placed there through the slow accumulation of ages due to the action of thunder storms causing the combination of the oxygen and the nitrogen of the air and through the agency of certain plants. It is estimated that over each acre of ground there are some 39,000 tons of atmospheric nitrogen, or in other words, 80 per cent. of the fifteen pounds pressure upon every square inch of surface is due to the valuable nitrogen. Only in comparatively recent years has the fixation of atmospheric nitrogen received the great amount of attention its fundamental importance merits.

Of so great moment is the fixation of atmospheric nitrogen both for its use in explosives as well as in fertilizers for food production that it is stated that Germany waited until the problem of fixation of atmospheric nitrogen had been solved before beginning the World War (see p. 12). A single plant in Germany in 1918 took approximately 100,000 tons of nitrogen from the air, an amount equivalent to one-fifth of the Chilean output furnished the rest of the world, and several times greater than the capacity of any American plant (16).

Fixation by the growth of leguminous plants such as peas and beans by the aid of bacterial action has been known for a number of years and is increasingly emphasized and applied in crop rotation. Chemical fixation is more recent and had of necessity to await the perfection of the electric arc and the electric furnace and the successful liquefaction of air.

By the use of a powerful electric arc, the action of nature during a thunderstorm is imitated, and the nitrogen and oxygen of the air by the influence of the electric discharges are made to combine to



Carbide Furnace Room in Cyanamid Plant

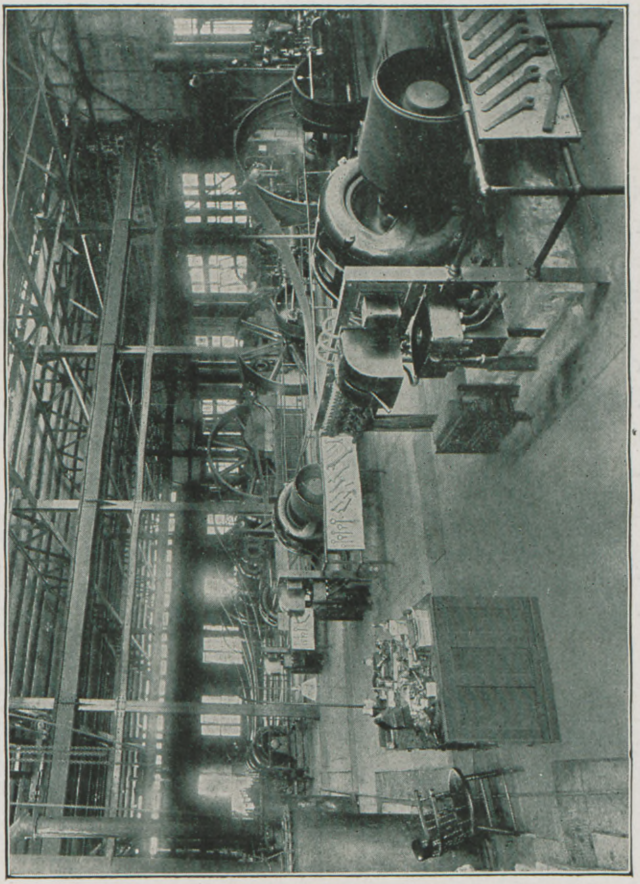
form nitrogen peroxide. This thru treatment with water forms nitric and nitrous acids, which by further treatment are changed to calcium salts or lime nitre.

Lime and coke heated in an electric furnace form calcium carbide. Nitrogen obtained from the air by removal of moisture, carbon dioxide and oxygen is passed over calcium carbide at a temperature of 1200° C. and calcium cyanamide is formed, which has proven successful as a fertilizer, being so produced commercially by an American company.

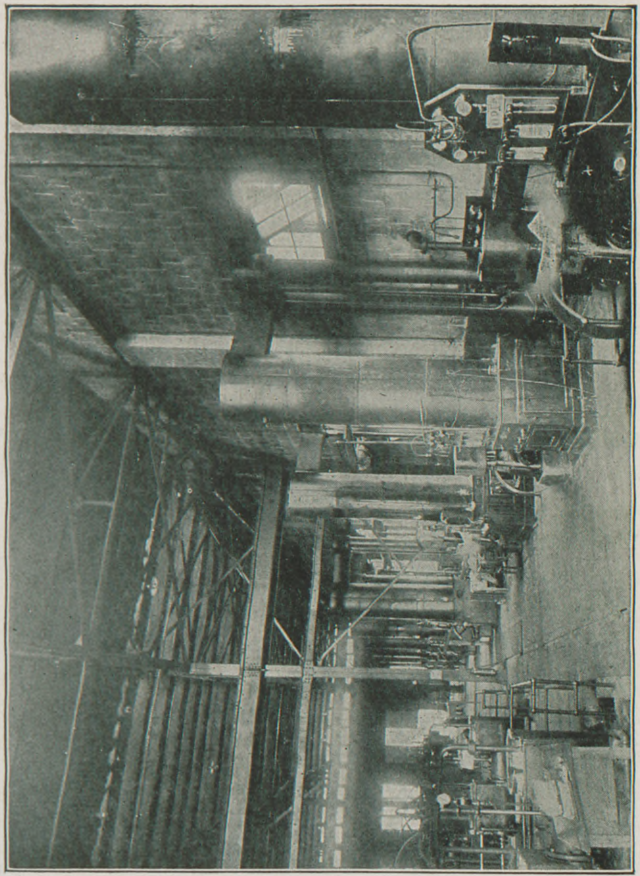
Nearly four-fifths of the air is nitrogen. When air is liquefied by cold and pressure and part of it allowed to boil away, the nitrogen having the lower boiling point tends to boil away first. If this purified nitrogen is heated with hydrogen under high pressure (200 atmospheres) in the presence of a suitable catalytic agent ammonia is formed. This ammonia may be held by any desired acid furnishing a valuable fertilizer. Further it has become possible to change this ammonia to nitric acid on an industrial scale (17).

Phosphorus.—" Of all minerals necessary for plant growth the compounds containing phosphorus are most liable to be deficient " (13). For our supply for fertilizers beside the small amount contained in animal manure and some vegetable products such as cotton seed meal, we must depend upon the phosphorus in bones and in rocks.

Guano is a combination of manure and bone phosphate found in certain dry regions. Here,



Interior Liquid Air (Nitrogen) Plant, Showing Compressors



Interior Liquid Air (Nitrogen) Plant, Showing Columns where Nitrogen is Separated from Oxygen because of the abundance of fish or for other reasons birds have gathered. Thru long ages deposits have been formed by the droppings and the bodies of the birds. From Chincha, one small island off the coast of Peru, more than a billion dollars worth of guano has been taken.

The bones are composed chiefly of normal calcium phosphate, showing on analysis 20–25 per cent. phosphorus pentoxide and 3–4 per cent. nitrogen as organic matter. As this is insoluble in water only a part of this phosphorus is at first available for plant use, but more of it gradually becomes so. Hence it makes an especially satisfactory fertilizer for certain purposes as in the growth of fruit trees.

The phosphate in rocks is also in the form of the insoluble normal calcium phosphate, and so is but very slowly available as plant food. This rock phosphate has been produced in enormous quantities in certain southern states, and large deposits, not yet worked, are said to exist also in Wyoming and neighboring states. To render the phosphate available the rock is crushed and treated with sulfuric acid which forms the more soluble acid phosphates, the primary salt being readily soluble in water and the secondary in weak organic acids. If this acid or super-phosphate is brought into contact with a basic substance such as limestone it is changed back to the insoluble form and this process is called reversion. Obviously then superphosphates should not be mixed with lime cyanamide or any basic substance.

So-called basic slag is an illustration of making a material harmful in one substance of real value for another purpose. Phosphorus in steel is a serious detriment and must be removed from the pig iron in steel making. This is done by lining the converter in which the pig iron is changed into steel with a basic substance containing lime or magnesia. Then this basic lining after it has removed the phosphorus is crushed and makes a good fertilizer, especially valuable on lands containing much organic matter or deficient in lime.

For years prior to the Great War the United States exported large amounts of phosphate rock and imported compounds of potassium and nitrogen, the total exports of fertilizers in 1914 being $12,000,000 with imports of $28,000,000. During the fifteen months before the armistice 3,600,000 tons of nitrates passed thru the Panama Canal.

Potassium.—Before 1914 the supply of potassium found in the Stassfurt deposits in Germany were the chief source of the world's supply. The United States alone imported approximately a million tons yearly of potassium products equivalent to about 240,000 tons of potassium oxide (18). Her confidence in this supposed monopoly was a part of the German scheme of world conquest. It will be remembered that though nitrogen and phosphorus occur in the earth in very small percentages, potassium is one of the eight most common elements. Why then is it difficult to obtain an abundant supply of the compounds of this element? The answer is that the element is so tightly locked up in the insoluble rocks in which it is found that it has been exceedingly difficult to free it and obtain soluble compounds except at prohibitive cost. A most fascinating story on the " Quest for Potash " could be written with no drawing on the imagination. How the United States met and in large degree mastered the situation confronting this nation from 1914 to 1918 is worth the telling (19).

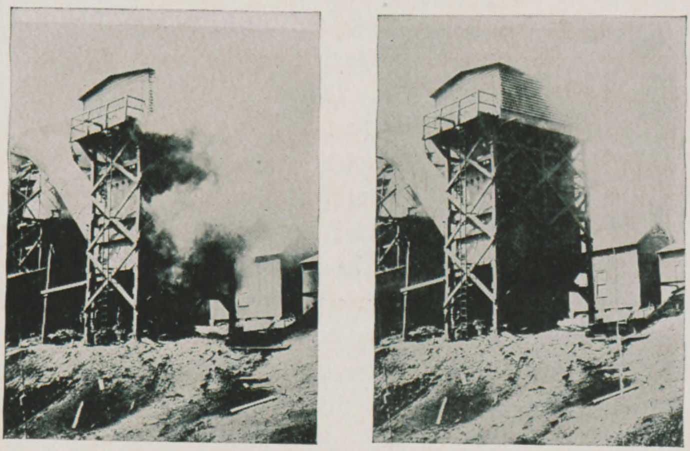
America and War Potash.—In 1915 in the beginning of the American potash industry the production was a little more than 1000 tons of potassium oxide. This increased to 9,720 tons in 1916, and to 32,000 tons in 1917, with a production in 1918 of 52,000 tons, and a capacity by 1920 of nearly 100,000 tons. This is still only one-fourth of the amount normally used, but in the sources developed and the methods used in securing this there is promise of an abundant and permanent supply eventually. The sources of this supply have been most varied and may be grouped as follows:

1. Lake brines
2. Ocean kelp
3. Dust from cement kilns and from blast furnaces
4. Wood ashes and various vegetable wastes
5. Wool scourings
6. Minerals rich in potash

More than half of the wartime potash came from natural brines mainly from Searles Lake in California and the lakes of Western Nebraska. Searles Lake is thought to contain ten to twenty millions of tons of potassium oxide. The amount in the Nebraska lakes has not been definitely estimated.

The idea of obtaining potassium from a sea farm is at least unique, and seems also to be practical since it has been in use for several years and in 1917 produced more than 10 per cent. of the total supply. The giant kelps of the Pacific Coast, growing from the Gulf of California to Alaska, furnish a vast field for this industry. These kelps are cut and dried, furnishing in some cases as much as 30 per cent. of potassium chloride in terms of their dry weight (20). There are, of course, difficulties in this work, and the use of this source will depend upon the cheapness with which other sources are able to supply the demand for potash. Both of these sources of supply are unfortunately located geographically because of freight costs, as more than 90 per cent. of the pre-war potash was used east of the Mississippi River.

To take the dust from any industry is a decided advantage, and when this dust can be made of economic value it is a still greater benefit. This is what the Cottrell method of dust removal has done for the cement industry. By passing a current of 50,000 to 100,000 volts thru flues the particles of dust charged with electricity fly to the sides of the flue oppositely charged, just as a comb will attract or repel small particles of paper. This problem was worked out by F. G. Cottrell now of the National Research Council, to whom the 1919 award of the Perkin medal was made for his services (21). By investigation of the Bureau of Soils it has been estimated that the cement industry could thus be made to furnish 100,000 tons of potassium oxide annually. The fact that 70 per cent. of the cement manufactured is produced east of the Mississippi River gives this method a geographic advantage and increases its promise of usefulness. At present not more than one-fifth of the estimated possible production of potash comes from this source. The possible production by applying this method to blast furnaces manufacturing pig iron has been placed at 300,000 tons of potassium oxide per year, more than our total pre-war demand, but not enough has actually been produced in this way to speak with definiteness.



Elimination of Dust or Smoke by Cottrell Process
Current off Current on

The term potash shows at once that ashes are rich in the sought-for potassium. There is doubt, however, as to this method competing on a large scale with others, though about 500 tons per year have been so produced. Dried banana stalks contain 10 per cent. of potash, while tobacco stems, beet sugar wastes, sugar refinery and distillery wastes, all contain appreciable amounts.

That crude wool contains about 4 per cent. of potash makes wool scourings a possible source of supply which may under favorable conditions be worth while.

Minerals rich in potash include alunite, a hydrated sulfate of aluminum and potassium, and a number of silicate minerals. By roasting the crushed alunite and leaching with hot water in a closed tank under pressure, more than 90 per cent. of the potassium was obtained as a sulfate of high purity. Some 2400 tons of potassium oxide were obtained thus in Utah in 1917. Among the silicate potash-rich rocks may be mentioned the green sands of New Jersey (22), the Cartersville slates of Georgia and the leucite rocks of Wyoming. Any one of these sources would furnish an ample supply for centuries, if only a cheap commercial process could be found to release the potassium from its tightly locked compounds.

Future of American Potash.—" Germany controls the market of the world for the metal, potassium, and its compounds." This statement from an American text (23), the second edition of which is dated January 2, 1915, was then entirely correct.

At present there are the beginnings of an American potash industry, which gives promise of being abundantly able to care for all of our needs. Whether it will succeed or fail depends in large measure upon whether or not it must meet the German competition under pre-war conditions.

Nature has furnished the United States with abundant supplies of phosphate rock, the fixation of atmospheric nitrogen offers several compounds of that element in sufficient quantity; potassium alone is needed and of the ultimate solution of this problem by American chemical ingenuity and perseverance there seems no room for doubt. Only thus can our independence in regard to the constantly needed agricultural triad be established.

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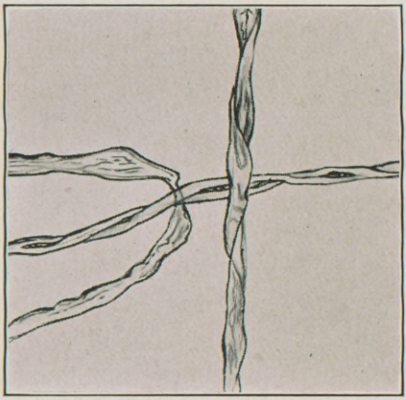
CHAPTER V

TEXTILES

The importance of textiles in our modern life is seen upon brief reflection. Almost all of our clothing and bedding, as well as most table and floor coverings are textile products. Not only luxuries but the necessities of life come under this head.

Classification.—Fibers may be divided according to their source into vegetable, animal and mineral. The last consisting of asbestos, mineral wool, glass wool, etc. are not so widely used and will not be further considered. Of the vegetable fibers cotton is by far the most important, with linen next in use; while silk and wool are the most commonly used animal fibers (1, 2, 3, 4, 5).

Cotton.—The cotton belt of the United States has for many years produced the largest part of the world's supply of cotton, the average crop of some 14,000,000 bales of 500 pounds each being about sixty per cent. of the total production. The possibility of using cotton in large quantities is due to the inventive genius of an American, Eli Whitney, whose well known discovery of the cotton gin was patented in 1794. The fiber in cotton is a seed hair composed mainly of cellulose; the length of this fiber or staple varies from less than one inch in the upland cotton to nearly two inches in the sea island variety. "Each fiber consists of a single long cell, whose cell walls become thinner as it grows, finally collapsing to form a flat tube."



Cotton Fiber

This cellulose, named from the plant cells of which it is made, is quickly destroyed by concentrated sulfuric or hydrochloric acids, while nitric acid forms nitrates used in the preparation of a variety of products, such as celluloid, and collodion, and in the manufacture of certain explosives. Long action of strong mineral acids tends to the formation of dextrin and glucose. Cold concentrated solutions of sodium or potassium hydroxide change in a marked degree the character of the fiber and give it a translucent appearance. This behavior first noticed by John Mercer, an Englishman, in 1844 was used by him in making "mercerized cotton" an artificial substitute for silk.

Linen.—The cotton fiber consists of a single cell, but in linen the fibers are formed by the grouping together of the cells in bundles. The preparation of linen from the flax is a fairly complex process, in which the plant is "retted" by treatment with water or exposure to dew to separate the fiber from the pith and woody matter, crushed, and combed to make the fibers parallel and suitable for spinning.

Linen Fiber

Linen does not contain so high a percentage of cellulose as cotton, is stronger, and has more natural luster. Since linen is a better conductor of heat than cotton it feels cold to the touch, a characteristic used to distinguish between cotton and linen goods. The action of acids and of alkalies upon linen is similar to that upon cotton.

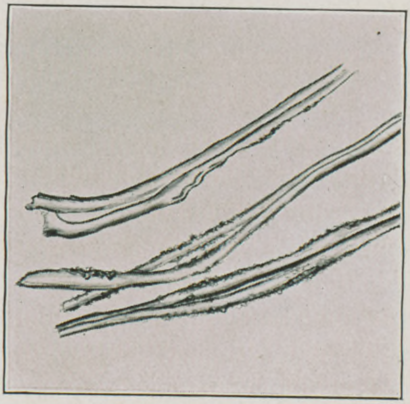
Bleaching.—Before goods are bleached they are washed or scoured to remove interfering substances which have come into the material either in the natural process of growth or during manufacture. This is followed by the bleaching proper.

Cotton is usually bleached in the yarn or woven piece, and the agent used is almost always a dilute solution of bleaching powder ($CaOCl_2$) or "chloride of lime," this solution being called "chemick." The details of the process vary with the subsequent use of the goods. Hydrogen peroxide in a basic solution containing soap, or potassium permanganate in slightly acid solution, bleach satisfactorily, but as yet these processes are too costly. The excess of permanganate is removed by sulfurous acid solution or that of one of its salts.

The bleaching of linen is similar to that of cotton, but because it contains more than 25 per cent. of coloring matter and other impurities, the process is more difficult and requires much more time. It is customary to " grass " linen for a week, thereby exposing it to the action of the sun and dew. Frequent dampening assists the process. It is supposed that the ozone in the air is the active bleaching agent in this part of the process. As linen is easily attacked by acids, alkalies or chlorine the bleaching solutions must be dilute and the process repeated several times. Linen is said to be quarter, half, or three-quarters bleached depending upon the amount of coloring matter removed. The whiter the fabric, the less the strength of the fiber.

Bleaching powder as well as permanganate and peroxide are used in the various methods of linen bleaching. The use of the two latter, though more expensive, reduces the time required.

Silk.—Cellulose, which is the chief constituent of cotton and linen, is made up of carbon, hydrogen and oxygen, the formula assigned it being $(C_6H_{10}O_5)_x$. Silk, though containing no cellulose, does have carbon, hydrogen and oxygen, and in addition has nitrogen to almost 20 per cent. The production of silk by the silk worm, the cocoon containing a fine continuous filament sometimes nearly three-quarters of a mile in length, is well known. After these cocoons are heated to kill the worm, the silk is reeled off, and the hanks must then be heated in a strong soap solution, which removes a considerable amount of the silk-glue.

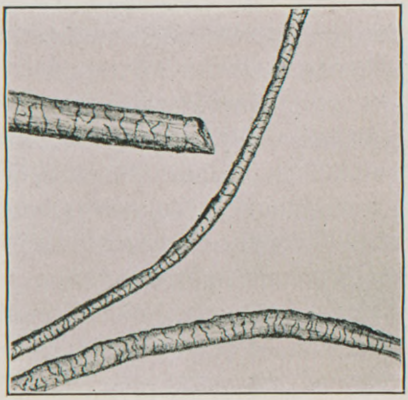


Silk Fiber

The power of silk to absorb metallic salts, especially tin, from solutions, fixing the metallic oxide in the fiber is the basis of silk weighting, by which the weight of silk is frequently increased 100 per cent. Silk is attacked by alkalies and by concentrated acids. Dilute acids are absorbed by the fiber and when dried in it, tend to increase the luster and to cause the silk to give a crackling, rustling sound, when rubbed or compressed.

Silk may be bleached by sulfur dioxide, or by hydrogen peroxide, or by potassium permanganate followed by sulfurous acid. Chlorine rapidly destroys silk fiber, except in very dilute solutions, and hence is not a suitable bleaching agent for silk.

Wool.—In addition to the four elements, carbon, hydrogen, oxygen and nitrogen, which make up the silk fiber, wool contains a fifth element sulfur, which is characteristic of it. Under the microscope the wool fibers are seen to be covered with a layer of broad scales arranged somewhat like "the shingles on a roof." When these fibers are placed



Wool Fiber

side by side and moved over each other in the process of "milling," felt is formed. The insulating effect produced by these scales holding small amounts of air is said to be the cause of the great warmth of wool.

Wool in the raw state frequently contains impurities which make up more than half of its weight. These are wool grease, a fatty substance serving as a protective covering to the fibers, suint, or dried perspiration, and outside materials, as burrs, straws, clay, etc. The suint is chiefly a potassium salt of certain fatty acids from which the potassium has recently been recovered commercially (see p. 63).

Test for Wool.—Dilute mineral acids have slight effect on wool. This fact is frequently made use of in distinguishing between woolen and cotton, or part-cotton, goods. This is done by treating the goods with dilute sulfuric or hydrochloric acids, and drying at 110° C.; when the cloth is handled the cotton crumbles and falls away from the unchanged wool. A similar process, called "carbonizing," is used in removing impurities from wool.

Wool Bleaching.—Since chlorine combines with the fiber of wool without removing the color, bleaching powder cannot be used with wool. Wool is generally bleached after a treatment to remove the tendency to twist and curl by "stoving." The hanks of wool are suspended on wooden pegs in a brick chamber in which sulfur is burned. Sometimes the same results are accomplished by soaking in a solution of sulfurous acid. These processes are not entirely satisfactory and the bleaching is only temporary, especially when the material is washed with soap or alkalies. A permanent bleach may be obtained by the use of hydrogen peroxide, but this is expensive.

Wool Substitutes.—The recent shortage of wool has made necessary the working over of old woolen goods and the intermixture of cotton with short fibered wool. There can be no objection to this, if the product is sold by its real name, and if the old material is thoroughly sterilized.

Artificial Fibers.—Much ingenuity has been shown in preparing substitutes for silk from the cellulose of cotton. These have something of the luster and appearance of silk. In the Chardonnet Process the cellulose is nitrated, though the process is not carried so far as in making gun cotton. The nitrated cellulose is dissolved in alcohol-ether, and the collodion thus formed is forced under heavy pressure thru capillary tubes. The alcohol and the ether after evaporation by an air current are recovered and used again, while the nitro-cellulose fibers, after denitration by immersing in a solution of ammonium sulfide, are washed, dried, combed and spun into yarn. Three other processes in use are the cuprammonium, where the cellulose is dissolved in an ammoniacal copper solution; the viscose; and the cellulose acetate.

Artificial Leather.—The manufacture of this material in many grades and imitating all kinds of leather, is carried out by coating a cloth or other fabric with a thick solution of pyroxylin, a nitrated cotton, in proper solvents, usually containing castor oil or a similar substance in addition to the alcohol-ether. After the solvents have evaporated, the surface may be embossed and finished ornamentally (6). The pre-war production of pyroxylin artificial leather in the United States exceeded 50,000 yards per day. A similar dope is used for making patent and enameled leathers, one in general use being a mixture of 6–10 per cent. pyroxylin, castor oil in wood alcohol, amyl acetate, fusel oil and benzine (7).

Celluloid.—When nitrated cellulose is worked together with camphor and alcohol at a suitable temperature, a tough pasty mass is formed. This is then forced thru fine sieves and passed thru rolls to remove all of the solvent, which is recovered. These films may be compressed to form blocks of practically any thickness, and from these films and blocks the many celluloid articles now commonly known are made. By suitable dyeing agents and other methods numerous colors may be obtained as well as imitations of horn, tortoise-shell and ivory. This is an American discovery patented in 1869 by Hyatt (8). On account of its ready imflammability there is some ground for objection to celluloid. A less imflammable substitute for it is cellulose acetate, made by treating pure cotton with acetic anhydride, diluted with acetic acid, until it dissolves; the triacetate formed is precipitated by pouring into water.

Photographic Films.—The first patent of a flexible photographic film was taken out by H. Goodwin in 1887. The nitrated cotton, or pyroxylin, and camphor in a suitable solvent (such as wood alcohol and amyl acetate) is poured on a smooth surface, and the solvent evaporates leaving a thin film. Because the film must be entirely transparent and uniform in appearance and thickness, great care in its manufacture is necessary. The development of moving pictures has tremendously increased the demand for this material, the daily output of which runs into hundreds of thousands of square feet.

Paper

The influence of paper as the bearer of thought thru the printed and written page cannot be estimated. So wide a variety of uses have paper and paper articles come to have recently, that it is not surprising that the manufacture of paper now ranks among the ten largest industries in the United States (9).

Until a little more than a hundred years ago paper was made out of cotton and linen rags. To-day rags are used only in the better grades of paper, while a very much larger amount is made from wood, though other materials, as straw, hemp, jute, esparto, are used to some extent. A certain amount of mineral matter, usually clay, talc or gypsum, is worked in with the paper to give weight and smoothness and to fill up the pores.

Manufacture.—Rags frequently come to the paper manufacturer in a dirty condition. After the buttons and hooks have been removed and the seams ripped by hand, the dust is beaten out and the rags are cut into small pieces and boiled under pressure with milk of lime for twelve hours or longer. After washing they are sent to the beater engine, sometimes called the Hollander, because of its invention in Holland. Here the material is thoroughly cut up and made into pulp, being at the same time well cleansed and then bleached, usually with bleacing powder. An antichlor is added to remove excess of chlorine, and the pulp is then weighted by the addition of mineral matter.

The pulp is run out on an endless belt of wire cloth, where it is spread out and loses part of its water by drainage and part by passing thru pressing and drying rolls. During this process, while the paper is wet, a stamp or " water mark " may be placed upon it by slightly raised letters on the so-called " dandy " roll. The paper is smoothed or polished in the calendar rolls. Paper on which ink is to be used must be finished by sizing, a process of filling the surface pores with gelatin, rosin or casein.

Wood Pulp.—Practically all newspaper, most of our book paper, and a large percentage of writing paper are made from wood. Spruce, fir, pine and poplar are frequently used for this purpose. Mechanical and chemical pulp are both made from wood.

The mechanical pulp is made by placing blocks of wood against a revolving grindstone, a spray of water being used to keep the wood from heating to the burning point. The pulp is screened twice and then is ready to be mixed with chemical wood pulp before being used in making paper by the process outlined for rags.

Three processes are in use for the making of chemical pulp: the soda, the sulfite and the sulfate. In the soda process the wood is chipped into pieces less than half an inch thick. These are placed in a digester with a 7 per cent. caustic soda solution and heated under pressure for about ten hours. The non-cellulose materials, such as lignin and resin, are decomposed by the caustic soda or combine with it, leaving a soft grayish-brown mass, which must later be bleached by chlorine. In the process the caustic soda is changed to sodium carbonate, and this after recovery by evaporation, is changed back to the hydroxide with slaked lime, and used again. About 40 per cent. of the weight of the wood is obtained as pulp.

In the sulfite process the chips are boiled under pressure with sulfurous acid or with an acid sulfite of calcium and magnesium containing about 4 per cent. sulfur dioxide. The sodium sulfate process depends upon the action on the non-cellulose material in the wood of sodium sulfide made from the sulfate by reduction. The organic matter in the liquor serves after evaporation to reduce any added sulfate. It is claimed that both the sulfite and sulfate processes give a stronger fiber than the soda process.

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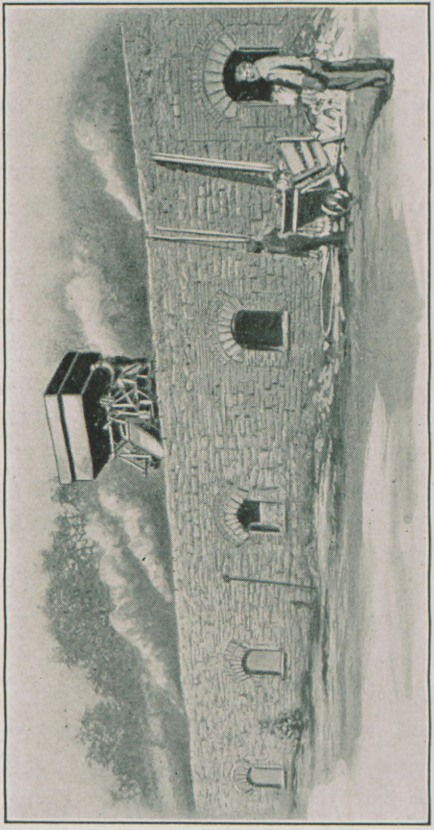
CHAPTER VI

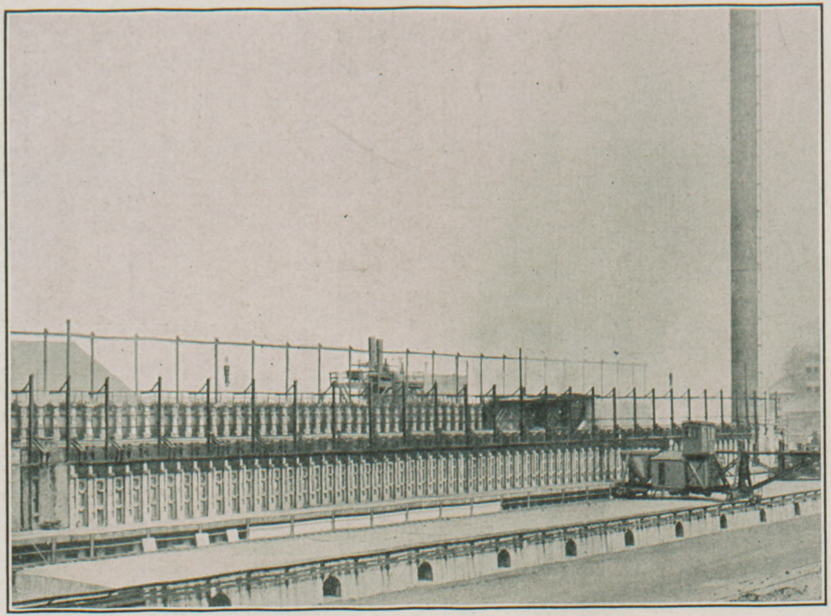
COAL TAR—DYES

Coal tar is a by-product in the destructive distillation of bituminous coal. Coal is heated in retorts closed from the air for two general purposes: either, to manufacture illuminating gas, the coke, coal tar and ammonia being by-products in this process; or, to prepare metallurgical coke, in which case these same by-products may or may not be recovered.

Coke from a retort manufacturing illuminating gas is not suitable for metallurgical purposes, such as the reduction of iron ore. Until comparatively recently by-products have been recovered in only a small per cent. of the plants making metallurgical coke in England and in the United States. Most plants used the beehive ovens which are exceedingly wasteful, more than one-third of the fuel value of the coal being lost as well as the by-products. Before the War a realization of the great value and importance of the by-products had caused an increase of the by-products oven used for such recovery. Still in 1914 only about forty per cent. of the metallurgical coke in the United States was produced in by-product ovens (1). While such ovens are somewhat more expensive to build than the beehive, they soon pay for themselves. With proper treatment more than enough



Beehive Coke-Ovens
Charging and Drawing



By-Product Coke-Ovens, pusher side.
Pusher and lorry shown, latter charging oven with coal

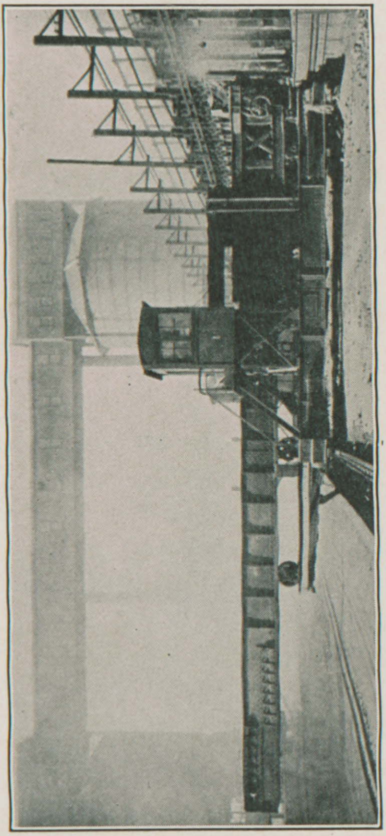
gas to heat the ovens can be produced and the excess sold. The yield of coke is increased and the by-products, coal tar and ammonia saved.

Products of Distillation of Coal.—The composition and amounts of the products vary with the conditions under which the distillation is carried out, but in general one ton of dry coal will yield (2)

11,000–12,000	cubic feet gas
1,400–1,800	pounds coke
56–120	pounds coal tar
20–35	pounds ammonium sulfate

The Demand for Coal Tar.—At first coal tar was considered a very objectionable and certainly a most disagreeable by-product. As more became known of its uses the demand for it has increased and in the years of the World War far exceeded the supply. Some of the excess of coal tar in the early days was used as a fuel, and from some of it a paint was made. A small amount was subjected to distillation and the products so obtained used as a substitute for turpentine in varnish making and also as a solvent for rubber. By this latter method in 1825 James Mackintosh began his manufacture of the waterproof garments which bore his name. In 1838 it was discovered that the dipping of posts and other timbers into coal tar or one of its distillation products greatly increased the length of time they would last, and thereby the demand was greatly increased.

In 1845 A. W. Hofmann of the newly-founded Royal College of Chemistry in London began really scientific investigations on coal tar, which have led



Pusher-Ready to push Coke from By-Product Oven

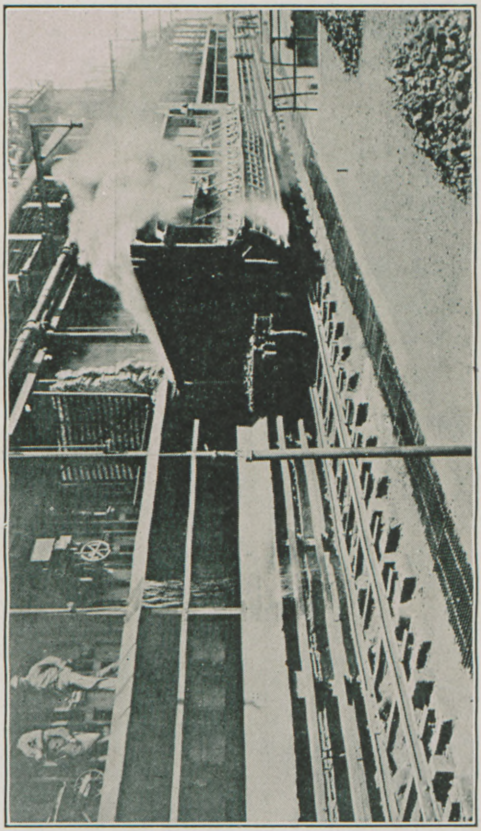


Fig. 11—Coke being pushed from oven on other side from pusher

to its many and valuable uses of to-day with constantly increasing demand. The systematic distillation of coal tar was first carried out by Mansfield, who had been a pupil of Hofmann, in 1848.

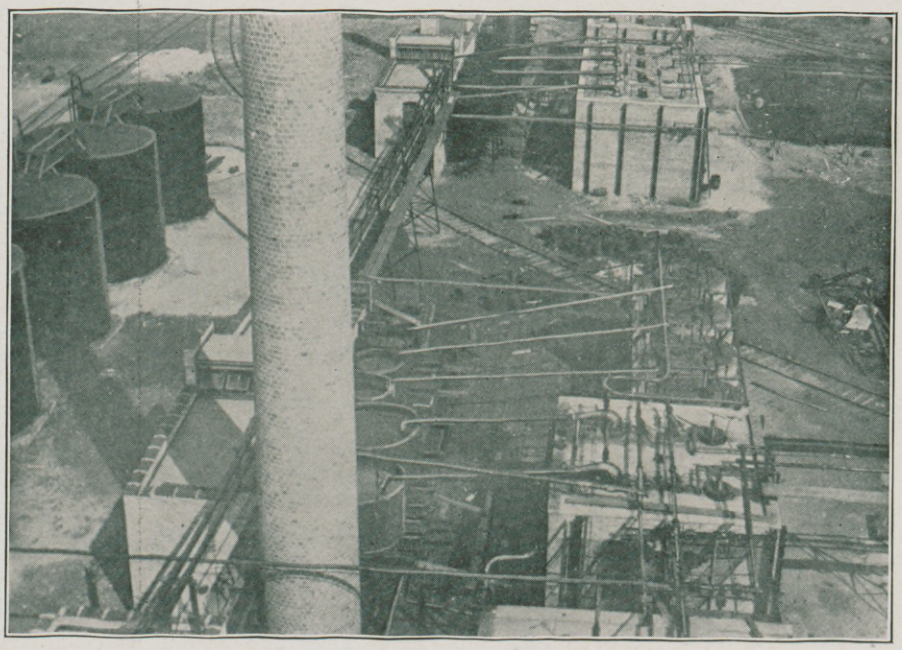
How great the demand must be is seen by the figures of production some years ago, which have, especially in the United States, greatly increased in recent years (2):

United Kingdom	1910	1,380,000 tons
Germany	1912	1,082,197 "
United States	1912	564,000 "
France	1909	214,800 "

Distillation of Tar.—Crude coal tar is by no means a simple compound, but a mixture of at least 200 different substances. A beginning on the separation of these numerous bodies is best obtained by fractional distillation. The procedure varies in different countries and also in different plants in the same country. The following will give an idea of the process and the products (3):

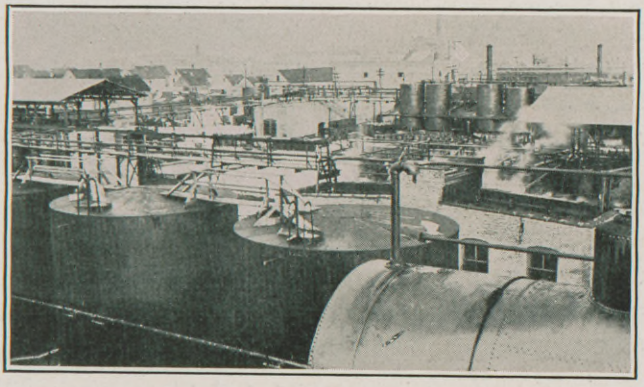
First Runnings	up to 105° C.	Ammonium salts, naphtha
Light oil	105–210°	Benzene, toluene, xylene
Carbolic oil	210–240°	Phenol, naphthalene
Creosote oil	240–270°	Naphthalene, cresols, liquid paraffins
Anthracene	270–	Anthracene
Pitch	residue in still	Pitch

More than 60 per cent. of the weight of the original tar is left in the still. Parts of the fractional distillate for which there is little demand are sometimes added to this pitch. Pitch is much



Birdseye View of Tar Stills

used in making of roofings and tarred paper, as a binder in road building, in the manufacture of briquettes and in black varnishes and paints.



A Corner of a Modern Coal Tar Plant

The higher boiling fractions of the light oil are used largely as solvents, as stated thus (4):

"In 1911 nearly 2,000,000 gallons of coal-tar solvents were produced in the United States, and were distributed among the different industries approximately as follows (Weiss):

Paint and varnish	47	per cent.
Rubber and rubber cements	18	"
Imitation leathers	10	"
Chemical manufactures	11	"
Miscellaneous	14	"

Coal tar compounds also find a very extensive use in the manufacture of explosives and dyes, many of them being classed as "intermediates." Carbolic acid and the cresols are active poisons and find wide use as antiseptics as in cattle washes and sheep dips. The creosote oil is much used in "pickling" timber, which trebles or quadruples the length of its usefulness. In 1913 the United States used 90,000,000 gallons of creosote oil for timber preservation, importing 62 per cent. of this from Europe (5). Somewhat similarly naphthalene is used, as in moth balls.

Thus from the vile smelling nuisance coal tar the magic of chemistry has produced valued aids to the art of healing, most beautiful colors to satisfy the eye, and explosives of tremendous power, in addition to hundreds of other equally useful, if not so noticeable, substances.

Dyes

Though the source of nearly a thousand different dyes, coal tar itself does not contain any substance that may be used as a dye. The great number of dyes of every possible shade and for the greatest variety of uses, which are now produced from coal tar, require painstaking care and in many cases processes of great length, involving as many as twenty chemical reactions. Conditions, apparently without significance at first, such as the use of a copper or of an iron lid, may decide the success or failure of a process (6).

> "Thus, from some eight or nine primary constituents of coal tar (benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene, etc.), there are produced, by the action of various chemical reagents—nitric acid, sulphuric acid, chlorine, caustic

soda, etc.—some two hundred and ninety 'intermediate' compounds, and from these 'intermediates,' by their mutual combinations and interactions, the finished dyes are prepared, of which upwards of nine hundred actually find application at the present time.

Constitution.—The wonderful success of the color industry has only been made possible by a most exacting study of the composition of the compounds involved, not only of the elements contained, but also the positions which these elements hold in the molecule. So important a factor has this proven, not only in dyes, but in practically every branch of organic chemistry, that the insignia of the Chemical Warfare Service, it will be recalled, contains the hexagon of the benzene ring, fittingly suggestive of the importance of constitution in the preparation and use of explosives and other war chemicals.

Early History.—From the earliest times man has delighted in brilliant colorings. Savages in all lands have been attracted by colored cloth, glass or beads. As civilization has advanced this love of color has remained, modified or refined, perhaps, but as powerful as ever. Animal, vegetable and mineral nature have been persistently searched to satisfy this demand. Tyrian purple, Turkey red and the blue of indigo are examples of dyes famous for generations.

Coal Tar Colors Appear.—In 1906 it was the writer's privilege to meet on his visit to America a very delightful old gentleman, whom many chemists and other Americans took pleasure in showing every honor and courtesy. This man was Sir William Henry Perkin, discoverer of the first coal tar dye, who was by special invitation visiting America during the semi-centennial celebration by the world of his discovery of the dye, mauve. At the banquet tendered him by American chemists in New York all of the decorations were in this shade made famous by his discovery in 1856.

This discovery of Perkin was made possible by two conditions: the one, the founding in 1845 of the Royal College of Chemistry in London with A. W. Hofmann, a pupil of Liebig as director; and the other, the discoveries which produced the aniline with which Perkin worked. In 1825 Faraday, an Englishman, discovered benzene, C_6H_6, which could be obtained from coal tar. In 1834 the German, Mitscherlich had prepared nitrobenzene, $C_6H_5.NO_2$, by treating benzene with concentrated nitric acid; while Bechamp, a Frenchman, in 1854 reduced this nitrobenzene with nascent hydrogen, obtained from iron and acetic acid, to aniline, $C_6H_5.NH_2$.

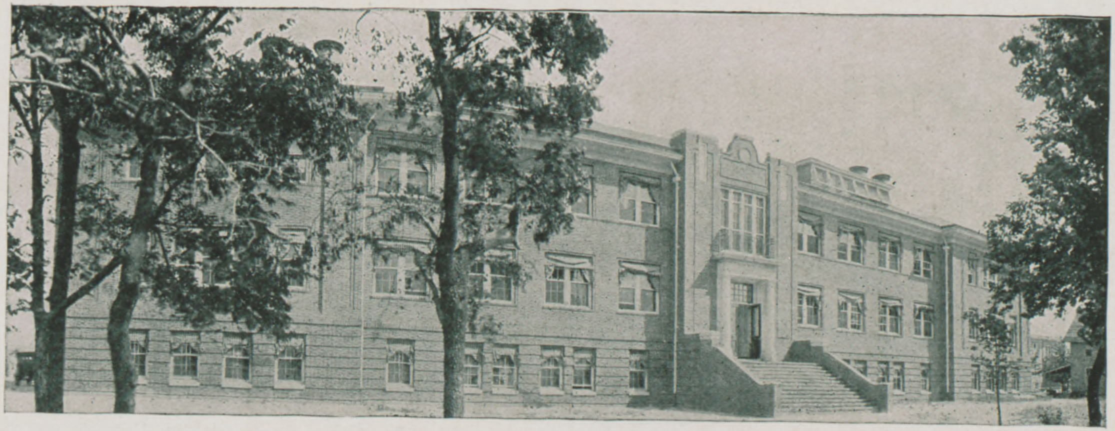
In 1856 Perkin, then eighteen years old, who had been a student of Hoffman, in an attempt to produce quinine synthetically oxidized a solution of commercial aniline in dilute sulfuric acid with potassium dichromate. As a result he obtained, not quinine, but a dark, resinous mass, from which by further treatment he separated a dye, to which was given the name of "aniline purple" or "mauve." It is interesting to note that this discovery would not have been possible had not the commercial aniline contained mixed with it variable amounts of the toluidines. In the course of a few years the use of this dye became so common both in France and in England that "Punch" referred to it as "The Mauve Measles."

Britain's Early Pre-eminence.—This discovery was quickly followed by others and the manufacture of dyes on a commercial scale was begun with England pre-eminent in this field. How this supremacy passed to Germany about 1871 is graphically told by Perkin himself, as recorded by Pellew (7). That this was possible was due not so much to the underhand methods of Germany, which were even then in evidence, but more to a failure on the part of the British to recognize the "vital importance of persistent chemical research." Sir William A. Tilden states two causes (8),

> "first, the neglect of organic chemistry in the universities and colleges of Great Britain, and then the disregard by manufacturers of scientific methods and assistance and total indifference to the practice of research in connection with their processes and products."

There is here for the United States a tremendously impressive lesson of the absolute necessity of co-operation between the university and other research and educational forces and the forces of industry.

German Dominance in the Dyeing Industry.—Thus for more than forty years before the World War the Germans had almost complete control



Research Laboratory for One of America's Newest and Biggest Dye Producing Works, Deep-water Point, N. J.

over the whole color business. There were some twenty German dye factories, some of them very large and exceptionally equipped, all thoroughly organized and working together. These presented a solid front against the relatively small dye firms in Switzerland, Great Britain, France and the United States, entirely unorganized, and producing all together only about ten per cent. of the output of their German competitors. While the total value of the dyestuffs consumed by the whole world was not relatively large, perhaps $70,000,000 per year, it was tremendously important, though not then generally so recognized, because from the "crudes" and " intermediates " required by the dyers, explosives could readily be made, and the transformation of a plant manufacturing these to a supplier either of munitions or of munition plants was an easy matter, requiring little time or trouble.

Further, textile and other industries with a yearly output in America alone of $3,000,000,000 worth of goods are dependent upon the dyeing industry (9). There was much of truth in the boast often made, " The dyestuff industry is a one-nation industry, and that nation is Germany."

An American Dyestuff Industry.—Under pre-war conditions four or five moderate sized factories were operated in the United States, but these were forced to depend in large measure upon Germany for their " intermediates," and were practically put out of business with the removal of the tariff protection in 1913. With the closing of the German ports by the war a number of small factories sprang up, and some of these have now become firmly established, manufacturing the standard colors in as excellent a quality as, or even better than, those formerly "made in Germany." In 1914 the United States imported 45,841,000 pounds of dyes, but in 1917 the United States manufactured 45,977,000 pounds, eight times our pre-war production, while the "intermediates" produced were 323,000,000 pounds. And this production has increased till now there is more money invested in dye plants in the United States than in any other country, in spite of the fact that under the stimulus of the War a single British plant covers 250 acres (10).

Dye Testing Laboratory of an American Dye Works

With this industry made permanent, which there is every reason to believe will be done, there is much of promise for the future, not only of dyes, but of many allied American industries. Truly A. Mitchell Palmer, while U. S. Alien Property Custodian, said (11)

"In peace, and even more in war, chemistry paints the whole picture of progress."

Classification of Dyes.—Because of their variety and complexity a system of classification of dyes is very difficult. One general method of classification depends upon whether the dye can be used alone, or whether some other substance must be added to hold it on the fiber. Dyes which can be used only with a mordant (from the Latin word to bite or hold) are called adjective dyes, those without a mordant, substantive dyes. Mordants are of two general classes; mineral, such as salts of iron, aluminum or chromium, and vegetable, such as tannin.

It was early recognized that the properties of a dye depended very largely upon its constitution. In 1876 it was pointed out by Witt that every dyestuff must contain one or more of certain groups, which he called chromophors (color bearers). The nitro group, $-NO_2$, and the azo group, $-N=N-$, are two of these chromophor groups. The simplest substance containing a chromophor was called a chromogen (color producer). The chromogens are not generally dyes themselves, but become dyes upon the addition of certain salt-forming groups, called auxochrome (color helper) groups. Thus benzene, C_6H_6, is colorless, but the introduction of the chromophor (color bearer), —NO_2, forms the chromogens (color producers): mono-, di-, or tri-nitrobenzene. These chromogens, though colored, are not dyestuffs, but by taking on an auxochromous (color helping) group, as —OH, the dyeing material, picric acid, or tri-nitro-phenol, $C_6H_2(NO_2)_3$-OH is formed from tri-nitro-benzene, $C_6H_3(NO_2)_3$. Substances which act as dyestuffs are either acidic or basic, and the salts have the more intense color.

A classification of dyes by Wood gives the following classes with certain typical members of each (12):

I. Basic Dyes	Triphenylmethane derivatives as Magenta, Methyl Violet, Malachite Green. Certain phthaleins, as Rhodamine.
II. Acid Dyes	Sodium salts of sulphonic acids and Nitrophenols. (Dye animal fibers directly.)
III. Direct Cotton	Azo compounds from diamines, as Benzidine, Tolidine.
IV. Mordant Dyes	Contain phenolic or carboxyl groups, as Alizarin.
V. Vat Colors	Reduction product fixed on fiber and then oxidized, as Indigo.
VI. Developed Dyes	Form on the fiber by chemical action, or within the fiber, as Chrome Yellow or Aniline Black.

Substitution of Coal Tar Colors for Natural.—There have been several striking cases in which coal tar colors have largely replaced the natural product, the most interesting being those of indigo and of Turkey red. One of the most widely used of all dyes is indigo, at first obtained entirely from the indigo-plant grown in India, China and Egypt.

In October 1897 after nearly twenty years of study and experiment on the part of German chemists artificial indigo was placed on the market. In that year India had over a million and a half acres under cultivation for indigo. In 1913 barely 200,000 acres were so in cultivation in India, so great had been the success of the artificial product, now made from naphthalene.

It is claimed that Turkey red was used in coloring the mummy cloths used ages ago in Eggpt, and much land was given a few decades ago to the cultivation of the madder plant, from the root of which this dye was derived. To-day alizarin, made synthetically from anthracene, a coal tar product, has practically stopped the cultivation of madder. Alizarin is widely used with a mordant for dyeing cotton, giving with iron oxide a violet color, with chromic oxide a brown, and with aluminum oxide a bright red.

Natural Dyestuffs Still in Use.—It would be unfair to leave the impression that all natural dyestuffs have been replaced by synthetic products. Such is by no means the case. Logwood, sumac, and recently Osage orange, as well as other woods have been used as a source of natural dyes. Even before the War more than 100,000 tons of dyewoods were used annually in the United States, and that amount was greatly increased during the war years (13).

Synthetic Drugs, Perfumes, Flavoring Extracts and Photographic Developers. A discussion of these products made from coal tar is beyond the range of this little book, but the naming of some of them will give some idea of their importance.

Drugs

antipyrin
antifebrin
phenacetin
aspirin
salol
salvarsan
saccharin

Flavoring Extracts

vanillin
oil of wintergreen
oil of bitter almonds
oil of cinnamon
pineapple

Perfumes

musk
meadowsweet
coumarin
hawthorn

Photographic Materials

orthochromatic plates
panchromatic plates
pyrogallol
hydroquinone
metol

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CHAPTER VII

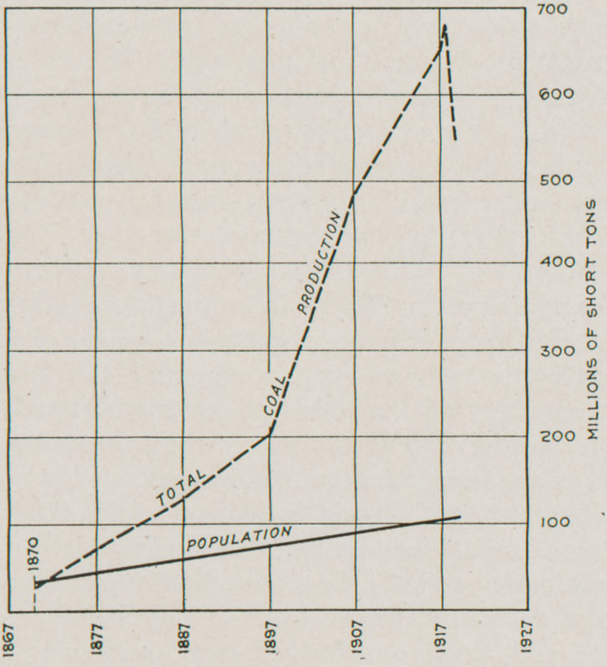
FUEL

With the possible exception of food nothing is so great a necessity for man as is fuel. The cheerlessness of a cold home largely disappears when it is filled with a comfortable warmth. Important as fuel is for domestic use, yet only a small percentage of the total production is so used, for fuel is equally a necessity in industry. To such an extent is this true that the coal production is sometimes called the barometer of business, an idea welcome to an American, because of the large percentage of the world's coal produced in the United States.

The world's production in 1913 given in short tons was (1):

United States	570,000,000
Great Britain	322,000,000
Germany	306,000,000
Austria-Hungary	60,000,000
France	45,000,000
Russia	35,000,000
Belgium	25,000,000
Japan	24,000,000
All others	91,000,000
Total	1,478,000,000

In the amount produced and the value, coal is by far the most important of our minerals, making up about half the value of the non-metal mineral products. Three states, Pennsylvania, West Virginia and Illinois produce nearly three-fourths of the total American coal. Together with that of oil and natural gas, the value of the coal produced yearly now far exceeds a billion dollars (1).



Curve Showing Relation of Increasc in Population in U. S. to Coal Production 1870–1921

The increasing demand of industry is seen in the relation of total coal production to population in the United States. Being less than one ton per capita in 1870 it has now become about six tons per capita, and that, too, in spite of the rapid growth in population (1) (see curve). The total coal production in 1918 was 678,212,000 tons, which fell because of unfavorable industrial conditions to 544,263,000 in 1919.

"*Stored-up Sunshine.*"—The energy which drives our industry, pulling our trains and propelling our steamships, comes from the sun. This is true, whether the source of that energy be the sunshine of recent days or weeks which lifts the water to later turn the dynamos of a powerful hydroelectric plant, or the sunshine of ages long past, now stored in the coal and oil and gas ready for use. Should wood be used for fuel, then the sunshine of recent decades is used. Thus it is interesting to think as this page is read, as to whether the source of light used by the reader is the direct sunlight of to-day, the sunlight of the past weeks transformed by water power, that of the past years from wood, or that of past ages from coal, oil or gas.

Classification.—Fuels are usually classified as solids, liquids, and gases, and their relative importance is in this order, though all three classes are of decided importance in the United States.

All solid fuels are derived from the woody materials of the trunk, stems or leaves of plants. These may be of recent growth, or, as we have seen, stored up thru long ages. In this latter case there is an increasing loss of volatile elements, as shown in hydrogen and oxygen, and an increasing per cent. of non-volatile carbon. These transformations, beginning with cellulose, the chief constituent of all plants, are well shown in the following table after Gebhardt (2):

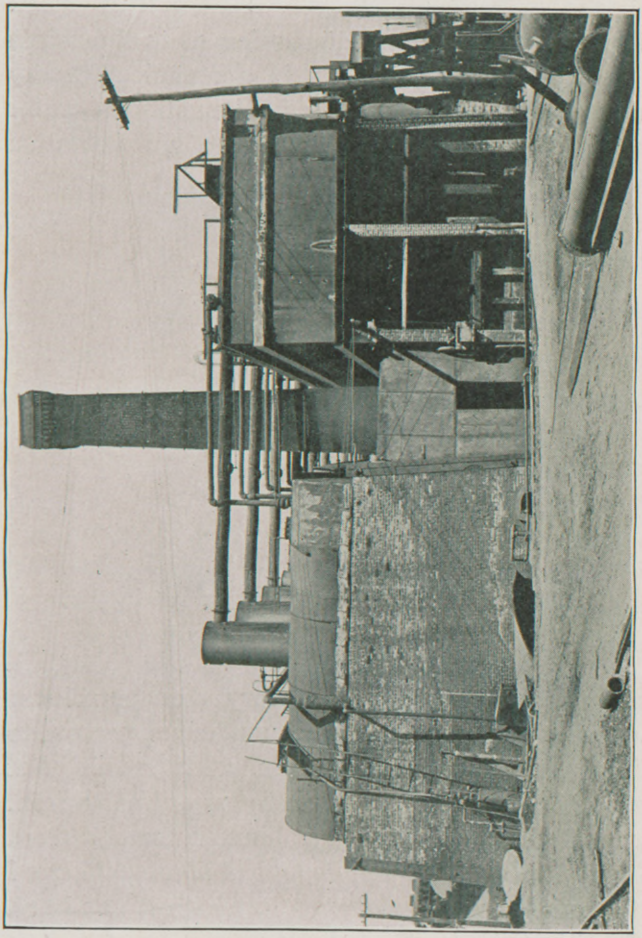
Composition of Solid Fuels

Substance	Carbon	Hydrogen Percentage	Oxygen
Pure cellulose	44.44	6.17	49.39
Wood	52.65	5.25	42.16
Peat	59.57	5.96	34.47
Lignite	66.04	5.27	28.69
Brown coal	73.18	5.58	21.14
Bituminous coal	75.06	5.84	19.10
Semi-bituminous coal	89.29	5.05	6.66
Anthracite coal	91.58	3.96	4.46
Graphite	100.00	....	....

Wood is widely used for domestic purposes, though its use is of necessity decreasing. In industry wood as a fuel is seldom used except in some special cases. The amount of water in freshly cut wood varies from 26 per cent. in the willow to 50 per cent. in the poplar. Thoroughly seasoned cord wood averages about 20 per cent. of moisture. This makes the heating power, or calorific value, of such wood greater than that of green wood but less than that of kiln-dried wood. Ordinary dry wood gives about 5600 British thermal units (B.t.u.) per pound, while kiln dried gives 8000 B.t.u. A cord of seasoned oak wood weighing about 3200 pounds nearly equals in heating value one ton of soft coal (3). Pound for pound, pine wood gives about 10 per cent. more heat units than oak; however a cord of pine because of its lightness furnishes much less heat than a cord of oak.

Coal occurs as hard coal, or anthracite, and soft coal or bituminous. Practically all of the anthracite coal is produced in Pennsylvania, and in 1917 and again in 1918 approximated 100,000,000 tons. The 1919 production was only 86,200,000 tons. The tonnage of bituminous coal is usually about five and a half times as great. The larger part of all coal mined is used for steaming purposes, the railroads alone consuming 150,000,000 tons in 1917. Approximately 75,000,000 tons of soft coal (about 14 per cent. of the total soft coal production) was used in 1917 for making coke. Forty per cent. of this was from retort or by-product ovens in which the coal tar was saved. This is a decided increase over the percentage of coke so made ten years ago, and will doubtless increase still more, if the demand for coal tar products remains steady. The largest by-product plant in the world is at Clairton, Pa. The use of coal briquets is desirable and should increase. These are made from coal dust, which would otherwise be largely wasted, held together by coal tar or pitch (5, 6).

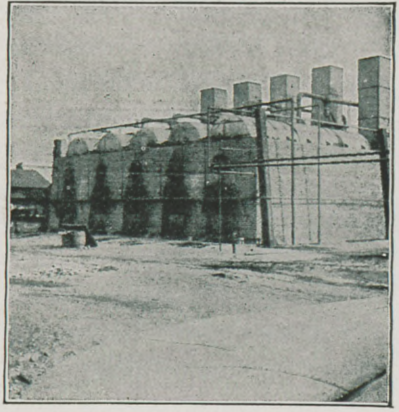
Petroleum.—While the inflammable gas issuing from the ground near Baku on the Caspian Sea had long been known and had attracted fire-worshippers from India centuries before (7), yet the practical use of the oil associated with this gas was negligible. The petroleum, or rock oil, industry may be considered as beginning in 1859 in which year the American petroleum industry had its birth when Drake sunk the first well near Titusville, Pa. For 200 years before this petroleum



Petroleum Refinery

had been used by the Indians as an external and internal medicine, frequently being sold as Seneca oil.

There has been much discussion as to the origin of petroleum. While there is a chemical theory that petroleum is the product of the action of water upon carbides of certain heavy metals, it is not so generally accepted as the theory that petroleum is of organic origin. Some evidence seems to indicate that it is of vegetable origin, while that from other sources is apparently of animal origin. It is not impossible that petroleum is formed from the remains both of animals and of plants, changed by the mighty physical forces to which it has been subjected in the earth (8).



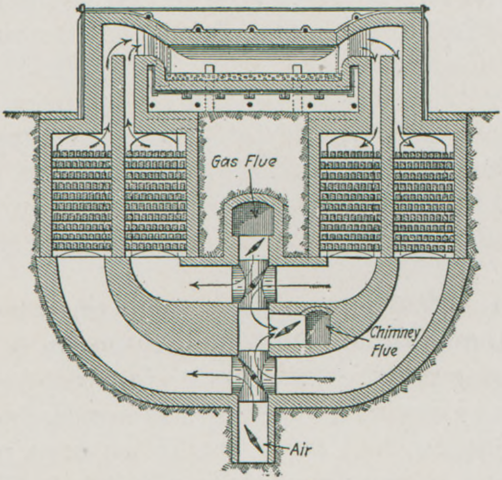
Oil Stills in Petroleum Refinery

The financial and industrial importance of oil has steadily increased with the growing production and the increasing demand for use in gas engines. More than a million barrels are now produced every day (9). In many ways oil is superior to coal as a fuel, occupying only half the space and weighing about two-thirds as much as coal required to give the same heat.

Oil Shales.—By investigations carried out by the United States Geological Survey it has recently been shown that oil shales in Colorado, Utah, Wyoming and Nevada contain vast supplies of oil, which can be obtained by distillation, usually at the rate of forty to fifty gallons per ton. It is claimed that this discovery has dispelled any danger of an oil shortage for at least several generations (10).

Alcohol.—While there have been repeated predictions that alcohol would find extensive use as a fuel, being prepared from waste material from the farm and elsewhere, and there has been an increase in production, still these prophecies have not, as yet, been in any large degree fulfilled. By the addition of certain substances to ordinary alcohol, " denatured " alcohol, which can not be used as a beverage, is formed and so is exempt from high taxation. The extent of the use of alcohol either from wood (methyl, CH_3OH) or from grain or other sources (ethyl, C_2H_5OH) will depend in the future upon the production and price of gasoline (11).

Fuel Gases.—In oil regions there is generally found, ready formed, large quantities of natural gas, often under considerable pressure. When this gas under pressure is tapped by a well, the gas for a time will flow, and this flow can be continued by pumping until the supply is exhausted. Natural gas, the chief constituent of which is marsh gas, or methane (CH_4), has a high calorific power and is a very satisfactory fuel. The chief difficulty in its use is in the maintenance of a steady supply. This can only be accomplished by continually sinking new wells to replace those that have become exhausted. The production of natural gas in 1917 was 670 billions of cubic feet with a value in excess of one hundred millions of dollars.



Furnace for Making Open Hearth Steel, Using Siemens Regenerative Principle

This natural gas sometimes contains helium, the lightest known element except hydrogen. On account of its lightness and incombustibility helium is useful for filling balloons, and the United States has established at Fort Worth, Texas, a large plant to utilize this gas found in natural gas occurring there.

That the gas flame can be so readily controlled and that the heat can be placed where it is needed are very real advantages in the use of gas as a fuel. Further by using the principle of the Siemens regenerative furnace, the incoming gas and the air required for combustion may be heated by passing thru flues containing brick checkerwork, which have already been heated by the escaping products of combustion. The flues are so arranged that the flow of the gases may be reversed from time to time, so that a decided saving in heat is effected.

There are other fuel gases in use, the most important of these being coal gas, water gas and producer gas. Coal gas formed by the destructive distillation of coal, that is heating coal away from the air, consists chiefly of hydrogen and methane, and finds wide use especially in domestic consumption. Water gas, made by passing steam over heated carbon in the form of coke was invented by the American, Lowe (13). It is made of carbon monoxide and hydrogen, and is used both in industry and for cooking. As the coke cools down, the process must be interrupted every few minutes and air blown over the coke to bring it back to the necessary temperature, the carbon dioxide formed being allowed to escape in the air.

Producer gas is sometimes made by passing an insufficient supply of air over a poor grade of coal, thereby forming a mixture of carbon monoxide with much nitrogen. In this way about two-thirds of the heat units from the carbon can be obtained in burning the monoxide to the dioxide, less, of course, the necessary loss in the process. More recently producer gas has been made by combining this process with that in use for water gas, admitting water and sufficient air to keep the coke hot enough.

The relative heating value of these gases is seen in the number of pounds of water evaporated by 100 cubic feet of each gas (14):

		Ratio
Natural gas	893 pounds	7.76
Coal gas	591 "	5.14
Water gas	262 "	2.28
Producer gas	115 "	1.00

Other Products.—By destructive distillation of coal and of wood, and by fractional distillation and refining of petroleum, many valuable products are obtained, some of which are given below:

From	Coal	Wood	Petroleum
	illuminating gas	some fuel gas	naphtha
	ammonia	wood alcohol	gasoline
		acetic acid	kerosene
		acetone	lubricating oil
	coal tar	wood tar	vaseline
			paraffine
	coke	charcoal	retort carbon

From this source we obtain practically our entire supply of ammonia used for refrigeration, in medicines, for fertilizers, and for domestic use. The value of coal tar has been shown in the preceding chapter. Coke is chiefly used for metallurgical purposes as in the reduction of iron ores (see Chapter XIII), but large amounts are also used in gas producers, and as fuel both in industry and for domestic purposes.

The pyroligneous acid obtained in the destructive distillation of wood is neutralized with lime and from the calcium acetate so formed, acetic acid is made by treatment with sulfuric or hydrochloric acid and distilling. Acetic acid finds a wide use in the making of white lead, in dyeing, in pharmacy and as a solvent in explosive and other industries. Acetone is a solvent for resins, fats and nitrated cellulose and hence finds use in the manufacture of celluloid, smokeless powder, and crude rubber. It is used also to manufacture chloroform and to denaturize grain alcohol.

On account of its freedom from sulfur and phosphorus charcoal is sometimes used in the production of a high grade of iron. Because of its power of taking up coloring matter, it is used for decolorizing and clarifying oils and solutions; this is especially true of animal charcoal, which is used in sugar refining. The use of wood charcoal in making gunpowder has already been mentioned. As a fuel it is valuable, but its use is not extensive.

Increased Yield of Gasoline.—Before the perfection of the gas engine every effort was made to secure from crude oil as high a percentage as possible of illuminating and lubricating oils. With the increased demand for gasoline due to the more general use of the automobile and airplane, and the decreased demand for kerosene due to the use of electric lighting, the method of refining petroleum has changed, the object now being to secure as much gasoline as possible. At higher temperatures the heavy oils with the heavier molecule tend to break up into oils with a lower boiling point and smaller molecular weight. This process is called "cracking" (13). Rittman, while in the employ of the U. S. Bureau of Mines, succeeded in so controlling temperature and pressure that the yield of gasoline was largely increased (15). McAfee increased the gasoline yield by heating the petroleum oil with 3–10 per cent. of anhydrous aluminum chloride (16).

The liquid products from petroleum are washed with sulfuric acid to remove tarry impurities, then with water, and with caustic soda to remove the acid. The water is allowed to settle out and the oil is exposed to light and air to give the clear, colorless product to which we are accustomed. Recently much light gasoline has been obtained by condensing it from natural gas (2).

Fuel Supply in the Future.—The tremendous increase in the consumption of fuels of almost every kind in recent years has caused alarm to some, and should, without doubt, call for a conservation wherever possible and the avoiding of wasteful methods. The immediate prospect of a fuel famine is by no means alarming. Predictions are at best unreliable as they are very likely to be upset by an increased consumption, by the discovery of some new source of energy, or of some hitherto unsuspected supply.

At any rate we can and should use this " stored up sunshine " of past ages for our legitimate needs, though we clearly have no right in our newly found knowledge and power to squander the birthright of coming generations. Just because the United States is exceptionally fortunate in her supplies of coal, of oil and of gas, so far as possible a careful use of these resources should be demanded that our industrial future may be all the more secure.

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CHAPTER VIII

SILICATE INDUSTRIES

Glass. Clay-Working Industries. Cement. (Lime).

We have seen (p. 49) that if we represent all the material upon the earth, including the atmosphere and the ocean, by a circle, then practically one-half of this circle is filled by oxygen; upon dividing the remaining half, we find slightly more than half of it, or 26 per cent. of the whole to be made up of silicon. With this fact as a background one is not surprised at the many substances of mineral origin which are made up largely of silicon and oxygen, and found as silicates. Some of these are mica, slate, asbestos, talc and certain building stones. Sand is made up of the two elements, oxygen and silicon only (SiO_2), which are likewise the constituents, of course, of sandstones, of quartz, and of a number of semi-precious stones.

Still more important silicates are found in the so-called silicate industries, in which may be included glass, clay-working industries and cement. These we shall now consider.

Glass

The making of glass was practiced in the early stages of Egyptian history, thirty centuries before the Christian era. In England it was first used for windows in the eleventh century (1). In 1608, the year after the founding of the first American colony, the London Company sent to Jamestown eight men to make " pitch, tar, glass and soap-ashes." With their work some writers date the beginning of chemical industries in America (see chapter I).

Manufacture.—The manufacture of glass may be considered in two distinct stages: the selection and fusion of the proper ingredients, which is essentially chemical, though carried out for ages without a thought of science; and the working of the glass, including the molding or blowing and other manufacturing processes, which are physical.

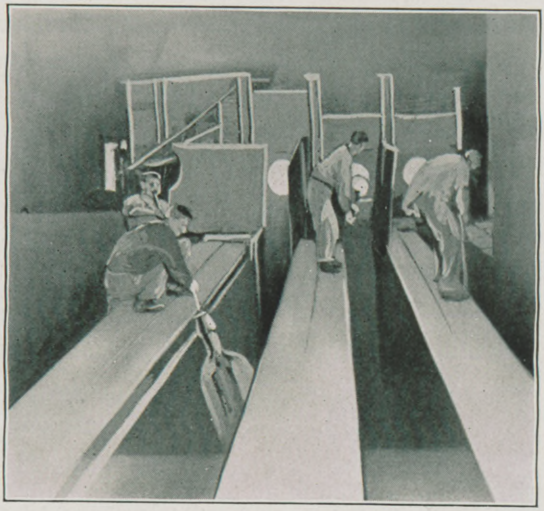
Composition.—Glass in ordinary use is generally either a lime or a lead glass, the former being a double silicate of calcium and of sodium and the latter of lead and of potassium. Soda-lime glass is given this formula ($Na_2O.CaO.6SiO_2$) and lead glass this ($K_2O.PbO.6SiO_2$), though probably the formulae are more complex (2). Other combinations of these elements are possible and more recently many varieties of glass using a large number of elements in a variety of combinations have been made, silica, of course being the basis of the product. Zinc oxide and boric acid are frequently used.

Lime glass is usually made by fusing in a specially prepared furnace sand and lime together with sodium carbonate, or sulfate. When sodium sulfate is used, charcoal or coal is added to reduce a part of the sulfate. Scrap glass, or cullet, is also frequently added. These minerals must be of a high degree of purity, the sand in use usually running more than 99.5 per cent. pure silica. Iron is especially objectionable as an impurity. To remove the effect of the small amount of this element almost invariably present, it is usually necessary to add manganese dioxide. This oxidizes the green ferrous iron to the less objectionable yellow ferric, and further the pink of the manganese silicate helps to neutralize the color from the iron. The use of phosgene, prepared in large quantities as a war gas, has been suggested for this oxidation, but such use has not been extensive.

In making lead glass, litharge (PbO) or red lead (Pb_3O_4) is used. This must be free from copper and silver. Alkali carbonates, and not sulfates, must be used with these oxides of lead, otherwise the sulfide present will darken the glass.

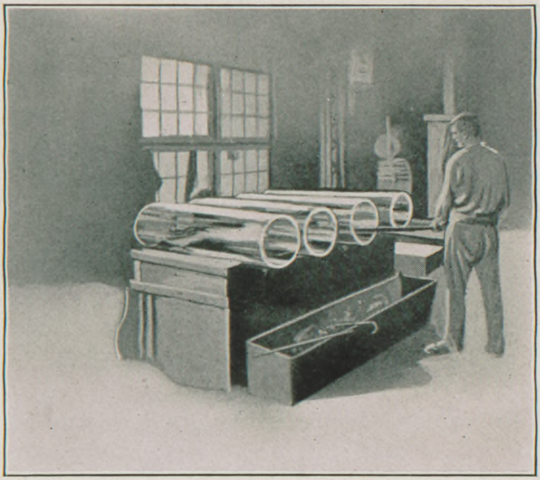
Fuel.—Coal, wood, oil, and natural gas have all been used as fuels in glass furnaces. A long flame and freedom from soot are necessary requisites. The possibility of using natural gas has frequently determined the location of glass plants. Furnaces vary greatly in size from pot furnaces holding only a few tons of the melt to tank furnaces of nearly a thousand tons capacity. These tank furnaces are charged from one side and the glass is withdrawn as needed from the other side, so that while the glass plant is in operation the furnace is kept in continuous fusion.

Glass-Blowing.—An iron tube, about five feet long, with a mouthpiece at one end is dipped into the molten glass. The workman removes this pipe from the furnace and by skillful blowing and turning causes the glass to become spherical in shape. If window glass is to be made, the large lump of glass on the end of the blow-pipe is extended changing into a hollow cylinder approximately six feet long and twelve to fifteen inches in diameter. To do this the glass must be reheated thru the "glory hole" of the furnace from which it was withdrawn, and to lengthen the cylinder the workman blows while swinging the glass and his pipe in a vertical semi-circle. While doing this he stands upon a bridge over a pit.



Blowing Window Glass

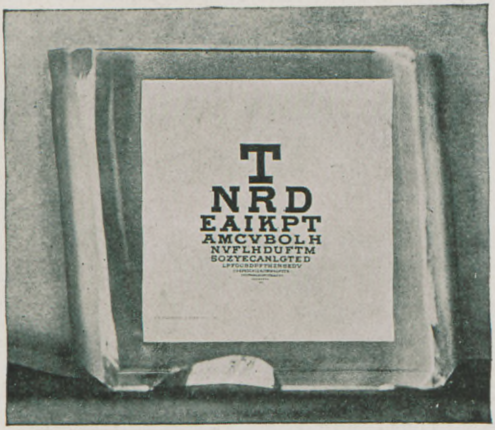
This glass cylinder, while still hot, is cut from the pipe by shears, and then split down the side. These split cylinders are placed in the flattening furnace, and on being heated open out flat thru gravity, and are made smooth by "ironing" with a block of wood placed on a handle. These sheets then go to the annealing furnace and from there to the cutting rooms. Twelve pieces of single strength glass and eight pieces of double strength make an inch in thickness (3).



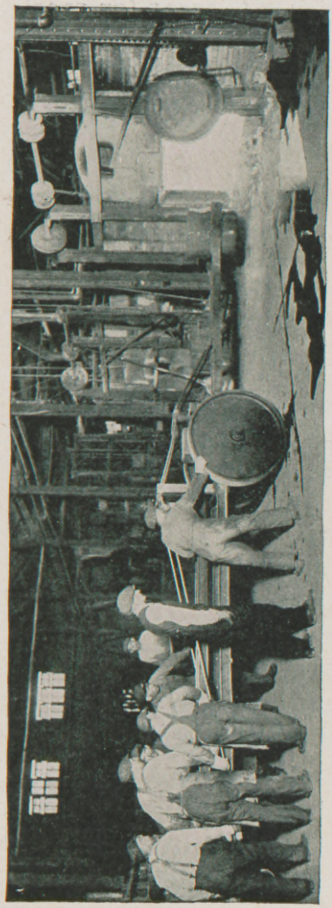
Splitting a Cylinder of Window Glass Preparatory to Flattening

Many forms of glass are blown in molds, which are opened to receive the molten lump of glass on the end of the blowpipe. After the mold is closed the glass is blown until it entirely fills the mold. Many bottles and other forms of glass are blown by machinery. Much window glass is also machine made. Plate glass is a soda-lime glass, similar in composition to window glass, but it is poured onto a large casting table and is not blown. After casting, the plate is ground and polished.

Optical Glass.—Until April 1917 almost no optical glass was made in the United States. The immediate and urgent demand for such glass, which was sorely needed by the government for range finders, gun sights, periscopes, measuring instruments, etc., offered a challenge to American ingenuity which was at once accepted. To understand the difficulty of the situation it is only necessary to remember that the modern range finder must be efficient at 20,000 yards instead of the 5,000 yards required before, and that in the periscope of a submarine twenty different pieces of glass are required. The immediate demand was for sixteen different kinds, totaling 2,000 pounds a day.



Photograph of Test Type Through Block of Optical Glass Five Inches Thick, Showing Remarkable Transparency



Taking Pot of Glass from the Furnace

Optical glass is made from materials of the highest purity in pots about 40 inches in diameter and 40 inches high. Glasses for special use must be of special composition, and various substances, such as boric acid, barium and phosphate compounds must be added to the usual ingredients. After fusion the glass is stirred and allowed to cool; at first, rapidly, and then slowly. The pot is broken and the yield of usable glass generally runs from twenty per cent. up. Special research has been carried out by the Bureau of Standards on the glass pots which must be particularly suited for the work in hand and not contaminate the mix (4).

Pot of Optical Glass After Cooling Several Days

By the combined efforts of the Bureau of Standards and some half dozen manufacturers enough optical glass was produced to enable America to meet her own demands and have some left for export. Thus we have as a result of this challenge so quickly and successfully answered, an American optical glass industry, which gives every promise of permanence and growth.

Pot of Optical Glass in Process of Being Broken Up

Laboratory Glassware.—This material is usually a potash-lime glass, frequently containing boric acid. Though at the beginning of the War there was much more laboratory glass than optical glass manufactured in America, the story of the increase in production is similar. It is gratifying to note that the recent report of the Bureau of Standards shows American made glassware entirely equal and in many respects superior to that imported from Germany previous to the War (5). The present production is greater than the pre-war importations.

Colored glass is produced by the addition of some coloring material, usually a compound of some metal. Thus, blue is given by cobalt or copper, green by chromium or iron, purple by manganese, red by gold or cuprous copper. Frequently a combination of two or more coloring agents is used to produce a certain effect.

Clay-Working Industries

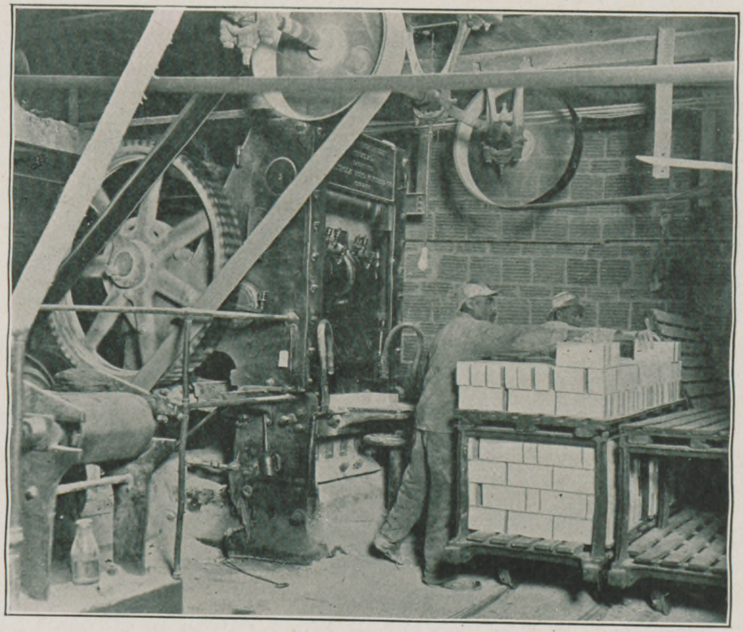
Clay suitable for the manufacture of useful products is " one of the most widely distributed of our minerals " (6). Every state in the Union contains clay-working plants.

These plants may be placed in two general classes upon the basis of their output: first, brick and tile; second, pottery in some of its many forms. Manufacturers of articles made from the lower-grade clays, such as brick, are usually miners also, while makers of high-grade pottery frequently buy their clay, sometimes importing. These imports in large measure ceased during the War, causing the development of American clays, a development which apparently will continue, for most, if not all, of the imported clays can be duplicated at home (7).

The value of the pottery produced in the United States in 1913, the last normal year of production, was slightly more than twenty per cent. of the total value of clay products, amounting to nearly $200,000,000.

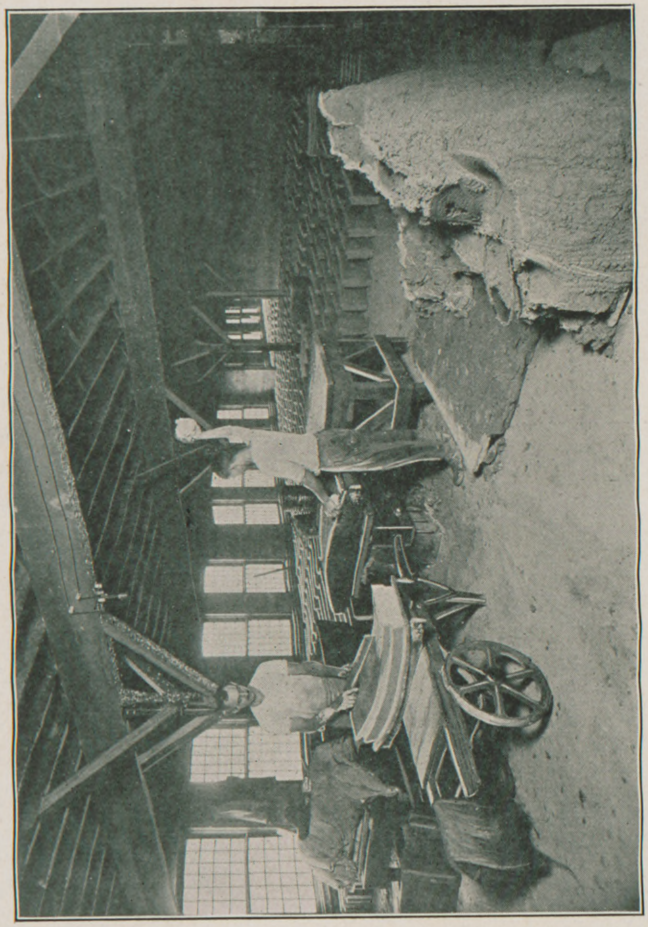
Brick.—Clay is a natural hydrated silicate of aluminum. An impure form of clay, containing lime and an oxide of iron, is used in making common brick. This industry is widely distributed, and the value of common brick is more than one-fourth that of all clay products. The clay is usually weathered after digging, is screened, and put into "pug" mill, where water and additional sand or other clay is added, if desired. After thorough mixing by revolving blades which cut up the clay and pass it to the discharge end, the clay is ready for moulding, which is done either by hand in wooden frames dusted with sand to prevent sticking, or it is forced out in a rectangular bar and machine cut into brick length. The "green" bricks are dried in the air, and then burnt either in open kilns built of the air-dried bricks with frequent openings for passage of the flame and the hot gases, or in a closed kiln which gives a more uniform product. For common brick the temperature does not usually exceed 1000° C., but for paving brick it is raised several hundred degrees higher to cause incipient fusion, which gives a hard surface. The heat and the amount of iron present determine to a great extent the color of the brick.

Fire brick are prepared from a coarse clay which contains less iron and more silica, the amount of the latter varying from 50 per cent. to 70 per cent. Sand-lime bricks are made by molding a mixture of sand with about 8 per cent. of lime and treating with steam at a pressure of 130–150 pounds for several hours.

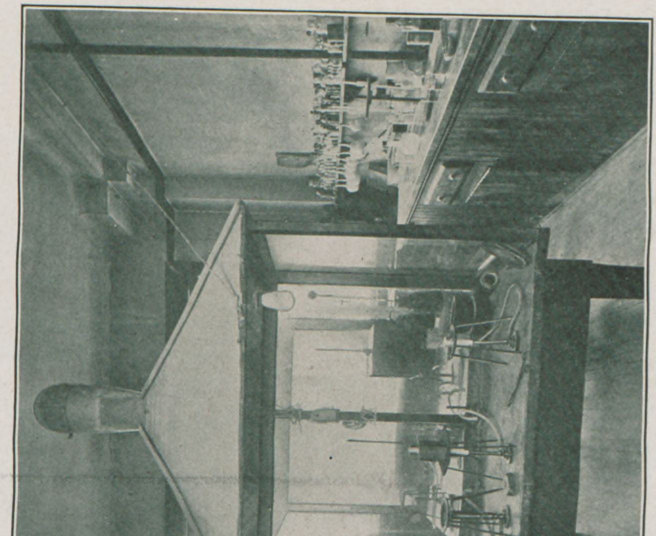


Making Fire Brick by the Dry Press Process

Sewer pipe and drain tile are made from materials similar to those used in brick making and burned in a closed kiln. Tiles for floors, walls, etc., are similarly manufactured from purer materials and may be vitrified by using a higher temperature, or they may be glazed.



Making Locomotive Tile



Ceramic Laboratory of a Clay Products Company

Pottery.—The purest clay found in nature is kaolin, and this kaolin is the basis of pottery manufacture. The articles classified under this head are quite varied, the following being some of those listed in the government report (6): red earthenware, stone ware, yellow ware, white ware, white granite, semi-porcelain ware, china, bone china, sanitary ware, porcelain electrical supplies.

The manufacture of unglazed pottery began in the earliest ages, reference to it being found in ancient Egyptian records. The Greeks and Romans covered their vessels with wax, tallow or bitumen to make them non-porous. While the invention of porcelain, a glazed form of pottery, is attributed to the Chinese, its manufacture seems to have been begun in Japan before the Christian era, and to have been carried to Persia, where the material was called " chini."

In the manufacture of pottery of all grades the same general principles apply. First, the article is shaped, either in molds or on the potter's wheel from a plastic mixture, the chief ingredient of which is kaolin. This is then dried and burned in a closed kiln. Unless a very high temperature has been used this leaves a porous body which must be glazed. In the case of cheap ware this is sometimes done by throwing salt into the kiln which forms a glaze on the surface of the ware by the fusion of the salt and the material in the ware itself.

In making the better grades the material is allowed to cool after burning and then dipped into water containing in suspension quartz, feldspar and various metallic oxides, and sometimes boric oxide. Upon again heating in the kiln after drying these materials melt at a fairly low temperature and form a glaze on the surface. Sometimes these materials are first fused alone, then crushed, mixed with water and placed on the article by dipping, and the whole fired after drying. Great care must be taken that the glaze formed has the same coefficient of expansion that the body of the ware has.

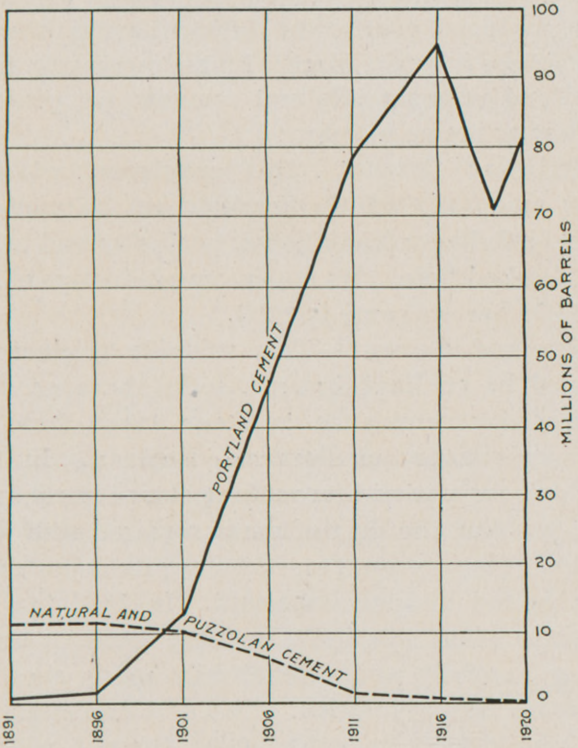
If the article is to be decorated, the desired design may be painted or stenciled on the unglazed piece in pigments usually made up of metallic oxides, and then fired. In other cases the decorating is done after the article has been glazed, using colored glasses which on subsequent firing melt into the glaze.

The term ceramics, derived from the Greek word meaning potter's clay, is applied to all such work, which offers an exceedingly broad and diversified field, ranging from the cheap article intended for the commonest use to the most exquisitely decorated and daintily molded vase. In laboratory porcelain a record of recent development like that for laboratory glass ware has been established, the product of American factories equalling or excelling the imported ware (8).

Cement

Next to steel and iron cement is our most important building material. Its general use is recent, for in 1895 the total production was less than

9,000,000 barrels, while the present production is more than ten times that amount (see curve).



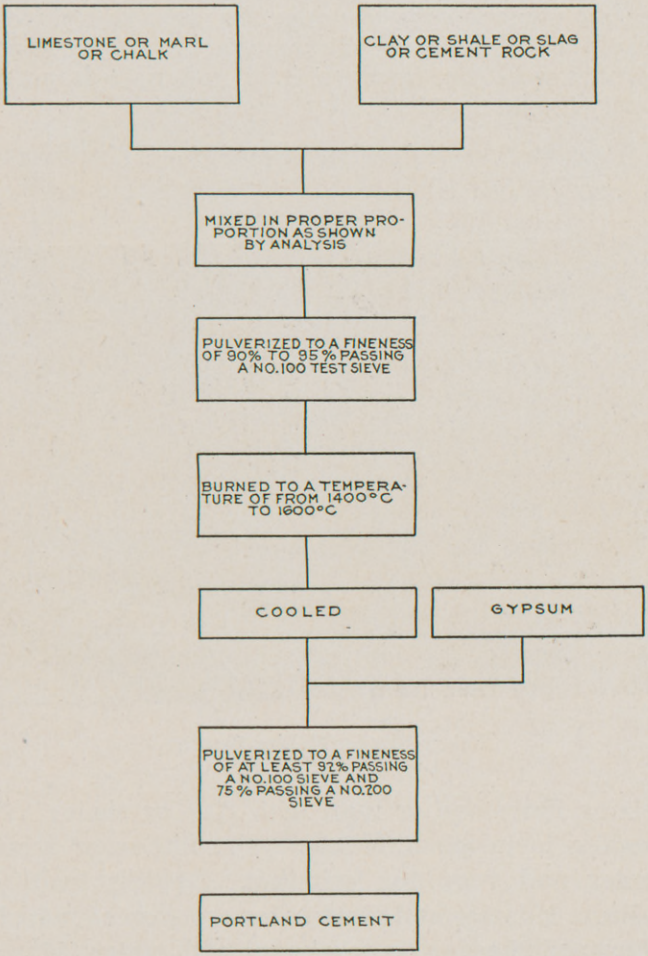
Production of Cement in U. S. 1891–1920

Natural Cement.—This material is made by burning and then grinding an impure limestone containing 13–35 per cent. of clayey matter, sometimes called cement-rock. Much of such cement was used in the construction of the Erie and other canals. In 1890 the natural cement produced was about 7,500,000 barrels, more than twenty times the then production of Portland cement. Now much less than a million barrels of natural cement are produced yearly, the article having been all but driven from the market by the increasing use of Portland cement. Natural cements are generally yellow or brown in color.

Puzzolan Cement.—This substance, which is now practically off the market, can be made by finely grinding volcanic ash or basic slag and mixing with slaked lime. Its maximum production of only 525,000 barrels came in 1903.

Portland Cement.—This valuable product was named by an Englishman, Aspdin, because of its supposed resemblance to stone taken from the famous quarries at Portland, England. In 1824 he took out a patent for making cement by burning and grinding the dust of roads repaired with limestone. Some years passed before its manufacture in England became important. In 1852 the first German plant was built, and the German output being carefully and scientifically made soon acquired a high reputation. The first American output was in 1875 from the Lehigh District, which is still by far the largest producer. The competition with the cement imported from England and Germany was keen and the amount of production increased slowly, not reaching a million barrels till 1896. Since then the increase has been phenomenal (see curve) (9).

According to Meade, a leading authority (10), "To-day undoubtedly the best Portland cement made in the world is turned out in America, . . . and it is now recognized as superior to that manufactured in any part of the world."

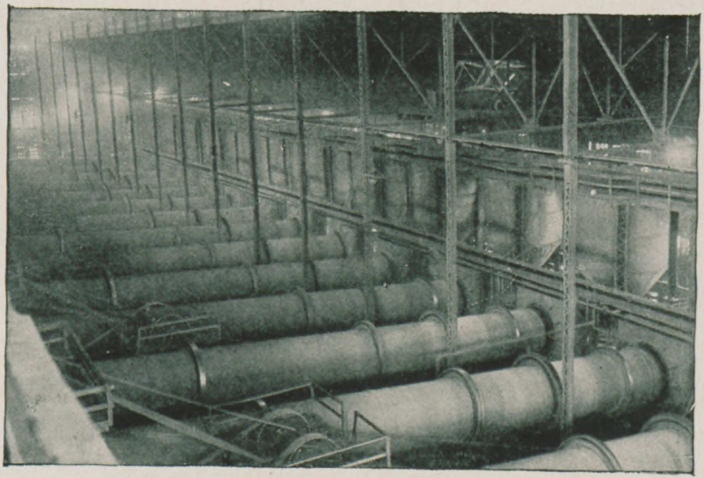


Steps in the Manufacture of Portland Cement

George Otis Smith, Director of the United States Geological Survey, in discussing our mineral reserves states (11):

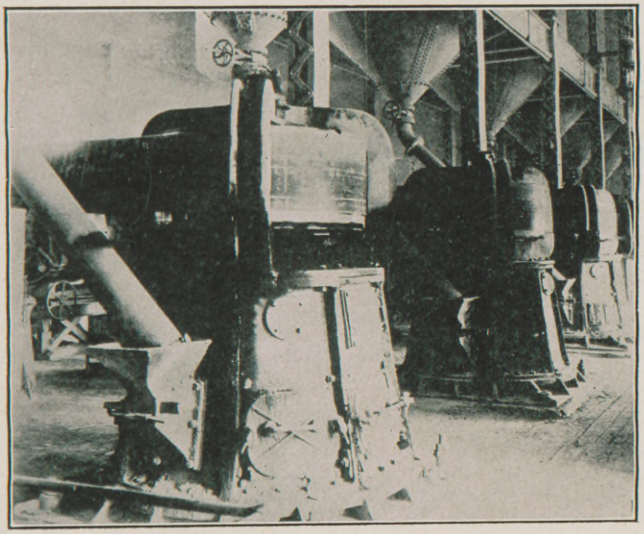
> " There is little or no need to import any cement, for all parts of the country are now fairly well supplied with mills for the manufacture of Portland cement, and the supply of raw materials is practically inexhaustible."

Manufacture of Portland Cement.—This process is carried out in three fairly simple steps: (1) mixing limestone or marl with clay or shale; (2) heating to incipient fusion; (3) addition of a retarder and very fine grinding. By this heating calcium silicates and aluminates are formed, which afterwards harden on treatment with water (12).



Rotary Kiln for Making Cement

1. The ingredients, which are usually quarried by the manufacturer, must be intimately mixed, which is accomplished by grinding. Careful chemical control is necessary to maintain certain ratios, as follows:

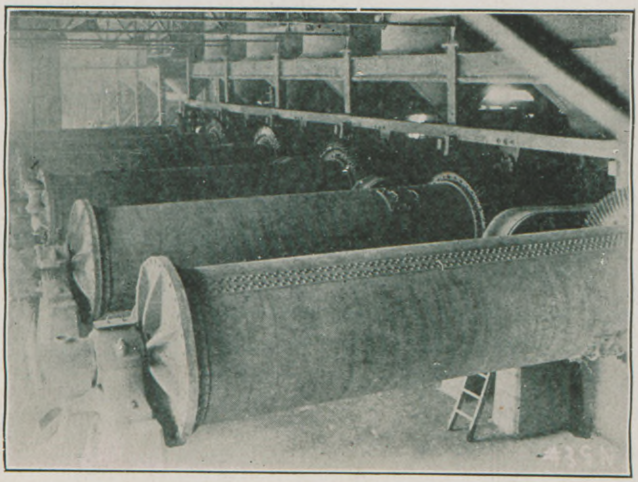


Mill for Preliminary Grinding of Cement

$$\frac{\%CaO}{\%SiO_2 + \%Fe_2O_3 + \%Al_2O_3} = 1.9 \text{ to } 2.1,$$

$$\frac{\%SiO_2}{\%Al_2O_3} = 2.5 \text{ to } 4.$$

According to United States Government specifications (13) cement must not contain more than 2 per cent. sulfuric anhydride nor 5 per cent. magnesium oxide. The grinding may be carried out by the dry process, which is an American invention and more economical, or it may be by the wet process, which varies according to the economic condition of the locality.



Tube Mill for Final Grinding of Cement

2. The finely ground mixture, either dry or mixed with water sufficient to allow pumping (the so-called slurry) is fed into rotary kilns which are universally used in this country, because they require less labor although using more fuel. These are made of steel, lined with firebrick, being 60–150 feet long and 6–8 feet in diameter. These kilns are inclined at a slight angle and are fired at the lower end, opposite to that from which the material enters. Most American plants (80 per cent.) use fine coal for a fuel, blown in by an air blast, about 25–40 per cent. of the weight of the cement being

required. In some places natural gas or oil is used. The material in passing down the rotary kiln is first dried, then loses its carbon dioxide, and finally forms small lumps or balls as it begins to fuse.

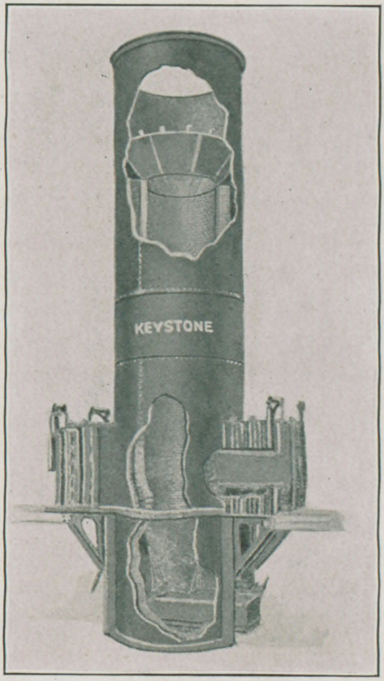
3. Upon coming from the kiln the material is either allowed to cool in piles, or, to hasten the process, is placed in the cooler and air is blown over it. After air temperature has been reached about 2 per cent. or 3 per cent. of gypsum, or other form of calcium sulfate, is added to prevent too rapid setting, and the whole ground so fine that 92 per cent. will pass a sieve containing 10,000 openings to the square inch and 75 per cent. a sieve containing 40,000 openings per square inch. It is then packed in 380 pound barrels or 95 pound sacks, and is ready for shipment.

The general process is clearly and graphically shown in the accompanying diagram after Meade (14).

The exports of cement from the United States have been less than those from several other countries, South America before the War obtaining cement from Europe. It is probable that our increased merchant marine will cause a decided increase in the amount of these exports, which in 1913 totalled only about 3,000,000 barrels, or 3.2 per cent. of the total production (9).

Lime

Lime is in no sense a silicate industry, but is placed at the close of this chapter solely for convenience. Lime (CaO), sometimes called " quick lime " (or with the old meaning of the word, " active lime ") is made by heating the sedimentary rock, limestone ($CaCO_3$), until all of the carbon dioxide is driven off. This process is usually carried out in vertical kilns, 30–50 feet high and 6–10 feet in diameter. In the best practice the process is continuous, the limestone being fed in at the top and the finished oxide drawn off at the bottom.



Lime Kiln

Wood is the best fuel as it gives whiter lime. When it can not be had, coal, oil or gas may be used. The coal may be mixed with the stone, though it is more frequently burned separately so that the lime will not be contaminated by the ash. Limestone with the smallest content of silica, alumina and iron oxide is used. If this contains less than 5 per cent. of magnesia it is called a high calcium lime. Magnesian limes contain more than 5 per cent. of magnesia and often as much as 30 per cent. In general these are not considered so desirable. A fat or rich lime contains less than 5 per cent. of impurities other than magnesia (15).

Hydrated Lime.—When treated with water calcium oxide is changed to calcium hydroxide and in this hydrated form lime is generally used. This reaction evolves much heat and must be carefully done if the product is to be of good grade. To reduce danger from fire in shipping and storage and to yield a uniformly satisfactory product, water sufficient to form the hydrated lime is frequently added at the kiln and the dry hydrated lime shipped in barrels or bags. On mixing this with more water no heat is evolved. Half a million tons of hydrated lime are now so prepared.

Upon exposure to air lime takes up moisture and carbon dioxide and deteriorates rapidly, finally forming air slaked lime, which is of the same composition as the original limestone and of no value for building purposes. When limestones containing 10–20 per cent. silica, alumina and iron oxide are burned, hydraulic lime is formed, so named because the product will harden under water. Hydraulic limes in their properties stand between ordinary lime and natural cement.

Production. Uses.—Forty-four states reported lime kilns in operation in 1913, the total production being 3,600,000 tons (16). The increase in production of lime has been gradual and steady, but not at the tremendous rate shown by cement, the total production of cement now being nearly five times that of lime.

While the largest single demand for lime is in the building industries, its uses are quite varied as seen in the following list taken from the report of the United States Geological Survey on " Mineral Resources of the United States, 1914 " (16):

building lime
sugar factories
slag cement
smelters
disinfectant
cyanide plants
chemical works
tanneries
alkali works
steel works
sheep-dipping
glue factories
paper mills
fertilizer
sand-lime brick
glassworks
manufacture of soap
purification of water

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CHAPTER IX

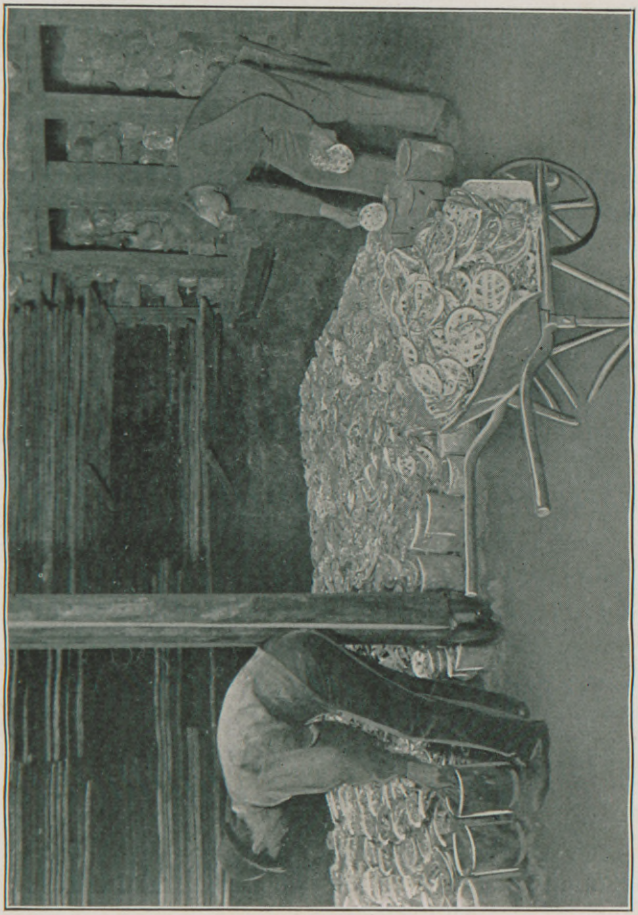
PAINTS AND VARNISHES

Paints usually consist of the mineral pigments (the body) ground in oil (the vehicle). They are applied as surface coatings for either decorative or protective purposes, or both. By painting the surface of material it is protected from the action of oxygen in the air, from moisture and from the borings of insects.

Pigments

Some authorities distinguish between the body or solid material of the paint used for covering and the pigment which gives the color. More generally both body and pigment are considered together, as the pigment frequently has body as well as coloring power. Some pigments occur in nature, as the ochers and Siennas and umbers, and after grinding are ready for use upon mixing with the vehicle. More often they are mineral substances which are prepared by certain manufacturing processes. Occasionally an organic coloring material, usually obtained from coal tar, takes the place of the mineral coloring matter, though this must be added to some mineral material to secure the desired body.

Some of the more commonly used pigments will be briefly considered, beginning with the white and then with those that are colored.

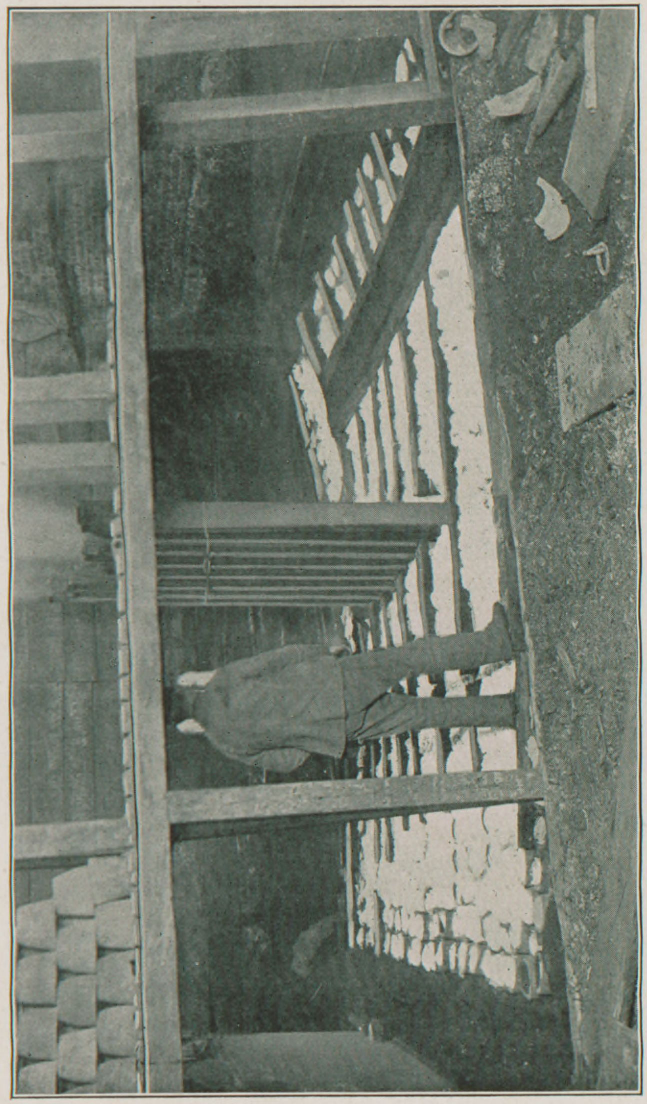


Setting Lead "Buckles" in Pots in Dutch Process for Manufacturing White Lead

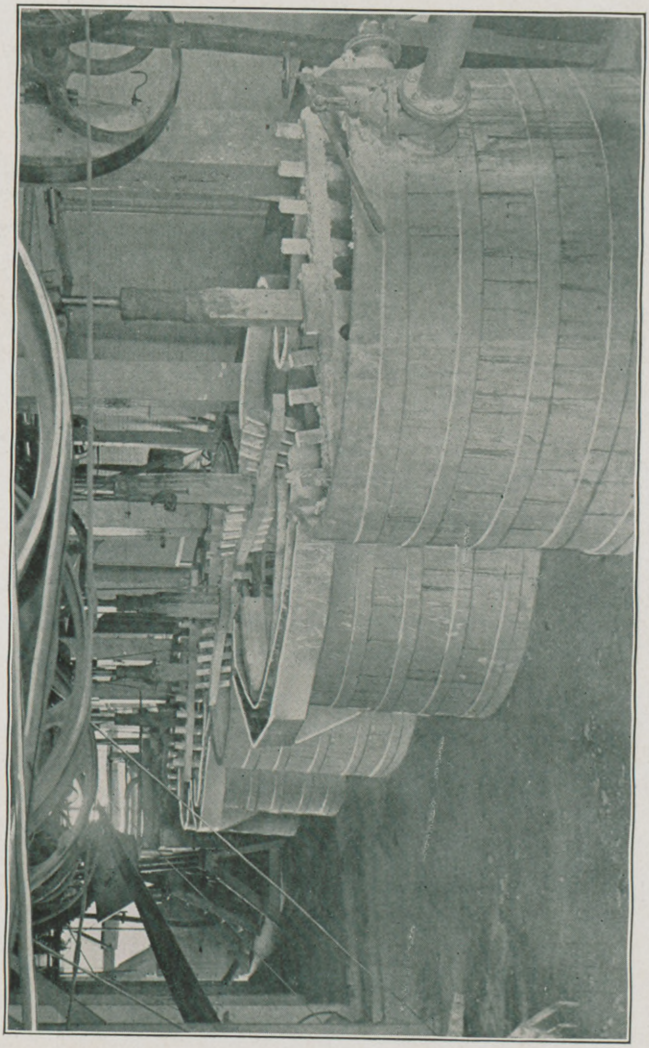
White Pigments.—Practically all of these are some form of lead or of zinc compounds. For some 2000 years white lead, a basic carbonate of lead containing about 85 per cent. of lead oxide and 15 per cent. of carbon dioxide and water, was the only widely used white pigment. Much less than a century ago the other white pigments made their appearance. To-day white lead is used as a basis for many paints because of the ease with which it may be applied, which makes it popular with the painter, and its great covering power, which brings it into favor with the manufacturer.

The old Dutch process for manufacturing white lead consists in placing lead buckles or grids upon supports inside of specially constructed earthenware pots in the bottom of which is acetic acid. These pots are placed in stacks surrounded by used tan bark, the carbon dioxide and heat liberated by the fermentation of this bark, causing the acetic acid to volatilize and changing the lead acetate formed to the basic carbonate. The process is very slow requiring about 100 days, which is a serious objection. The corroded material is ground in water, and floated to separate it from the unchanged lead, and dried in copper pans. It is sold either as a dry powder or ground in oil.

There are several other shorter processes for the manufacture of white lead based upon the same general chemical principles. In some cases the molten lead is obtained in very small particles by spraying. These are treated with acetic acid and corroded in revolving drums into which carbon



Starting to " Strip Stack " Note White Lead Formed



Rake Tubs, through which White Lead is Floated dioxide is passed. In spite of the time consumed the old Dutch process is still largely used, the claim being made that the product is better from a practical viewpoint (1).

Sublimed white lead, a basic sulfate of lead, the analysis of which shows about 75 per cent. lead sulfate, 20 per cent. lead oxide and 5 per cent. zinc oxide, is made directly by subliming galena or lead sulfide, the most common ore of lead. It has attained a very rapid prominence in recent years. Ozark White is also a lead sulfate product but contains besides about 60 per cent. zinc oxide (2).

The discovery of zinc oxide as a paint by LeClaire in France, who made it by subliming the metal about the middle of the nineteenth century, and by Samuel T. Jones in America, who made it directly from certain zinc ores, marks the introduction of pigments whose importance is equalled only by that of the lead pigments (2, 3). The purest zinc oxides made by the sublimation of the metal are chosen as the standard of whiteness in paints. Zinc oxide is peculiarly adapted for mixing with other pigments, especially white lead. Toch, a leading American authority on paints, says (2):

> " The great competitor of white lead is zinc oxide, and the weakness of white lead is the strength of zinc oxide, and vice versa. White lead, for instance, is a soft drier and zinc oxide is a hard drier. White lead finally becomes powdery; zinc oxide in its eventual drying becomes hard, and it is for these reasons that a mixture of zinc oxide and white lead forms such a good combination."

It also retards the rusting of iron. On account of its gloss and whiteness zinc oxide is much used for enamels.

When solutions of zinc sulfate and barium sulfide of the proper strength are mixed, double decomposition occurs and the two insoluble compounds, both barium sulfate and zinc sulfide, are precipitated. This mixture has no value as a pigment. When this mass is filtered off, heated to about 1000° F., suddenly plunged into water, ground to the pulp state, and thoroughly washed and dried, a brilliant white pigment of extremely fine texture and high covering power is formed. The manufacture of this *lithopone* was begun in England in 1880 and has been perfected until within the last ten years it has come into quite general use, especially for interior work, as it darkens on exposure to direct sunlight unless some additional material is added to it (4).

Red Pigments.—Red lead, or minium (Pb_3O_4), is one of the most commonly used. Metallic lead is heated in the presence of air and oxidized to litharge (PbO), which is then heated in a muffle furnace at 600–700° F., forming red lead. Ferric oxide is also widely used, either as the natural pigment (Indian Red) made by grinding the mineral hematite, washing with water and drying, or by heating a mixture of ferrous sulfate and quick lime (Venetian Red). The latter of necessity contains 60–80 per cent. of calcium sulfate.

The use of mercuric sulfide to give the brilliant red color, vermilion, has now been replaced by organic color materials, such as para-vermilion. This material is soluble in linseed oil and has high coloring power, the average pigment containing only 5 per cent. of this para-red with 90 per cent. of barytes and 5 per cent. of zinc oxide.

Blue Pigments.—These are usually made of Prussian Blue or of ultramarine. The former is made by treating ferrous sulfate solution with a solution of potassium ferrocyanide, and oxidizing the resulting bluish-white precipitate. Ultramarine is a complex compound, formed by the fusion in crucibles of silica, clay, soda and sulfur. Other blues are obtained from compounds of copper or of cobalt.

Green Pigments.—The most satisfactory and permanent is chromium oxide (Cr_2O_3), made by fusing potassium dichromate with boric acid, washing in hot water, grinding and drying; also by the precipitation of a chromic salt with soda, followed by calcination at a red heat. On account of its expense its use is restricted to paints of a high grade. More brilliant greens are obtained by mixing Prussian Blue and chrome yellow, from salts of copper, and from aniline compounds. The last, being affected by direct light, are used chiefly for interior work.

Yellow Pigments.—Chrome yellows and yellow ocher are the most important. The various shades to be obtained from lead chromate and other lead compounds are seen in this table rearranged from Toch (5):

Light Chrome Yellow	lead sulfate and lead chromate or basic lead carbonate and lead chromate or lead citrate, or tartrate, and lead chromate
Medium Chrome Yellow	lead chromate
Orange Chrome Yellow	lead oxide and lead chromate

The yellow of the lead chromate is lightened by the white of the lead sulfate or basic carbonate, or deepened by the lead oxide in combination.

Yellow ocher is " simply clay stained with rust " and usually contains 10–30 per cent. of ferric hydroxide. Sienna, named from the Italian town where it was first obtained, is darker in color because of a higher iron content and the presence of some manganese.

Black Pigments.—Nearly all of these contain carbon as a base. Lampblack made from burning oily materials with an insufficient supply of air contains about 98 per cent. carbon, while carbon black of similar composition is made by burning gases in like manner and collecting the soot upon a rotating plate against which the flame strikes.

Graphite, the allotropic form of carbon, formerly obtained as a mineral, but now chiefly manufactured by the Acheson process (see chapter XI), is much used, better results being obtained by mixing it with a liberal amount of a lead or of a zinc compound.

Ivory, cocoanut shells, soft wood, bones and various other vegetable and animal materials have been heated to form materials for black paints.

Reinforcing Pigments.—It was at first thought that a pure white lead or zinc oxide paint was most durable and gave the most satisfactory results. The addition of other materials was considered as adulteration. Gradually it came to be recognized that such addition in reasonable amounts was of advantage, the percentage allowed depending entirely upon the circumstances in each case. Lithopone contains 70 per cent. of barium sulfate and the para-red paints used on agricultural implements contain 90 per cent. of barytes. The materials commonly used as reinforcing pigments, sometimes called inert fillers or extenders, are

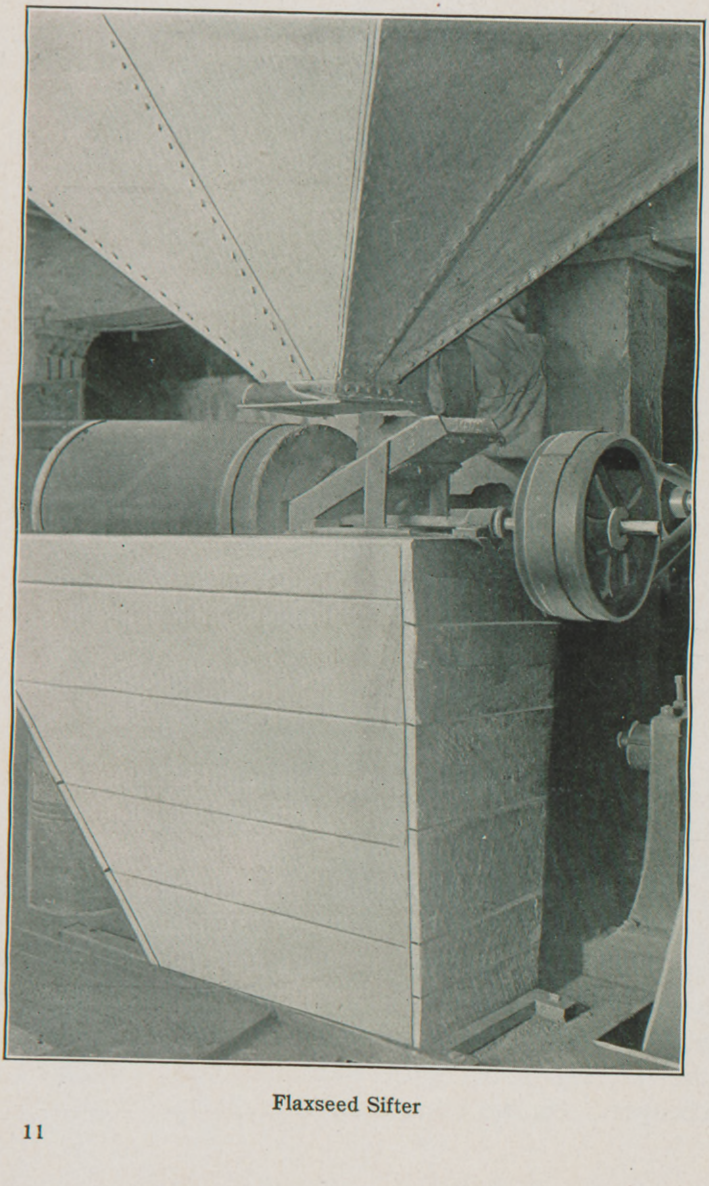
Barium sulfate	the naturally occurring barytes or that prepared by precipitation
Calcium carbonate	natural chalk or finely ground marble or that prepared by precipitation
Gypsum	natural hydrated calcium sulfate
Silica	ground sand or infusorial earth
Asbestine	finely ground asbestos
Kaolin	clay

These materials are all white in color and, either occurring in nature or readily prepared from substances so occurring, are inexpensive. Most of them are inactive chemically, though the alkalinity of the calcium carbonate is at times an advantage in neutralizing traces of acid impurities. Alone they are of slight value as paints but by mixing these coarse pigments with those of finer particles, a skeleton of the larger particles is formed, giving strength and rigidity. This is filled in by the finer particles, making the mass more compact and more permanent (4).

Vehicle

The various materials used to form the body of the paints having been discussed, it now remains to consider the vehicle, or liquid medium. This is always a drying oil or mixture containing drying oil or oils. Drying ordinarily means the giving off of water and consequent loss of weight. In the case of drying oils, however, it means the taking up of oxygen from the air and consequently an increase in weight. Hence all drying oils are chemically unsaturated compounds, that is all of their valency bonds are not satisfied, and these bonds are filled by the oxygen upon exposure to the air. In doing this the oils are changed from a liquid to a solid, forming a hard, transparent film.

Linseed Oil.—This oil possesses the power of absorbing oxygen to a greater degree than any other oil. It consists of glycerides of isolinolenic, linoleic, linolenic and oleic acids, all of which are unsaturated. Its name comes from the *line*, or fiber, of the flax stalk, the oil being obtained from the seeds of the flax plant. Flax is grown over central, northern and western United States, Minnesota and the Dakotas being leading producers of seed. Plants when raised for their fiber are pulled up before the seeds are ripe. These seeds must be allowed to age several months before pressing, and then the quality of the oil obtained is not nearly so good as that from the ripe seed. However, the seed is generally the object of cultivation, the fiber not being used.

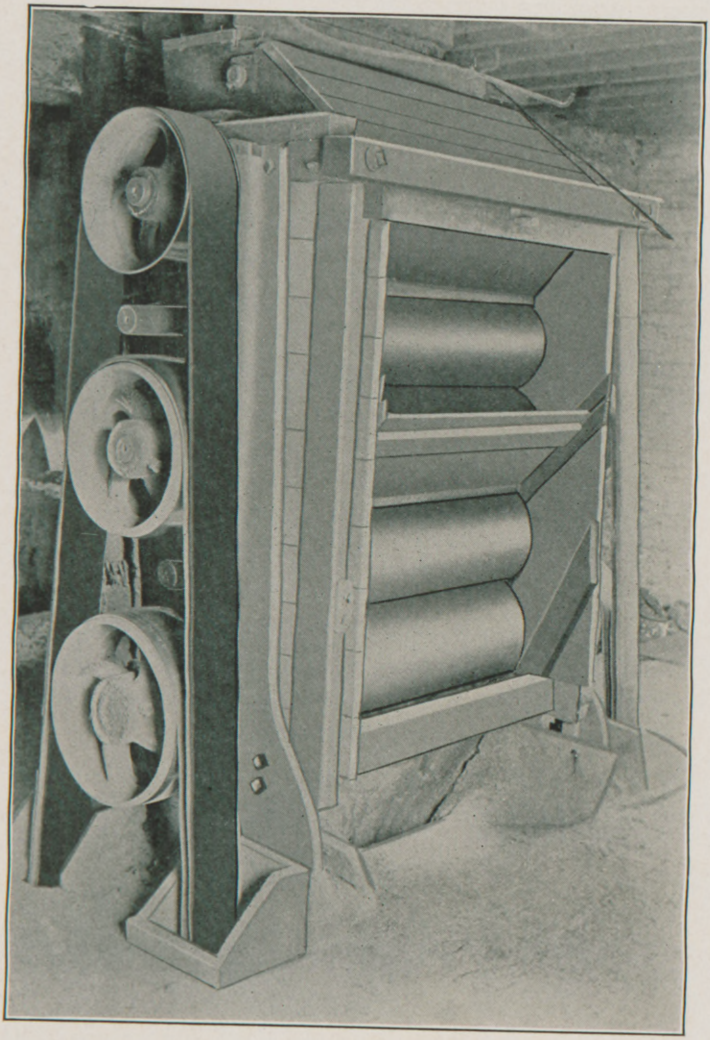


Flaxseed Sifter

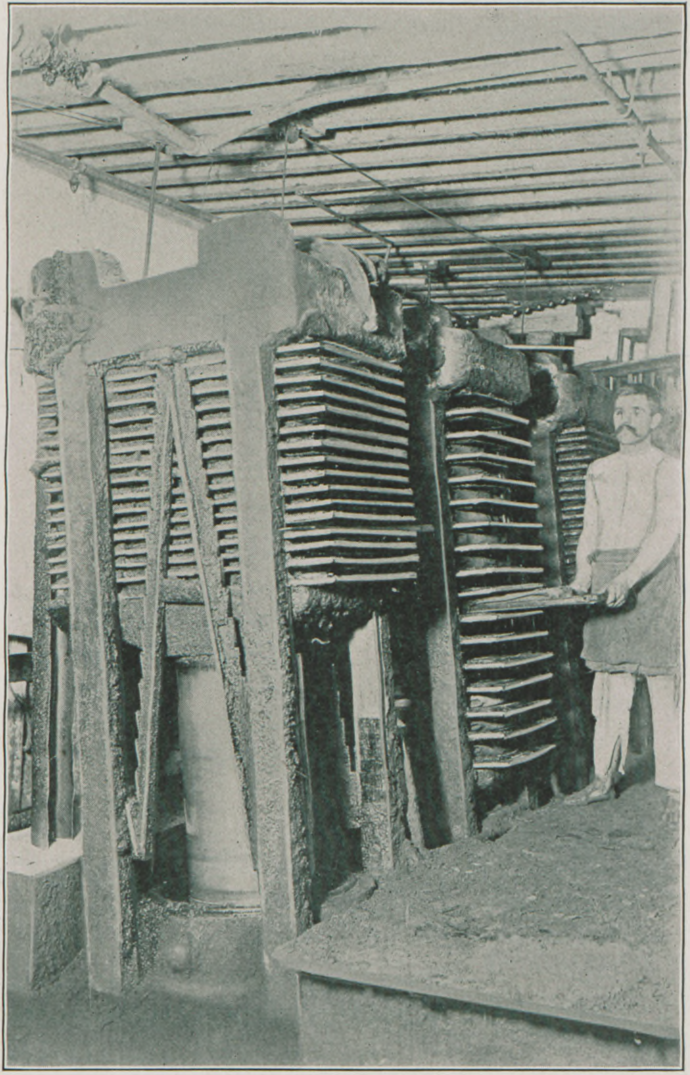
The oil may be separated from the seed after crushing, either by subjecting the meal previously heated to 80° C. to a hydraulic pressure of two tons per square inch, or by a continuous process in which the crushed seeds are fed in at one and and the pressed meal comes out at the other. The oil may also be extracted by naphtha, though there are some objections to this process. To remove impurities the oil is allowed to stand from four to six months, the clear layer resulting being the raw linseed oil.

The drying of oil is made more rapid by heating it at about 150° C. with small amounts of lead or manganese compounds. As the lead compounds tend to cause contraction of the oil upon oxidation and the manganese compounds to cause expansion, it is customary to use small amounts of both, the metallic lead content being about 0.5 per cent. and manganese about 0.02 per cent. By such treatment the so-called boiled oil will dry in from 8 to 24 hours while the raw oil requires 72 hours.

Other Oils.—For twenty years before 1909 the price of linseed oil averaged forty cents per gallon. In that year a notable advance occurred and by September 1910 a price of one dollar was reached. The result of this increase in price caused the introduction of a number of other oils. Among these were Chinese wood, fish (such as menhaden), soya bean, rosin and mineral oils. The addition of these oils is under certain conditions an adulteration, the last two being more commonly used because cheaper. On the other hand it is claimed that for



Flaxseed Crushing Rolls



Hydraulic Press for Extracting Linseed Oil many uses, such as the manufacture of linoleum, lithographic inks and patent leathers, the addition of given amounts of certain of these oils is a decided advantage.

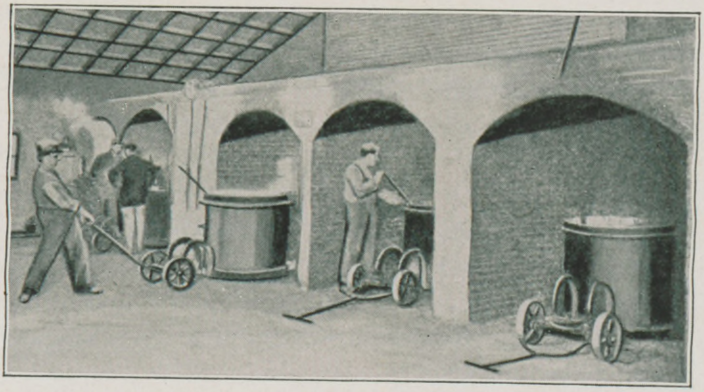
Driers.—These substances seem to depend for their efficiency upon catalysis. They may be considered under two classes: oil driers and japan driers. The use of oil driers has been previously mentioned; litharge, red lead, lead borate or acetate and manganese dioxide are the materials generally used. The japan driers are liquids, being rosinates or linoleates of lead or of manganese, dissolved in turpentine. In this state they mix readily with oils at ordinary temperature and their action is rapid (4).

Solvents and Diluents.—A number of light, volatile liquids which dissolve oils are used to thin paints. Of these turpentine for many years was practically the only one used. This liquid is a product of the long-leaf pine growing in southeastern United States, and is obtained from the distillation of the sap, or as wood turpentine by distilling the chips (6). Rosin or colophony is left in the still when the sap is distilled. Because of its long use, the substitution of any other liquid for turpentine was considered an adulteration. This is clearly an adulteration, if it is claimed to be pure turpentine. Though many still claim turpentine to be entirely superior to all of its substitutes, it is stated by others that benzine made by passing certain paraffine oils with wood turpentine over red-hot coke gives equally satisfactory results.

Petroleum is, of course, the source of paraffine oils. Other mineral products such as those obtained by the distillation of coal tar are also used as turpentine substitutes.

Varnishes

The term resin is applied to a variety of products obtained from the exudation of trees and these may be considered as recent or soft resins, and fossil or hard resins. When resins are dissolved in some suitable solvent a varnish is formed which may be applied to form a hard, lustrous and usually transparent coating upon wood or other material (7).



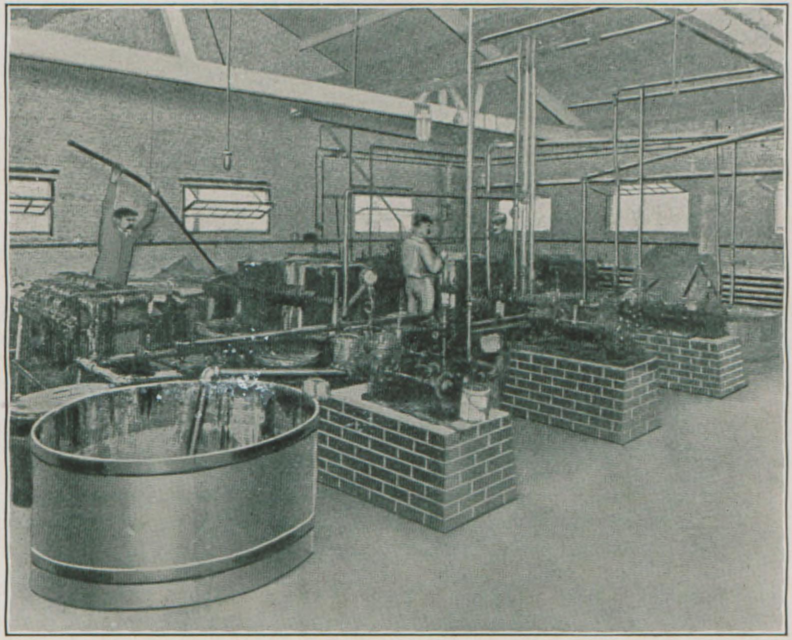
Varnish Stacks and Kettles for Dissolving Resins

The recent resins are the products of trees now living, the most common being rosin from the pine, dammar, a product usually obtained from southern Asia, and lac. Lac, which is the material from which shellac is made, is not the direct exudation of the tree, but a resinous excrement of a parasitic insect, a native of India. The name, lac, is an Indian term for 100,000, indicative of the number of these insects (8). The purified shellac is dissolved in alcohol or other volatile solvent and gives a hard and highly elastic coating.

Lacquers are spirit varnishes made from shellac or similar material, dissolved in a volatile liquid. They are applied to metals as well as to wood. In addition to those made from the resins lacquers are also made from pyroxylin, which is a nitrated cotton (see p. 73).

The fossil resins have been formed by the exudations of trees of a previous age and are dug from the earth frequently at a depth of several feet. These include amber and the copals. Amber makes the hardest of varnishes, but on account of the expense of it and the hard copals, kauri is widely used in place of them. This is a soft copal from New Zealand and Australia. The fossil remains are always used as oil varnishes, the oxidation product of the oil remaining in the coating with the resin. If desired, coloring matter may be added to varnishes before application.

Bakelite is an artificial resin-like substance perpared by boiling equimolecular proportions of carbolic acid and formaldehyde under carefully controlled conditions in the presence of small amounts of ammonia or caustic soda. By condensation and the giving off of water a product is formed which is soluble in alcohol, acetone and other solvents, making possible its use as a varnish. This material discovered by Dr. L. H. Baekeland, an American, was patented in 1907. Since that time this form A and both Bakelite B and Bakelite C formed from A by heat, have had a wide variety of uses (9).



Varnish Filtration

Prepared Paints and the Chemist.—Half a century ago each painter mixed his own colors, frequently hand ground, with his white lead at a great cost in labor and time and with the impossibility of reproducing exactly a given product. The growing conviction that the addition of some other material to white lead made a better paint, together with the well known difficulties encountered in hand mixing, made possible the introduction of prepared paint products. At first prepared paints were not successful because not mixed with brains, that is not carefully or scientifically prepared.

As stated by Gardner (10):

> " These conditions, however, soon changed, and with the introduction of laboratories under the supervision of trained chemists, the manufacture of prepared paints rapidly developed into an industry in which the processes were controlled by the application of scientific principles and in which the raw materials used were most carefully examined for their chemical purity and physical properties."

According to the Census of Manufacturers in 1914 the paint and varnish industry totalled nearly $150,000,000, three-fourths of which was for paint.

Paints, stains and varnishes for almost every conceivable use are now on the market in a generally satisfactory form. Cement, metal, marine, bituminous, wall, barn, enamel, automobile, floor paints give some idea of the extent and variety possible. The use of paint ingredients extends to many industries which do not occur to one on first thought. Thus, in the manufacture of oil cloth and linoleum, of wall paper and window shades, of leather and of rubber goods, many of the materials used are the same as those used by the paint manufacturer.

Of their use in printing the following list of purchases of the Bureau of Engraving and Printing, Washington, for a pre-war year will give an idea:

White	Pigments	802,200 pounds
Black	"	297,500
Blue	"	52,000
Green	"	180,000
Red	"	68,200
Yellow	"	200,000
		1,599,900 pounds

Of this Toch says (11):

" These pigments are identical in every respect with those used for general painting, and yet all these pigments are used for the purpose of printing the currency and the postage stamps of this Government."

The increased use of paint materials has without doubt made, not only for improved sanitary conditions and more beautiful surroundings, but also for economy on account of the protection from rot and rust resulting from the action of the atmosphere and of moisture.

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CHAPTER X

RUBBER

When first introduced rubber was considered largely as a luxury. At present in its wide variety of manufactured products, it is a necessity for the carrying out of many lines of industry, and at the same time adds much to the comfort of life. Though known for more than two centuries before, its present name was given to it by Joseph Priestley in 1770, because it removed pencil marks by rubbing. This was four years before his noted discovery of oxygen.

Source.—Certain tropical plants are noted for a milky juice or latex (different from the sap), which is found in the stems, leaves, bark and roots of trees, vines and shrubs. This latex is an emulsion somewhat similar to that of our common milkweed. Upon analysis of the latex from plants growing in the Amazon jungles of Brazil, which furnish the best rubber, these results are obtained (1):

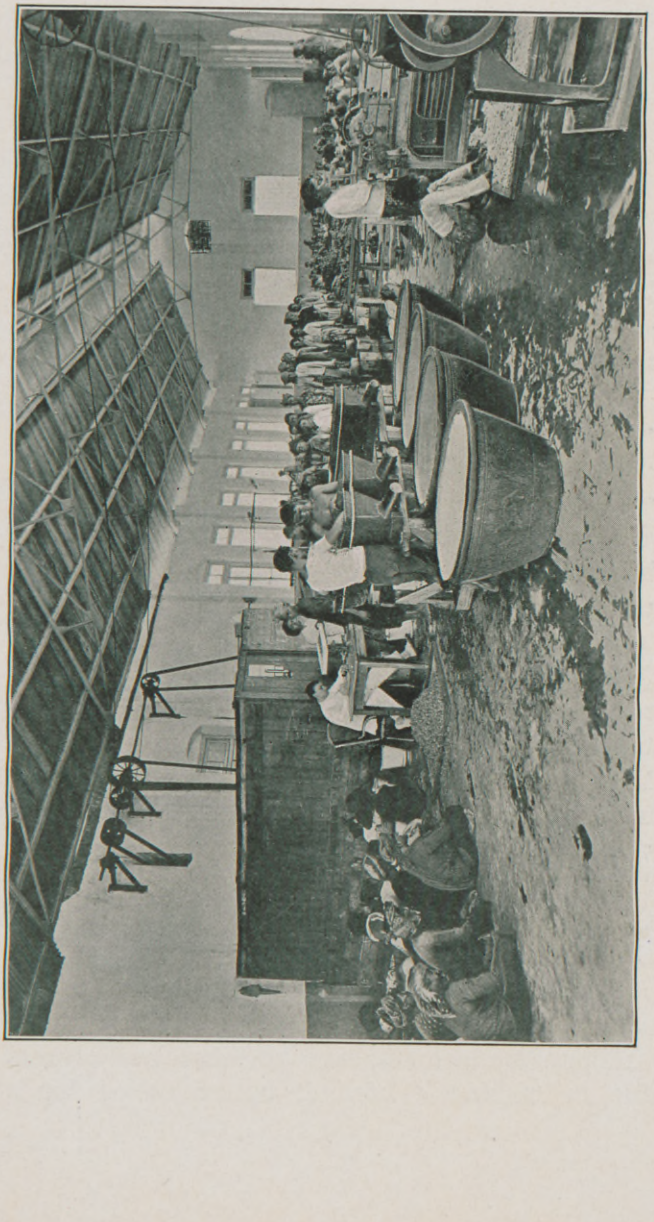
	Per Cent.
Water	55.
Rubber	38.5
Proteins	3.
Resins	3.
Mineral matter	0.5
	100.0

This analysis gives an idea of the composition of this latex, but there is considerable variation.

Java-Tapping Rubber Tree

In Brazil the trees are tapped when twelve to fifteen years old, the season being from July to November. The yield per tree is about ten pounds of milky juice, or three to four pounds of rubber daily (2). Rubber plantations are now in existence in many tropical countries using plants brought from the Amazon. The cultivated plants are tapped in the fifth or sixth year. Two-thirds of the world's production of 427,000 pounds in 1916 was plantation rubber, though this cultivated rubber does not seem to be exactly the same as the product of the wild varieties with which most of the plantations were originally stocked (3). In addition to the 2,000,000 acres of rubber plantations in the tropics, another possible source of supply is from the guayule shrub grown by irrigation in the United States (4). This is considered by some as a substitute.

Preparation for Market.—The rubber globules must be caused to unite and fermentation of the protein material must be prevented before shipment. This is done in several ways: by heating and exposing thin layers to wood smoke, by the use of a centrifugal machine, or by the use of chemicals. Dilute acetic or formic acid, solutions of salt, alum or carbolic acid may be used. Originally in the Amazon region, called the Para district because of the shipping port, a paddle was dipped into the latex and turned in the smoke of a slow fire; this was repeated until a considerable ball or " biscuit " was formed. In the Congo, natives are said to drive off the water of the latex by smearing it over their naked bodies.

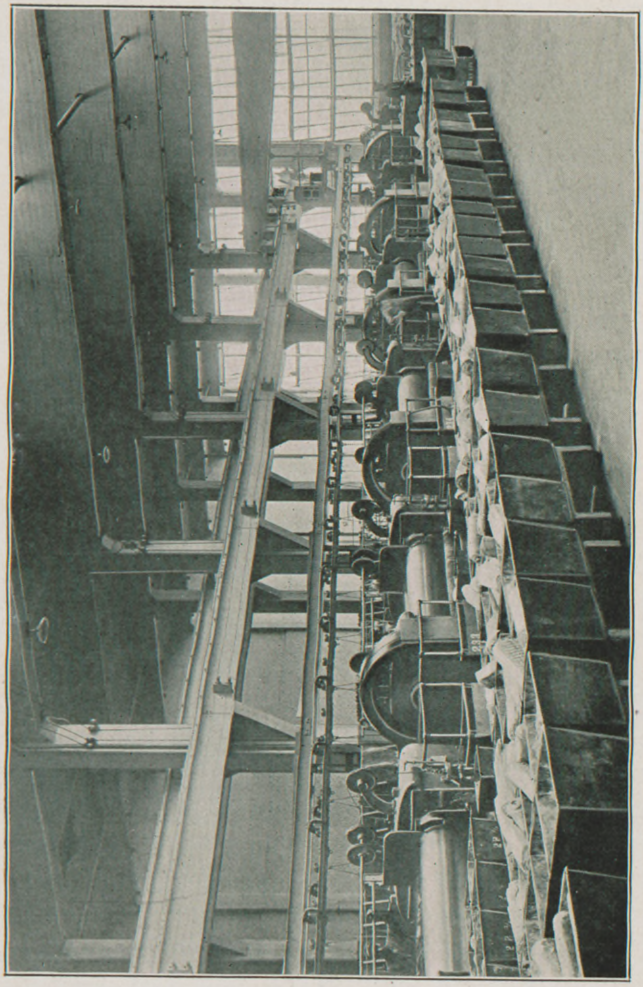


Java—Interior of Treating Plant of an American Rubber Company

For the removal of bark, twigs and mineral matter from the crude rubber, it is sliced and macerated between rolls and washed with water. This causes considerable loss in weight, especially in the poorer and more impure grades.

Vulcanizing.—Rubber would never have obtained its present wide usefulness, except for the marked change in its properties when it is treated with sulfur. Pure rubber is soft and sticky in hot weather, and hard and brittle in very cold weather. After being treated with sulfur, or vulcanized, it becomes much less sensitive to temperature changes, increases in elasticity and tensile strength, and becomes much more durable when exposed to the weather or to the action of chemical reagents. Vulcanization is usually carried out by heating the rubber with sulfur. When more highly heated 100 pounds of rubber will take up as much as 30 pounds of sulfur, which is the amount used in the making of hard rubber or ebonite. For ordinary vulcanization, however, much less is used, soft rubber frequently containing not more than two per cent. of sulfur. After proper vulcanization rubber material containing 40 per cent. pure rubber should stretch seven times its length and return to its original shape. The vulcanizing of rubber was first discovered by Charles Goodyear of New Haven, Conn., in 1839 (5).

Added Materials.—Many materials of both mineral and organic origin are added in the manufacture of rubber products. Some of these are of real value in making a product better suited for a



Mill Room Showing Mix Mills and Bins Containing Rubber and its Compounds of an American Rubber Company special use, while others are mere fillers. In the former class may be placed certain metallic oxides or sulfides, such as those of lead, zinc or antimony, while powdered chalk and barytes are frequently used as fillers. Manufactured goods containing textiles make up a very large and important part of the rubber industry.

Synthetic Rubber.—Rubber, or caoutchouc, is a polymer (many parts) of polyprene ($C_{10}H_{16}$), that is, it contains a number of molecules of polyprene which are in some way combined, the formula for rubber being $(C_{10}H_{16})x$; in other words a molecule of rubber contains x molecules of polyprene. The power of taking up sulfur in vulcanization seems to be due to the presence of unsaturated valency bonds (6).

When subjected to destructive distillation rubber yields among other products the compound, isoprene (C_5H_8), which can be caused to polymerize with the formation of rubber. Erythrene (C_4H_6) under proper treatment can be changed to rubber. If, therefore, these substances can be produced in sufficient quantities and at a low enough cost, the preparation of synthetic rubber would seem to be assured. Isoprene has been made from turpentine, from fusel alcohol, and from starch, sugar, and sawdust. Erythrene has also been made from acetone and other materials. Based on this and similar principles, several processes for the manufacture of synthetic rubber have appeared. Whether or not it will be done on an extensive scale is largely an economic question depending upon the cost of the materials required and of the process of manufacture, as compared with that of producing the natural rubber.

Synthetic rubber was produced on a large scale at Leverkusen in Germany during the War, though the process was very expensive (7).

Reclaimed Rubber.—After removing as much of the fiber as possible by mechanical means the old rubber products are treated with warm dilute sulfuric acid to destroy the vegetable fiber remaining. This is followed by heating with dilute caustic soda solution under pressure, which removes the remainder of the fabric and the uncombined sulfur. This process devised by Mitchell of Philadelphia does not devulcanize the rubber, but does give a product which is preferred by manufacturers to other organic fillers. In fact it is considered superior to some of the poorer grades of crude rubber.

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CHAPTER XI

ELECTROCHEMISTRY IN INDUSTRY

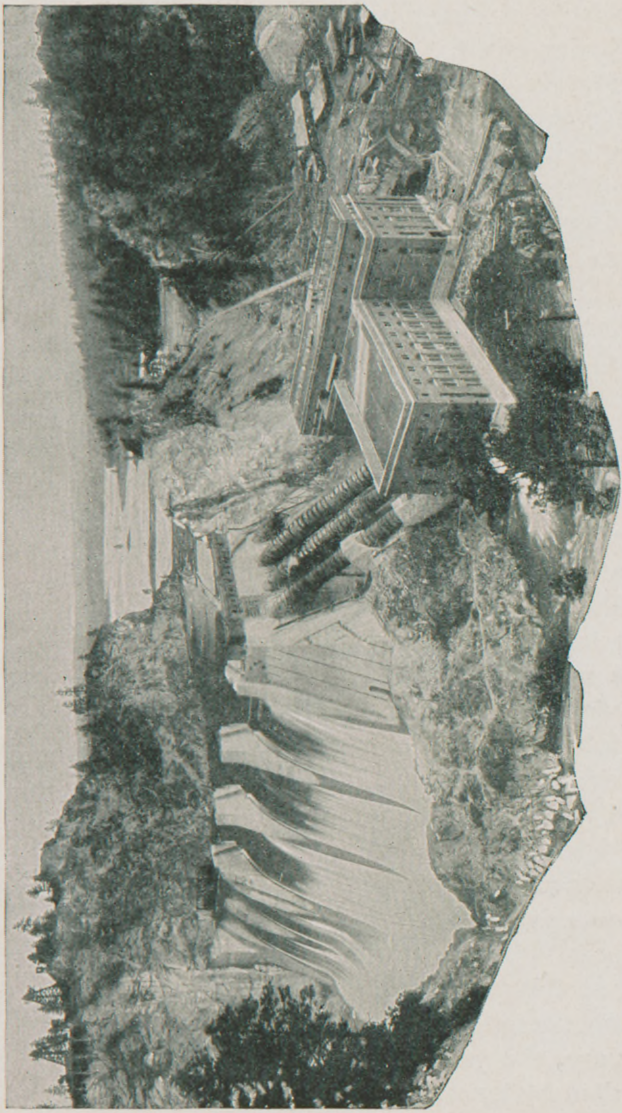
Although Davy more than a hundred years ago used the electric current for the discovery of the alkalies and the alkaline earth metals, and his assistant and pupil, Faraday, made most valuable contributions to the field of electro-chemistry, yet any extensive use of the current in industry must of necessity date from its production upon a commercial scale. Hence practically all of the applications of electro-chemistry to industry are confined to the present generation.

In this development America has played a most important part. The magnificent electro-chemical industries at Niagara Falls continually testify to the genius and perseverance of such chemists as Hall, Castner, Acheson, Willson and Baekeland, as well as to the energy and business ability of many other Americans (1).

The electric current has two distinct uses in chemical work: its use upon substances in the liquid form, either in solution or in a fused state; and its use as a source of heat. We shall briefly review first this electrolytic use and then the electrothermal.

Electrolytic

The electrolytic action of the current may be considered under three heads: (1) metals, (2)



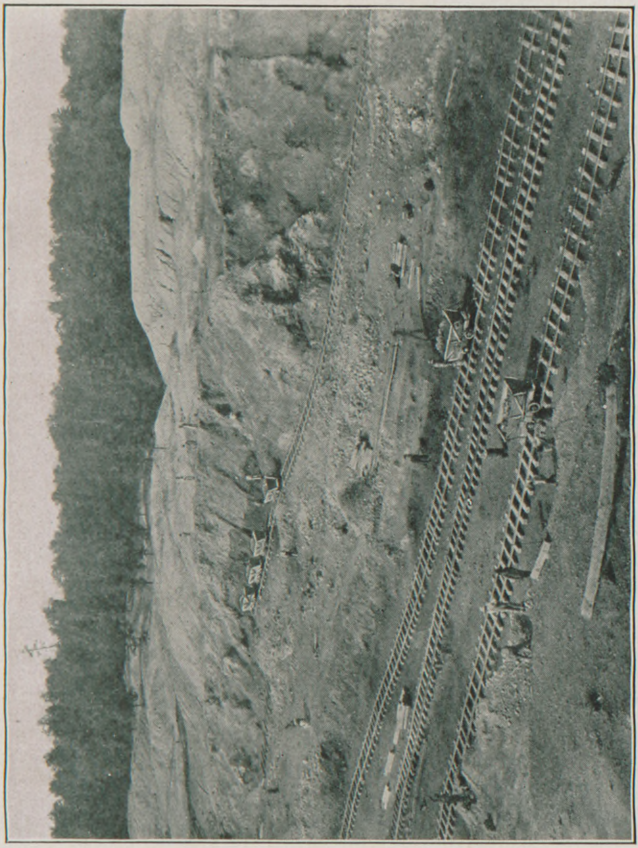
Hydro-Electric Plant and Development—Power From one of the Greatest Natural Resources products of electrolysis of salt, (3) oxidizing and reducing effect.

Metals.—The first use of the current commercially was in the electroplating of metals, and this method is still widely employed for a number of metals, such as copper, silver, gold, zinc and nickel and even in the plating with an alloy, such as brass from a cyanide solution of both copper and zinc.

The electro-refining of copper surpasses any other process for the production of pure copper, a purity of 99.9 per cent. being obtained. Lead, silver, gold, nickel, bismuth and antimony can also be so refined.

Davy's principle of obtaining sodium, potassium and calcium is applied to-day upon a commercial scale by using the current upon fused salts of these metals.

Probably the most important metal prepared by electrolysis is aluminum, in the preparation of which the method proposed by Chas. M. Hall, while a student at Oberlin College, is commonly used. Aluminum oxide obtained from bauxite is dissolved in melted cryolite, which is a double fluoride of sodium and aluminum. To set free the aluminum a high power current is required and 25,000 kilowatt-hours per ton of metal are consumed. Consequently it is cheaper to bring the purified ore to a point where electricity can be cheaply obtained as at Niagara Falls. In 1883 shortly before the announcement of the American college boy's discovery, the yearly production of aluminum in the United States was 83 pounds. Now it is more than



Mining Aluminum Ore, Bauxite, Arkansas

a million times as much. Silicon is also prepared by the electrolytic use of the current.

Electrolysis of Salt.—The electrolysis of a salt solution is by no means so simple as it may appear, and to meet the difficulties that have arisen in the commercial process much ingenuity has been shown. The sodium liberated at the negative pole at once tends to form sodium hydroxide with the evolution of hydrogen. The chlorine liberated at the positive pole forms with the sodium hydroxide sodium hypochlorite in the cold and the chlorate if heated. By combining hydrogen with chlorine by properly controlled explosions hydrochloric acid is produced.

To prepare metallic sodium fused salt and a mercury cathode are used. With both the fused electrolytes and with solutions diaphragms are used to prevent premature mixing of the products of electrolysis. From common salt and the electric current as a beginning, metallic sodium, chlorine, hypochlorites, chlorates, perchlorates and hydrochloric acid may be prepared, the hydrogen and oxygen when needed being furnished by the water (2). For this process we are largely indebted to the labors and discoveries of Castner in the early nineties. Baekeland later did valuable work along the same line (1).

Oxidation and Reduction.—Upon the electrolysis of water containing a small amount of sulfuric acid, hydrogen and oxygen are liberated. These gases are now collected and put on the market on a commercial scale. The oxidizing effect produced at the anode and the reducing effect at the cathode are used in the production of a number of organic compounds, only a few of which have as yet been produced upon a large commercial scale. Thus a 20 per cent. salt solution to which acetone has been added gives chloroform upon the passage of the current (3).

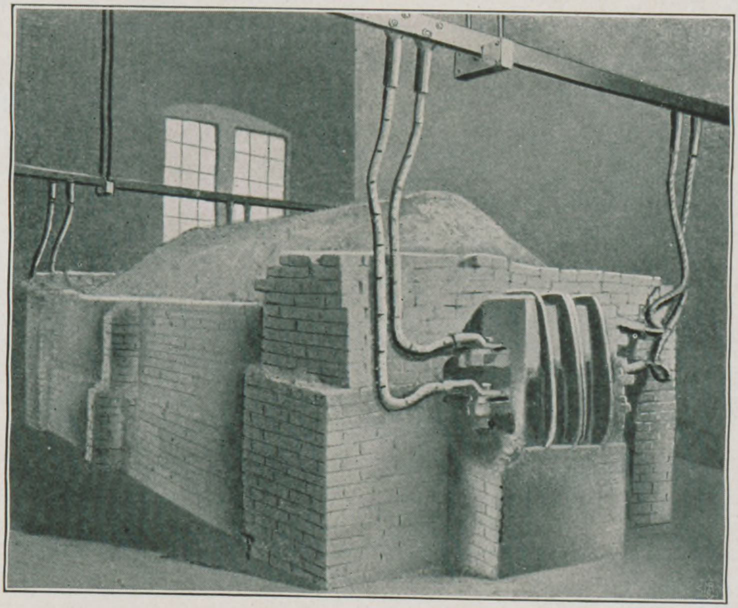
Much might be said of the use of the current in electroanalysis, in the development of which Americans have been leaders. Thousands of rapid determinations accurately and easily made by its aid assist the chemist in his control of industry (4). Other electrical laboratory appliances are of the greatest convenience and help.

Electrothermal

The successful use of the electric furnace by Messrs. Cowles of Cleveland in 1883 showed possibilities before unknown, for by this use of the current the highest known temperatures at the exact point desired can be secured with accuracy of control. This may be done under special conditions, if desired, as for example, in a reducing atmosphere. Of all the applications of the electrothermal effect of the current it is impossible to write, but some of its products may be thus classified: (1) carbon compounds, (2) nitrogen compounds, (3) iron and steel alloys, (4) a variety of products, such as phosphorus, ozone, alundum, etc. (5).

Carbon Compounds.—The commercial production of calcium carbide about 1899 by " Carbide "

Willson at Spray, N. C. by heating a mixture of coke and lime in an electric furnace, not only furnished a valuable product, which later became an efficient source of acetylene, and still later of the fertilizer, calcium cyanamid, but under the stress of the recent war this acetylene was transformed into acetone, acetic anhydride and cellulose acetate, materials much needed in the manufacture of explosives and airplane " dope."



Electric Furnace, Making Carborundum

Silicon carbide, or carborundum, is formed when silica in contact with an excess of carbon is heated to the high temperature obtained in an electric furnace. This artificial abrasive has very largely replaced the natural corundum, or emery, being in almost universal use except in glass grinding. The overheating of a carborundum furnace led to the discovery of artificial graphite, which is in many ways far superior to the natural product. Pure carbon alone does not change into graphite on heating, as it must first be changed to a carbide of some metal. To accomplish this anthracite coal with 8–10 per cent. of ash evenly distributed thru it is used. This material may be molded into the desired shape and made into graphite, or it may be graphitized and then molded, the product being quite pure, running 99.5 per cent. graphite. This purity is due to the volatilization of other material at the high temperature of the furnace. The use of this graphite for electrodes has been so perfected that it is now possible to screw a new electrode onto the end of the old without interrupting the process. Electrodes with a diameter greater than 17 inches are now made. The processes for both carborundum and graphite were invented by E. G. Acheson of Niagara Falls, the one in 1892, and the other in 1895 (6).

Carbon disulfide is made by heating a mixture of sulfur and charcoal in an electric furnace in which the sulfur vapor combines with the heated charcoal. The process is practically an automatic one.

Nitrogen Compounds.—The use of electricity in the fixation of atmospheric nitrogen has already been discussed, as has the use of the electric furnace in the making of calcium carbide to be changed into calcium cyanamide. (See chapter IV.)

Iron and Steel. Alloys.—For a number of years electricity has been used for heating iron and steel furnaces, more especially the latter, in which steel was purified at a very high temperature after having been treated by the Bessemer or open hearth process. On account of freedom from dissolved gases and oxides as well as from phosphorus and sulfur, this duplex process gives a superior steel.

In the preparation of alloys which were formerly made in crucibles of imported clay, the electric furnace has in recent years been particularly useful. In 1913 there were 19 furnaces in use in the United States for this work, while in 1917 233 furnaces thus made 750,000 tons of alloy steels. The metals used with the iron are chromium, manganese, molybdenum, nickel, silicon, titanium, tungsten, uranium and vanadium, adding when properly used, toughness, hardness, strength and elasticity. For example ferrochrome is used in making armor plate, ferro-tungsten in giving a tool which holds its cutting edge at a high temperature (7). In his address before the American Electrochemical Society, April 3, 1919, President Tone said (8):

> " No one now doubts that we shall soon attain to supersteel and it is no less clearly indicated that this will be accomplished by the electric steel furnace and electrically produced alloys. . . . Such steel produces rails which do not break and plates which do not fracture. . . . The alloy steels have made possible the modern automobile, the aeroplane engine and the farm motor tractor."

Quantity output of quality steel by means of the electric furnace is to be expected. The largest plant of this kind in the world is at South Chicago (9).

Varied Products.—Phosphorus is obtained from the calcium orthophosphate of either rocks or bones by heating it with sand and carbon. Ozone is formed from the oxygen of the air upon passing air between the terminals of a high-tension alternating circuit. Alundum is an abrasive made by the electrical treatment of a mineral containing aluminum oxide.

These materials differing so greatly are indicative of the very wide field of usefulness open to electrochemistry. There are many processes now in the laboratory stage which are not mentioned here, but some of these are certain to become of commercial importance.

During the War our Government invested a billion dollars in electro-chemical plants. This large production and application of electric power is bound to have an increasing effect upon industry.

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CHAPTER XII

ACIDS

In the consideration of acids the chief emphasis will be laid upon the three common mineral acids, sulfuric, nitric and hydrochloric, or muriatic, not only because of the larger amounts of these acids manufactured, but also because of their use in the manufacture of other acids.

Sulfuric Acid the Most Important.—It has been often stated that the consumption of sulfuric acid is an indication of the degree of civilization a nation has attained. This far-reaching statement can be justified by thinking of the use of this acid in the preparation of fertilizers, in the refining of petroleum, in the reclaiming of rubber, in the manufacture of dyes, and in the preparation of very many chemicals. Hundreds of industries which contribute largely to man's progress, prosperity and happiness depend either directly or indirectly upon this acid. Not only is the amount of its production indicative of the progress of a nation in times of peace, but because of its use in the manufacture of explosives it is even more exactly a measure of the war activities of any people.

This acid has been long known, the earliest record being that of the Arabians in the eighth century. As early as 1740 its manufacture on a commercial scale was carried out by an Englishman, Ward, who burned sulfur and nitre together, condensing the vapors in glass vessels containing small amounts of water. The largest plants to-day are in the United States (1).

In principle sulfuric acid making is exceedingly simple. Sulfur burned in air, or a sulfide roasted, that is, heated in air, forms sulfur dioxide. If this sulfur dioxide can be made to combine with another atom of oxygen forming sulfur trioxide, and water is added to the trioxide, sulfuric acid is formed. But sulfur dioxide does not easily take up an additional oxygen atom, and to cause it to do this cheaply and readily is the problem of the sulfuric acid manufacturer.

Two methods are in use for the manufacture of this acid: the lead chamber and the contact. The one is carried out in lead lined chambers, where oxides of nitrogen cause the increased oxidation of the sulfur dioxide and form the acid in a rather complicated series of reactions; in the other sulfur dioxide and oxygen are passed over heated platinum black (asbestos covered with a thin coating of platinum) or other catalytic agent, contact with which causes the formation of sulfur trioxide. In recent years lead chambers of very large size have been built, one in use at the plant of the Tennessee Copper Co. being 59 x 236 x 40 feet, enclosing more than half a million cubic feet. The total chamber space in use at this plant is over 6,000,000 cubic feet, and the daily capacity is 900 tons of sulfuric acid (60° B.) (2).

The sulfur dioxide used in this country was largely obtained before the War by burning or roasting pyrites, or iron sulfide, brought from Spain. In many plants by-product sulfur dioxide, obtained from copper, zinc or other metal smelters, is used, thus making valuable a very objectionable by-product, hitherto wasted.

Acid made by the lead chamber process is not concentrated and its concentration is difficult. The contact process, however, gives a concentrated acid of any desired strength and of a greater degree of purity than that readily obtained from the chamber process. On the other hand, the contact process requires greater care in operation, as the reaction is reversible, and the presence of certain impurities in the sulfur dioxide will " poison " the catalyzer and make it inactive.

Much sulfuric acid is manufactured and consumed in the same plant, so that an exact statement of the total production is difficult. The approximate production of sulfuric acid in 1913 is given in the table below. The present production is considerably higher, while the production of the United States while engaged in the World War was fully twice the figure here given (3).

United States	3,500,000	long tons
Germany	1,650,000	"
Great Britain	1,150,000	"
Italy	640,000	"
France	550,000	"
Belgium	350,000	"
Russia	260,000	"

Nitric Acid.—This acid, also long known, was called by the ancients aqua fortis, or strong water.

It is usually made by treating sodium nitrate, or Chile saltpeter, which is brought from South America, with concentrated sulfuric acid. The production in 1914 calculated from figures given in the U. S. Census of Manufacturers was an equivalent of 89,000 tons of 100 per cent. nitric acid made from some 160,000 tons of nitrate. As actually used this amounted to 78,589 tons of acid of average strength and 112,124 tons of mixed acid (sulfuric and nitric). During the War the tremendous demand for nitric acid needed in the manufacture of explosives caused an estimated yearly production of 650,000 tons of 100 per cent. nitric made from 1,000,000 tons of nitrate (4).

The increased ratio of nitric acid produced to nitrate consumed shows that during the war period the efficiency of the process was increased. This was due to many improvements. High silica iron, which is acid proof, was used to largely replace other kinds of apparatus. Economy in operation was practiced, so far as possible.

The preparation of nitric acid by sparking the air has not thus far been successfully carried out on a large scale in the United States. However, nitric acid formed by the oxidation of ammonia, has been made on a commercial scale, and at the time the armistice was signed a number of plants for this purpose were under construction. It is claimed that this process will be the chief one in use in this country (5). Whether this is correct, or not, will depend entirely upon economic conditions, in which our enlarged merchant marine may be a decisive factor. (See chapter IV.)

Hydrochloric Acid.—Originally this acid was a very troublesome by-product in the Leblanc process of manufacturing soda. It is still manufactured, as in that process, by treating common salt with concentrated sulfuric acid and heating, the hydrochloric acid passing off as a gas. This gas is cooled and dissolved in water, in which it is very soluble, either by passing it thru tall towers filled with coke over which the water trickles, or thru several large wash bottles containing water. The sodium sulfate, or salt cake, is in considerable demand, being used by glass makers, in dyeing, and to some extent in medicine. The normal sulfate is called Glauber's salt after purification and recrystallization, in which process it takes up ten molecules of water of crystallization (6).

Muriatic acid is the commercial name given to this acid, being derived from the Latin word for brine. Though frequently used in the chemical laboratory and in some industries, this acid has not the importance of sulfuric acid. This is seen in the fact that its production in 1914 was 168,000 tons, less than one-twentieth of that of sulfuric acid.

Acetic Acid.—This organic acid is obtained in an impure state in the destructive distillation of wood. To purify it calcium acetate is formed by neutralization with lime followed by evaporation. Upon distillation of the calcium acetate with sulfuric acid pure acetic acid is obtained. It is used in the making of acetates, some of which are of value in medicine, in the preparation of white lead, and in the manufacture of dyes and explosives. It is found in a dilute form in vinegar, being formed by the oxidation of the alcohol present in the cider. The 1914 production of 37,000 tons was greatly increased during the War.

Other Acids.—Oleic and stearic acids, obtained from animal fats, rank next in the amount produced. These are followed by phosphoric, boric, hydrofluoric and citric acids, the production of each being less than 10,000 tons annually.

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CHAPTER XIII

METALS

Importance.—The total value of all mineral products in the United States in 1913, the last normal year, because the last before the World War, was approximately two and a half billion dollars. Of this a little more than one-third, or $883,000,000 was for metallic products (1).

Occurrence.—Some metals occur in the native or free state, as is frequently the case with gold. In most cases, however, the important ores are the oxides and sulfides, with the carbonates and silicates being of less importance. The term mineral is sometimes used to designate any substance which comes from the ground, being derived from the same root word as mine. An ore is a mineral containing a metal which may be extracted with profit. Thus ordinary sandstone is a mineral containing some iron, but it could not be called an ore of iron.

Metallurgy.—The science of extracting metals from their ores is called metallurgy. Due to increased application of chemical principles and to the use of the electric furnace this science has advanced very rapidly in recent years. Mainly because of this has the increased use of metals been made possible. During the 33 years preceding the outbreak of the War in Europe the population of the

United States approximately doubled. Comparing this ratio in population with that of the value of the metals produced in 1880 with the production in 1913 we have calculated these ratios (1):

	1880		1913
Population	1	:	(nearly) 2
Silver	1	:	1.2
Gold	1	:	2.5
Lead	1	:	3.7
Iron	1	:	5.2
Copper	1	:	16.5
Zinc	1	:	16.6
All metals	1	:	(nearly) 6

It will be noticed that while the population has doubled, the production of metals has increased in value six times. In other words the increase in value in metallic production has been three times as great as increase in population; and this, too, before the high level of war prices.

The two methods in general use for the extraction of metals from their ores are: the reduction of the oxide with carbon in the form of coke, and in some cases coal; and by electrolysis. Iron and zinc are metals produced by the first of these methods and aluminum by the electric current. The use of one metal to set free another from its compounds, as the liberation of antimony from its sulfide by heating with iron can obviously be used only in the case of the more valuable metals. The use of hydrogen to reduce oxides is too expensive except in unusual cases. Crude petroleum for the reduction of zinc ores has been suggested, but thus far has not proven practical on a large scale (2).

Iron

Of the total value of metals mentioned at the beginning of this chapter almost exactly one-half is due to pig iron (1). The United States produces far more iron and steel than any other nation, her total output being fully forty per cent. of the world's production.

In the production of iron ore Minnesota, Michigan and Alabama are the leading states. The first two states furnished more than four-fifths of the entire output of the United States in 1914. In 1917 the iron ore mined in this country was 75,000,000 tons, more than four times the 17,000,000 produced in 1897, twenty years before (3).

Supreme Importance.—Iron is undoubtedly the most important of the metals. Were all the gold of the world destroyed by magic, after the financial convulsion had adjusted itself to the loss of this measure of value and some new standard had been agreed upon, industry would move on at its usual speed. With iron similarly removed, industry would be pitifully helpless. There would be practically no tools or machines with which to work, and worse still nothing to make them with and little from which they could be made. The abundance of iron, the comparative ease with which it may be obtained from its ore, its strength and its adaptability are the chief reasons for the wonderfully important part it plays in human affairs. Of its adaptability Bradley Stoughton says (4):

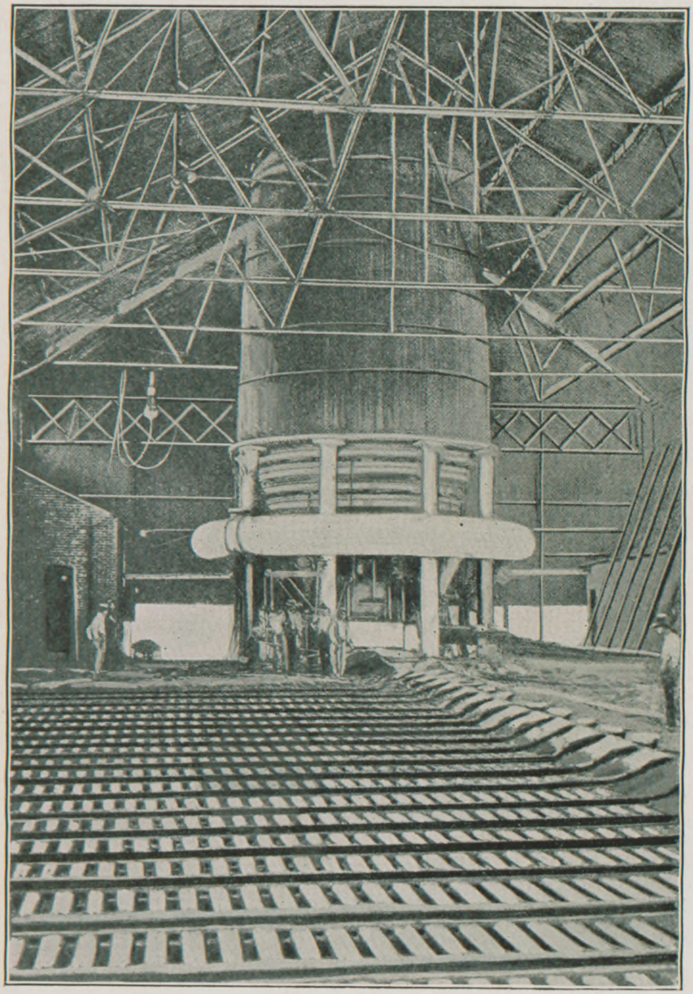
" Iron can be made either the strongest or one of the weakest of metals; either the most magnetic or one of the non-magnetic metals; one of the hardest or one of the softest; one of the toughest or one of the most brittle; it may have a coefficient of expansion with changes in atmospheric temperature varying from almost zero to a maximum, 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 per cent. of the mass, or by giving it a different heat treatment, or by both together."

Ores.—The important ores of iron are all oxides:

Hematite, sometimes called red hematite	Fe_2O_3
Limonite, sometimes called brown hematite, which is a hydrated form	$2Fe_2O_3.3H_2O$
Magnetite, a ferrous-ferric oxide, usually written Fe_3O_4	$Fe_2O_3.FeO$

Hematite is by far the most important of these, making up more than 90 per cent. of the iron ore mined in the United States.

Reduction. Cast or Pig Iron.—If necessary to remove moisture the ore is heated. But usually together with coke and a flux, limestone for most ores, it is placed in a cylindrical blast furnace, generally 12–14 feet wide and 90–100 feet high. Under the influence of the blast of air the carbon reduces the iron oxide, either directly or more generally by the reducing action of carbon monoxide. The molten iron is drawn off at the bottom in the form of pig iron. The process is continuous, ore, coke and the flux being fed in at the top, and the slag and iron drawn off separately from the



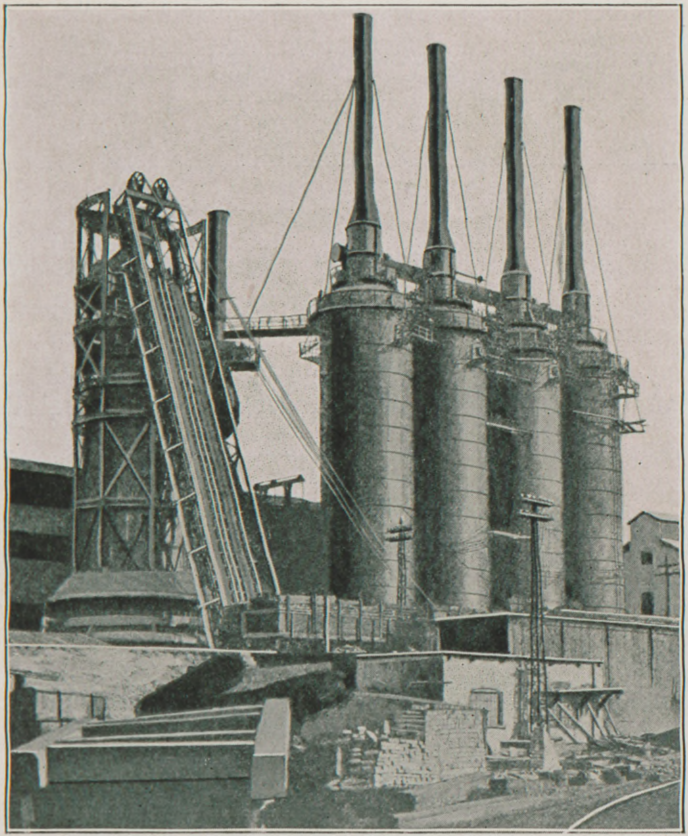
Pig Iron Casting

bottom. Throughout the entire process there are two streams flowing through the furnace: the one of melted iron and flux moving slowly downward as the coke is consumed and the ore reduced, and the other the swiftly moving stream of heated reducing gases and nitrogen from the air moving upward and out into a special pipe at the top.

Air is fed into the blast at the rate of 40,000 cubic feet per minute. The moisture is removed from this air blast by artificial cooling, since cold air does not hold nearly so much moisture as warm air, a fact illustrated by bringing a glass of cold water into a warm room. This invention by the American, Gayley (5), put into operation in 1904 gives a uniformity of product, regardless of the daily and seasonal moisture variation, and reduces the fuel cost more than 10 per cent. It is claimed that this process reduces the cost of production of iron from 50 cents to $1.00 per ton, so that with an annual production of 40,000,000 tons the saving would amount to a clear gain of twenty to forty millions of dollars.

To attain the requisite temperature the air, after the removal of the moisture, is heated in so-called stoves before being turned into the blast.

Composition.—The pig iron from the blast furnace contains approximately 93 per cent. of iron, the other materials present being carbon, sulfur, phosphorus, manganese and silicon. Its relation to wrought iron and steel is seen in the following analyses given by Newth (6):



Blast Furnace and its Hot Blast Stoves

	Per Cent		
	Cast Iron	Steel	Wrought Iron
Carbon	3.81	0.65	0.10
Silicon	1.68	0.07	0.05
Phosphorus	0.70	0.03	0.15
Sulfur	0.60	0.02	0.05
Manganese	0.41	0.40	0.07
	7.20	1.17	0.42
Iron	92.80	98.83	99.58
	100.00	100.00	100.00

Wrought Iron.—To form wrought iron or steel from pig iron, most of the impurities must be removed. When this process is carried out in the puddling furnace, which is lined with hematite to furnish oxygen, the flame from a fire at the side being led over the charge, the product is called wrought iron, for the iron is wrought or worked

Puddling Furnace

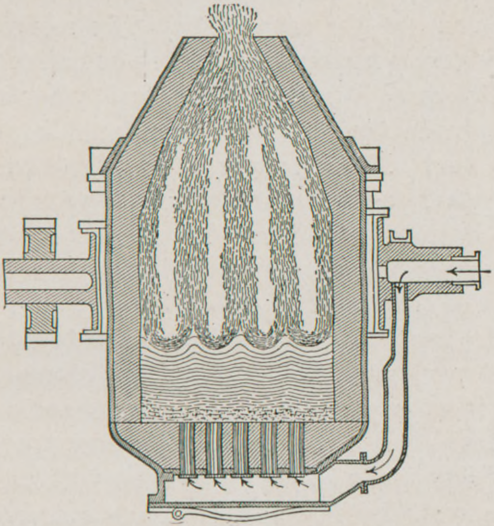
during the process and finally hammered or rolled to remove the slag. Wrought iron is a term now little used for it has in a large measure been replaced by soft steel, but there is still a demand for it for certain special purposes.

Steel.—Steel may be made either in the Bessemer converter, the open hearth, or the crucible process, though the latter has recently been largely replaced by the electric furnace. In the Bessemer process the molten cast iron is placed in an iron converter lined with some difficultly fusible material and a current of air turned on. This blast burns out the impurities of the iron within a few minutes, no other fuel being required. As chemically pure iron has little practical use, pig iron containing known amounts of carbon and manganese is added to give the proper amount of these two elements required for steel. In this barrel shaped converter ten to twenty tons of steel can be made in as many minutes.

In 1907 practically the same amount of steel was produced by the Bessemer converter and in the open hearth process; in 1917, however, the production of the Bessemer converter was somewhat less than that of ten years before while the open hearth production had trebled (3). The principle of removal of impurities from the pig iron by oxidation is the same for both processes. But in the open hearth the pig iron, to which some scrap steel or iron ore is generally added, is placed in a reverberatory furnace, the hot gases passing over it to burn out the impurities. Fuel in the form of gas

A Bessemer Blow

or sprayed oil is used, being burned with air previously heated by the regenerative system. When an acid (siliceous) hearth is used phosphorus and sulfur are not removed. But if the hearth is lined with lime or burned dolomite the acid elements unite with the basic lining and are removed in the slag. This process can be used with a number of ores containing phosphorus, which would not be available otherwise.



Section Bessemer Furnace

Factor in Locating Cities.—The location of certain American cities because of their ready access to iron ore, coal and the needed flux is significant. Thus the location of Birmingham was largely determined during the geological ages in which these materials were deposited. Chicago's importance as an iron center is due not so much to the nearness of mineral deposits as to the ready transportation by both rail and water of the materials required in the reduction of iron ore and of the products made from it.

Non-Ferrous Metals

Copper.—While the United States produces 40 per cent. of the world's iron and steel, it furnishes 70 per cent. of the copper (7). The mines in the Lake Superior region furnish free or native copper, while Arizona, Montana, Utah and other western states obtain their product from sulfide and carbonate ore. Much copper is obtained from ores giving other metals such as zinc, lead, silver and gold. Besides Michigan, Tennessee is the only state outside of the west producing any considerable amount of copper.

While good iron ore will frequently run more than 50 per cent. iron, the average of copper ores mined is often less than 2 per cent. and in some cases less than 1 per cent. The fact that copper ores of low grade could be worked with profit was demonstrated by Jacklin (8), and recent production has been largely from low grade ores. Only in unusual cases does the percentage of metal in copper ores run as high as 10 per cent.

Copper is obtained from its ores by smelting, which produces a matte, containing 35–50 per cent. of the metal mixed with heavy other metals and containing much sulfur. For fine ores this is done in a reverberatory furnace and for coarse ores in blast-furnaces. These are similar to those in use for iron, but are specially adapted for copper ores.

The crude copper obtained by either of these processes must be refined by casting into thin plates, which are used as anodes. By this electrolytic refining the impurities are either dropped into a sludge which collects at the bottom of the containing vessel or remain in solution, while the copper separating out on the cathodes has a purity of 99.9 per cent. (9).

Lead and Zinc.—In the production of both of these metals the United States leads all other countries, the production in each being about one-third of the world's supply. Missouri is the ranking state in the production of the ores of each, the other leading lead producers being found in the West, where gold and silver are frequently found in lead ores, while New Jersey and Wisconsin are leading producers of zinc, as well as Montana, Oklahoma and Colorado (10).

Both metals occur most commonly as the sulfide and the principle of roasting and then reducing the oxide formed is carried out for each, though the method in which the process is carried on varies widely (2). Both metals form compounds widely used as pigments and these are frequently made directly from the ores (11). (See chapter IX.)

Gold and Silver.—Both of these metals occur native, that is in the metallic state, most of the gold being so found. The greater amount of silver produced, however, is obtained in the smelting of other ores, especially lead and copper. In the world's production of gold the United States ranks second, first place having been held since 1905 by South Africa, though the margin of lead recently has become quite small. In the United States western states lead as gold producers, California being first. In silver production Nevada, Idaho and Montana lead (12).

More than three-fourths of the silver but less than one-fourth of the gold produced in the United States comes from the smelters. For the remainder of the silver cyanidation is the process now in use. In this process the metal is dissolved from the gangue by a solution of sodium cyanide, of about 1 per cent. strength, the silver being recovered from this solution either by precipitation with metallic aluminum or zinc, or by electricity. The same process is in more general use for the recovery of gold from low grade ores, the cyanide solution being weaker than that used for silver. Considerable gold is obtained from its ores, when high grade, by placers, in which process the gold because of its greater density (specific gravity 15.6–19.5) is separated in water from the crushed ore, the lighter materials being carried away by the force of the stream. Almost as much gold is recovered by amalgamation, in which process the gold is taken up by mercury which is generally held as an amalgam on copper strips. A summary of the output of gold and silver by these methods is shown in this table adapted from Mineral Resources of the United States, 1914 (12):

	Per cent			
		Gold		Silver
Placers		25.3		0.2
Gold and silver mills:				
By amalgamation	20.9		0.4	
cyanidation	31.4		22.1	
chlorination	0.2		0.0	
Total Milling		52.5		22.5
Smelting—crude ore and concentrates		22.2		77.3
		100.0		100.0

Gold and silver are separated, or parted, by dissolving out the silver in sulfuric or in nitric acid and by other methods, including chlorination and certain electrical processes. In the acid methods there must be two or three times as much silver as gold, or silver must be added to make this proportion, if the method is to work satisfactorily.

Other Metals.—Of most of these in common use the United States either does produce or could produce a reasonable amount, the possibility of domestic production being emphasized during the War. For economic reasons several of these metals are imported; thus nickel is imported from Canada and after refining is exported (13).

In the case of some metals it has not yet been possible to indicate a total production equal to the demand for the metal. Thus the United States is the largest consumer of tin and of platinum, much of the tin being imported from Banca in the Malay peninsula, and the Ural Mountains being the chief producer of platinum prior to the disturbance in Russia.

Certainly it is true, that with few exceptions, the

United States could, if necessary, be independent in the matter of metals, and in the case of the most important metals our production far exceeds that of other countries (14).

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CHAPTER XIV

AMERICAN CHEMISTRY AND THE FUTURE

The preceding pages have given some idea of the achievements of the American chemist. Even before the World War there was practically no industry of consequence in the United States that did not depend directly or indirectly upon his industry and insight. Then we not only produced more chlorine and more sulfuric acid than any other nation, but we also led the world in petroleum refining and furnished 90 per cent. of its supply of aluminum (1).

War Development.—We have seen that the development during the War was unprecedented and astounding. The sulfuric acid produced in a single year was greater than that of the combined weight of the more than a hundred millions of the country's inhabitants. In 1913 there were 19 electric steel furnaces in the United States; in 1917, 233, while other electrochemical industries increased in like manner (2).

Not only were old industries developed but new ones were created. The optical glass industry, as Minerva of old, sprang into being full grown. One American company produced 144 pieces of porcelain ware in 1914 and 1,347,235 pieces in 1918. In a single year the production of dyes and synthetic medicines increased 5000 per cent.

Growth under such conditions can not all be permanent. Only by readjustments accompanied by heavy loss can any of the hundred millions of dollars invested in war gas plants be saved.

In the light of this development should we not by a survey of our country's resources be able to learn something of the promise of the future, and of how that promise is to be best made a reality?

Resources.—Looking back over the resources of the United States, as we have had occasion to recount them, we find no ground for empty boasting, but a very real occasion for realization of the responsibility that rests upon this nation and the limitless opportunity that opens before us. Already the United States produces

25 per cent. of the world's wheat
60 per cent. “ “ “ cotton
75 per cent. “ “ “ corn.

From our mines and wells come

40 per cent. of all the iron and steel.
66 per cent. “ “ “ oil
70 per cent. “ “ “ copper.

One little state, West Virginia, has greater stores of coal than Great Britain and Germany combined (3).

Power.—Looking out over America's vast resources of fertile field and rich mine, and remembering that civilized man is by the help of science just beginning to make adequate and full use of the forces of nature, we gain some conception of the possibilities ahead and how great, how tremendous power rests in America's hands! Writing several years ago Harrington Emerson states (4):

Costs, per Horse Power Year of 7,500 Hours

At $2.00 per day man power costs	$54,000
Gasoline in a small engine costs	300
Steam, for large power installations	20 to 200
Gas " " " "	
Electricity " " "	

" One hundred and sixty years ago the use of coal had not been begun on a commercial scale; all the work was done by man and beast. Sixty years ago in the United States the consumption of coal, used most wastefully, was one-quarter ton per adult male, each ton able to do the work of five men."

To-day there are consumed annually between five and six tons, not " per adult male," but for every man, woman and child in the entire country. " And the energy from oil, from gas, from distant waterfalls, is not included."

Waste.—Though blessed with mammoth coal supplies, we allowed valuable by-products to escape and bought our dyes from Germany till war's necessity forced a change. For every board foot of lumber cut during the past few years we have wasted in the forests and at the mills nearly two feet more. Because of lack of application of general scientific principles to our agriculture our crop yields per acre are far below those possible. Thus, we produce only 14 bushels of wheat on the average, while Germany grows 28 and England 32. If forced to do so, it is claimed that the United States could double her acreage of cultivated land and quadruple her agricultural production.* Thru unsanitary conditions and impure water supplies,

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* Already America's agricultural production per man employed is much higher than that of other countries.

tolerated still in certain communities, we waste life by typhoid and other preventable diseases in a manner altogether without excuse. Arthur D. Little from whose excellent article many of these facts are taken, says: (3)

> "We are indeed a prodigal people, prospering for a time by methods, which would end European civilization within a generation."

Spirit of America.—It has always been possible to depend upon the American people to eventually do the right thing. Mistakes innumerable may be made, hasty actions may be taken, strikes and lockouts may come, but in the main the American ideal of fairness and the square deal has always finally dominated. This is why it is America. And so, facing squarely the situation as it is, with the wonderful resources and undreamed of power, not forgetting the all but criminal waste, we are forced to these conclusions:

1. That with all our development we have only touched the border of the promised land; that we have but seen the dawning and the sunrise of America's chemical development and that the glory of the noon lies ahead.

2. That the future will demand of the American chemist and of all of his fellow Americans these things:

(a) Efficiency
(b) Alertness
(c) Co-operation

Efficiency.—There will be small place in the day that is coming for the man or woman who is not thoroughly trained and thus capable to readily meet the issues that must arise and to efficiently deal with them. Business men and the public generally must recognize the fundamental importance of chemistry in the life of the nation and it must be given the support it deserves. That this is assuredly coming, events of recent years clearly show.

Alertness.—Always must the chemist be ready to sense the reality of the time in which he lives and alert to meet the future. Even now, Germany's chemical factories stand intact; her force of trained chemists, because busy behind the lines, has been little impaired by the War; and denied world domination thru military power, undoubtedly she will seek it thru a combination of trade and science. Unrepentant, as she clearly is, Germany's methods now will be as unprincipled and merciless as they were before and during the War.

A number of new American industries can not yet meet German competition. Will all of us have the patriotism, even at some financial sacrifice, equal to that of the more than one hundred leading textile and other manufacturers, all consumers of dyes, who petitioned President Wilson to use his influence to place a high protective tariff on dyes? At the head of every request for quotation for college or university laboratory supplies should be the slogan

"American chemicals and apparatus preferred"

till these American industries can readjust themselves to new conditions.

Co-operation.—If the farmer insists on buying his fertilizer in Germany and that tariff shall not interfere, then he must be prepared, at best, for the increase in German prices when German monopoly has been reestablished by the destruction of the American potash industry. Possibly he may be called upon to see his sons and his grandsons face a foe thrice-armed by chemistry, while they lack the safeguards the chemist could have given them. Producer and consumer, capitalist and laborer, banker and business man, must all be willing to co-operate each with the other and with the chemist in the day that lies ahead.

American Chemical Independence will thus come, not in the narrow sense of using only American goods under all circumstances, but in the far more real sense of carefully surveying, planning and developing our resources, so that we may be ready should the day of need ever come.

In the early history of chemistry we learn that the alchemist strove to turn other metals into gold. Later the goal of the medical chemist was the elixir of life, which would keep him who drank it always young and ever free from pain.

Already the American chemist has, in part, achieved the objects of each, bringing wealth and health to many by the application of his science. Far more in the future in co-operation with American business genius and energy, he will give to the United States a security and a production that will bless not only our own country but all mankind.

May every American, young or old, realize the wonderful development ahead, and place himself in line with the mighty onward sweep of this resistless current.

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