CHAPTER XII

INDUSTRIAL CHEMISTRY¹

BY CHARLES E. MUNROE

Introduction

Anniversary celebrations offer a fitting occasion for reviews in which either to beat the drum and scatter compliments, or, perhaps more wisely, to take account of stock for future guidance. A considerable feature of the celebration of the Priestley anniversary in 1874, almost two years before the founding of the AMERICAN CHEMICAL SOCIETY, was the three addresses, respectively, by T. Sterry Hunt on "A Century's Progress in Chemical Theory;" by J. Lawrence Smith on "The Century's Progress in Industrial Chemistry;" and by Benjamin Silliman, Jr., on "American Contributions to Chemistry;" the first, philosophical in treatment; the second, historical with a slightly statistical tone; and the third, bibliographical with much delightful biographical matter intercalated. Together they formed a datum mark for this Society.

The influence of these men was marked, as is evident by an inspection of the record of the celebration of our Twenty-fifth Anniversary, and especially the "Report of the Census Committee," which consisted of Charles Baskerville, chairman, Louis Kahlenberg, Charles E. Munroe, William A. Noyes, and Edgar F. Smith. This report reviewed the state of preparedness of this country in the field of chemistry, and supplied a mass of useful information and data of permanent value in historical comparisons. Dr. Baskerville rendered yeoman's service in producing such a report under somewhat unfavorable circumstances.

1 This chapter was to have been prepared by W. A. Hamor, assistant director of the Mellon Institute of Industrial Research, University of Pittsburgh, but after having collected his data and partially outlined his plan of treatment he became physically disabled. He most generously turned over all his material to me for use. I am also indebted to W. M. Steuart, director of the Census, to C. A. Browne, chief of the Bureau of Chemistry, and to many members of the American Chemical Society, who, either directly or through Dr. Browne, have sent me valuable information and memoranda. To all of these I express my appreciation, with the regret that I have been forced to leave unused so much of the material that was placed at my disposal.—C. E. M.

The report will be found to deal largely with education, though the section on Industrial or Technical Chemistry treats principally of the condition or status of the chemist. The subject of the education of technical chemists was omitted because it had been so fully treated by William McMurtrie in his presidential address in 1900. Statistics of the industry did not appear: first, because reliable ones were then so few; and, second, because the first systematic survey of "Chemicals and Allied Products" was then being made, and its "finals" had not been reduced and authenticated. The results appeared later as Bulletin 210 of the twelfth census of the United States by Charles E. Munroe and Thomas M. Chatard, accompanied with an appendix by Story B. Ladd, entitled "Digest of United States Patents Relating to the Chemical Industries (Products and Processes)." This latter was intended to cover every United States patent relative to the industries treated from the founding of the United States Patent Office up to 1900, but, though this digest covers 306 quarto pages in small pica type, the crowded condition of the Patent Office rendered it uncertain that we had "pulled" every patent, while other circumstances prevented a résumé of apparatus patents.

Subsequent bulletins, not only on "Chemicals and Allied Products," but on "Precious Metals Recovered by Cyanide Process," "Petroleum Refining," "By-product Coke," "Salt," and "Gas," were issued, and résumés were prepared for them which were substantially complete because the Patent Office had caught up in its classification, and because it was found possible to abstract apparatus and analogous patents. Emphasis has been placed here on patents because no complete picture of progress in an art or industry can well be formed without a knowledge of the progress of invention in that art or industry and this is chiefly recorded in patents.

Originally the United States Census of Manufactures was taken every decade; beginning with 1905, every fifth year; and beginning with 1919, every second year. It is hoped that this country may soon make an annual accounting, because such statistics, properly compiled and presented, not only promote industry, foster commerce, inform the financier and the legislator, guide the historian and interest many, but they are essential to the permanence of the Nation. When forced by the exigencies of the World War to ascertain our degree of preparedness and the extent of our resources, those statistics then collected, though not complete, were invaluable.

The census is given prominence in this introduction because we must now go to its records and to those of the Tariff Commission, the Bureau of Foreign and Domestic Commerce, the Geological Survey, and the Bureau of Mines for the quantities and values of the chemical industries through which to gauge and evaluate the progress of any one of them. This matter is germane to our title in that the first effort of the census to collect statistics on Chemicals and Allied Products was made in 1880, while all the other agencies enumerated here have been created during the last fifty years. Furthermore, there is not one of these agencies that has not relied upon the technical chemist for aid and advice. A notable example of the fundamental importance of such statistical inquiries is found in "A Census of Artificial Dyestuffs Used in the United States," by Thomas H. Norton, 1 which was the initial step in releasing us from the forced payment of tribute to a dominant foreign power. Many may recall the protests against the publication of this record, compiled from our Nation's archives, and that certain, most critical, data were suppressed. It is hoped that never again shall vital statistics such as these, entered on the national records, be concealed from our manufacturers, our consumers, or any party in interest.

There were few, if any, men in 1874 so well qualified by training and experience to review the century's progress in industrial chemistry as Dr. J. Lawrence Smith. At twenty-one years of age he had already won his C.E. degree from the University of Virginia and his M.D. degree from the South Carolina Medical School and had an intervening year of experience in railroad construction. Following the attainment of his medical degree he spent three years in study with Pelouze, Orfila, Dumas, Liebig, Elie de Beaumont, and with eminent physicists, physiologists, and mathematicians of Europe. He became state assayer of South Carolina; he served several years as consultant to the Sultan of Turkey, developing the resources of the Ottoman Empire; he was president and general manager of the Louisville Gas Light Company; with Dr. E. R. Squibb he engaged in the commercial manufacture of analytical reagents and fine chemicals. He was United States commissioner to the Paris Exposition in 1867 and wrote an extensive report on its chemical exhibits, and also one on petroleum which was published in Germany. Yet in his introduction to his Northumberland address Dr. Smith questions the scope of his subject and found difficulty in delimiting it since chemistry reached so far into

¹ J. Ind. Eng. Chem., 8, 1039-48 (1916).

the industries. The topic as now viewed goes beyond chemical manufactures and includes the applications of chemistry that affect industry. Hence, the multitude of subtopics can be dealt with only in outline.

To give an idea of the magnitude of the chemical industry of that time Dr. Smith records that "In France alone, the annual value of chemical products is over \$250,000,000." The returns for the United States census of 1923 give \$708,372,249 for the substances it classes as "Chemical Products." In analyzing its returns for 1909 I found that the value of those substances treated in chemical technologies even then amounted to \$4,859,964,000, and it is unquestionably many-fold that amount now.

Gases-Normal, Compressed, and Liquefied

Turning now to the historic gases of Priestley's time, Dr. Smith enumerates eleven different methods of isolating oxygen, refers to the recognition of ozone by Schönbein and, speaking of the, as yet, limited applications of oxygen in the arts, notes that a 500-pound ingot of platinum and iridium, for use in making the standard meters for the United States and other governments, had recently been produced by means of the compound blowpipe, using oxygen in conjunction with hydrogen or hydrocarbons. He expresses the conviction "that the day is not far distant when Priestley's name will not only be connected with the discovery of the corner-stone of modern chemistry, but will also be associated with one of the most useful agents in the chemical arts." With what satisfaction would Dr. Smith learn that in 1923 the United States produced commercially 379,780 thousandcubic feet of oxygen by the electrolysis of water (his eleventh method) and 2,057,526 thousand-cubic feet from the liquefaction of air, the total having a value of \$23,382,236; that oxygen was widely used in therapeutics and industries; that the compound blowpipe was a part of the equipment of most machine shops for use in cutting and welding metals, and that, following Cottrell's suggestion, we now contemplate its use in the blast-furnace and other metallurgical operations.

Compressed and liquefied gases appeared for the first time as a distinct category in the census of 1899 and it included not only oxygen but chlorine also, with SO₂, CO₂, N₂O, NH₃, and others. The oxygen then reported was largely used in the calcium light, which is now displaced by electric lamps. Scheele's gas or chlorine was then principally used in bleaching and disinfection, but the remarkable application of it to water purification and to

the chlorination of compounds on a large commercial scale are developments of the last half-century, the chlorine now being largely isolated from chlorides by electrolysis, a process not enumerated by Dr. Smith, and one which has supplanted the chemical processes described by him. The pioneer work in this field in the United States was done by Ernest A. Le Sueur, starting first with Charles N. Waite in 1887 at Newton, Massachussetts, and erecting in 1892 a plant at Rumford Falls, Maine, where caustic soda and bleaching powder were produced.¹ The Dow Chemical Company began producing bleaching powder from electrolytic chlorine in 1898, and many other manufacturers, using a variety of cells, followed. The manufacture of poison gas by the aid of chlorine gave a great impetus to its production and a multitude of uses were developed for it. It is estimated that, in 1925, the yearly capacity of all commercial plants in the United States and Canada was 185,000 tons, to which may be added the idle plant at Edgewood Arsenal, Maryland, with a capacity of 36,500 tons. It is figured that about 65 per cent of the output is consumed in the paper industry, 22 in the textile industries, 10 in sanitation, and the remaining 3 per cent in all other uses.2

Of the chlorine produced in 1925, 46,000 tons were liquefied. Liquefied chlorine is shipped in steel cylinders of 10, 20, 100, 150, and 2000 pounds capacity, or steel tank cars, the single-unit ones having a capacity of 15 tons and the multi-unit ones carrying 15 one-ton tanks. There are over 300 steel tank cars and 80,000 steel cylinders in use or available.

To the compressed and liquefied gases above enumerated as entering commerce in the United States may now be added acetylene and other hydrocarbons and hydrogen cyanide, the total value for this category reaching, in 1923, to \$54,401,591, the quantity of chlorine attaining 125 million pounds. Recalling our indebtedness to Priestley for carbonated beverages,³ which in our day have been greatly improved by A. P. Hallock and C. A. Catlin, we note the value for carbon dioxide in 1923 nearly approached \$5,000,000, though in 1919 this value was surpassed by \$1,500,000. One queries whether, following the outburst of that critical year, there is a falling off in the consumption of soft drinks.

¹ Parsons, C. L., "The Le Sueur Process for the Electrolytic Production of Sodium Hydroxide and Chlorine," J. Am. Chem. Soc., 20, 868-77 (1898).

² Pritchard, D. A., "Economics of the Chlorine Industry," Chem. Met. Eng., 33, 350-53 (1926).

¹ Friend, J. Newton, Chem. Ind., 45, 145 (February 26, 1926).

Chemical Substances Produced by Electricity

Another category first appearing in the census of 1899 was "Chemical Substances Produced by the Aid of Electricity," in which sodium, caustic soda and hypochlorites, chlorates, lead oxides, graphite, calcium carbide, carborundum, carbon disulfide, phosphorus and phosphates, were then reported as entering commerce from this source, the total value of these products being given as \$2,045,535. It will be noted that aluminum and many of the other metals, and alloys produced by electrothermic methods were not included in the above list. In this connection we may recall the names of Hamilton Y. Castner, J. D. Darling, E. A. Le Sueur, Pedro G. Salom, E. G. Acheson, T. L. Willson, F. A. J. Fitzgerald, and Edward R. Taylor among the pioneers in the development of these new industries. Darling's process for isolating sodium from sodium nitrate, while producing nitric acid, was in operation at the works of Harrison Bros. & Co., Philadelphia, and it was reported that, in December. 1902, the amount of sodium on hand had become so great the city authorities, fearing accidents, compelled the operation of the process to cease. Of the many chemical works which I have visited and of the operations which I have viewed none has given me the sensation with which I witnessed at Taylor's plant, in Torrey, New York, the large-scale continuous production of a low-boiling point, easily ignitable, endothermous substance, such as carbon disulfide, in a large stack furnace in which the melting of the sulfur and its combination with the carbon was effected by electric arcing. It was a most daring development and one little to be expected from a man of Taylor's appearance and bearing. This development came at an opportune time, for though there was use for it as a solvent in many arts, as an efficient insecticide, and as a parent substance in the manufacture of thiocyanides, carbon tetrachloride, sulfocarbonates and other sulfur-containing substances, the great viscose industry, in which carbon disulfide is used to form the cellulose xanthate, was forging to the front. Of special interest among the industries with which I was associated was that operated under Salom's patents wherein native galenite was reduced to metallic lead, this spongy lead then being used as such in the grids of storage batteries, or oxidized to litharge, minium, or peroxide as desired. One of my prized exhibits was a mass of galenite crystals reduced by this process to sponge lead, the mass still retaining the dominant and all the modifying planes of the original crystals. The rate of growth of the industries embraced in this category is shown

in that the value of the products returned at the census of 1923 was above \$107,000,000, making an increase of over \$105,000,000 in 14 years. It is observed that at the 1923 census hydrogen, bromine, ferro-alloys, halogen derivatives, rare metals and alloys, together with other metals and miscellaneous compounds, were added to the list of products reported.

Sulfuric Acid

In dealing with this topic Dr. Smith recalls that pyrites was adopted in England as a source of sulfur because of the shortsighted policy of the King of Naples in granting a monopoly of the Sicilian sulfur and that the use of pyrites spread to other countries, but that the use of sulfur would be resumed when better transportation facilities gave access to our sulfur deposits. The existence of sulfur in Calcasieu Parish, Louisiana, has been long known and some sulfur was secured from the deposit by the Confederates during the Civil War, but though repeated endeavors were made to gain access to this sulfur all failed of economic success because of the nature of the overburden until Herman Frasch devised and developed his ingenious system of annular tubes through which superheated steam might be forced down to the sulfur deposit and the water, primed with molten sulfur, forced to the surface. The effect is seen in the quantities of pyrites used in the chemical industries which fell from some 900,000 tons in 1914 to 471,000 tons in 1923. The use of pyrites will continue as long as they contain values. An achievement of the present half-century is the abating of fume nuisances from smelting operations, such as at Ducktown and Anaconda, through the conversion of the fume contents into useful products, such as sulfuric acid, and in this F. G. Cottrell's precipitator has been an important factor. In 1923, 384,489 tons of 60° Bé. acid were recovered from zinc ores, and 401,300 from copper ores.

Dr. Smith also made the following interesting forecast, "Döbereiner's suggestion of making sulfuric acid in very much smaller apparatus than that now used (by the agency of sulfurous acid, air and spongy platinum) has been tried and worked successfully on a small scale, and its extended success belongs to the future of chemistry." The records show that in the United States in 1923 sulfuric acid (50° Bé. basis) was made by contact processes to the extent of 1,812,341 tons and 4,743,176 tons by chamber processes. Of course the contact-process acid was produced in the higher concentrations known as oleum.

The contact process for the production of sulfuric acid is now a firmly established and thoroughly practicable process but enormous amounts of money and much effort, exerted by many able chemists, have been required to reduce Döbereiner's ingenious idea to practice, even after it has been successfully demonstrated in the laboratory. Among those contributing to this success is J. B. F. Herreshoff, who also devised a very satisfactory and muchused pyrites burner. The developments in chamber processes during the last forty years have recently been admirably set forth by P. C. Hoffman.¹

Nitric and Mixed Acids

While nitric acid has been used in the manufacture of nitrates, such as those of silver, mercury, lead, and other metals, and in assaying and analytical operations through centuries, it assumed no great commercial importance until its use in nitrating organic substances in the dye and explosives industries began about the middle of the last century. Even in 1899 the quantity produced as compared with sulfuric, or even hydrochloric, acid was relatively small, so that at the census of 1900 but 15,487 short tons (of all grades) were reported. In 1923 this had risen to 113,116 tons. Nitric acid was, and largely is, made by the reaction of sulfuric acid and sodium nitrate. A marked improvement in this process occurred about 1898 with the introduction of the condenser, invented by Edward Hart. More revolutionary methods adopted later were electrical processes for the direct production of nitric acid from atmospheric nitrogen and oxygen, or indirect conversion into nitric acid through cyanamide. The most practicable method appears to be to form ammonia from atmospheric nitrogen and water-gas hydrogen, and then to oxidize this ammonia to nitric acid. This latter method is now established in this country.

It has been found that nitration may be most smoothly and efficiently carried on, to produce either nitric esters or nitrosubstitution compounds, by using accurately proportioned mixtures of sulfuric acid with nitric acid, both being of the proper strength. This material in the market is styled "mixed acids." In the census of 1900 the production of mixed acids in 1899 is reported as 21,185 tons. The amount recorded for 1923 was 156,467 tons, of which 102,000 tons were produced by the explosives industry.

But little of the sulfuric acid of mixed acids is expended in nitration and not all of the nitric acid. Hence large quantities

^{1 &}quot;Progress in Sulfuric Acid Manufacture," Chem. Met. Eng., 33, 406-8 (1926).

of spent acids result from the process. These spent acids have become diluted by the water produced in the reaction and contain dissolved nitrogen oxides resulting from oxidation that runs on concurrently with nitration. Of course they are too valuable to waste, while their disposal as waste would be well-nigh impossible. Practice has varied from time to time as to the methods of recovery of spent acids. They have been treated by steam in towers to separate the nitric acid (and oxides converted to acid) from the sulfuric acid, the latter being reconcentrated for re-use as such, and the weak recovered nitric being used in the manufacture of ammonium nitrate. G. W. Patterson devised a plan for rebuilding spent acid. With oleum at command, rebuilding is a relatively simple matter and is now much practiced.

Nitrogen Fixation

The synthesis of nitrogen compounds from atmospheric nitrogen together with atmospheric oxygen, or hydrogen from various sources, especially as a by-product from many processes, has become one of the most important of chemical industries. I have previously pointed out the military importance of this industry. Although Bradley and Lovejoy had, prior to 1909, demonstrated the feasibility of nitrogen fixation, little commercial or political interest was manifested in these operations in this country until after the World War broke out, when their significance dawned upon the consciousness of our leaders. Hasty efforts were made to remedy the oversight. Norton's report was widely read. C. L. Parsons and Eysten Berg were sent to Europe to report on developments at first hand, and many firms and persons with special processes, such as that of John E. Bucher, were subsidized to promote development. But, except in pricefixing, and in its strategic effect, our activity was too belated. A beneficent outcome, however, was the establishment of the Fixed Nitrogen Research Laboratory, where the economics of the various processes have been investigated and their suitability for use under the varied conditions arising in this vast country determined. Research work, looking to the further perfecting of processes, has also been actively carried on and to such effect that some eight plants are now in operation and others are building. Nevertheless, we are yet but seventh on the list of producing countries, and our output is still less than 10 per cent of that of Germany. Among those active in these investigations may be

¹ Munroe, Charles E., "The Nitrogen Question from the Military Standpoint," Proc. U. S. Naval Inst., 35, 715-27 (1909); Smithsonian Inst. Ann. Rept. 1909, pp. 225-36 (1910).

mentioned F. G. Cottrell, A. B. Lamb, R. C. Tolman, Graham Edgar, S. C. Lind, A. T. Larson, H. A. Curtis, J. M. Braham, W. C. Bray, J. A. Almquist, and F. A. Ernst.

Soda

Under this heading Dr. J. L. Smith discussed at length the Le Blanc process, which is now a vanishing one and one which never gained a foothold in the United States. He gives an interesting chronological table of the progress of the soda industry from 1790, when soda was obtained from barilla and kelp; refers to cryolite as a source; and mentions the recent perfecting of the bicarbonate of ammonia process by Solvay & Company of Belgium who, in 1873, produced 5000 tons of soda by this process. At the census of 1923, 1,707,987 tons of soda ash were returned, of which 1,674,234 tons were produced by the ammonia-soda (Solvay) process, to which are added 33,753 tons of "natural and electrolytic soda." The production of soda from natural brine was thoroughly investigated by Chatard, while J. D. Pennock was an active factor in the development of the ammonia-soda process in this country.

Potash

According to Wilbert,² the Jamestown Colony, as far back as 1608, produced pot or soap ashes which were shipped to England. Although Henry Wurtz in 1850 found that considerable quantities of potassium existed in our greensand marls and described processes for its extraction, wood ashes, except for India saltpeter, remained the chief source of potash and potassium compounds until the extraction of the latter from the abraum salts of the Stassfurt deposits began, about 1861. In that year we imported from this source the potassium chloride used to produce, by metathesis with sodium nitrate, potassium nitrate for the gunpowder used in the Civil War.

At about this time our fertilizer industries, started in 1850 for the treatment of guano and coprolites, began compounding fertilizers, and they found their potash in Stassfurt salts. This source was so fostered that our native industry sank from a value of \$1,401,533 in 1850 to \$104,000 in 1905, while in 1913 we imported potash salts to the value of \$13,200,413. Therefore in 1914, on the breaking out of the World War, we were so dependent on these foreign sources that when commerce was inter-

 $^{^1}$ Chatard, T. M., "Natural Soda; Its Occurrence and Utilization," U. S. Geol. Survey, $\it Bull.~60~(1888).$

² J. Franklin Inst., 157, 366 (1904),

rupted our condition was desperate. Steps were taken at once for governmental surveys of the country's potash resources, which were found not only in wood ashes but also in many minerals, such as greensand marl, alunite, leucite, feldspar and shales, in kelp, in surface brines and their deposits, likewise in industrial wastes from the manufacture of sugar and alcohol, and in the dusts from blast furnaces and cement mills. The story of effort and accomplishment has been admirably told by J. W. Turrentine in his recently published book¹ in which he says:

It was the threat of the late German Empire that, because of the potash monopoly which it held, the world could be subjected at its will to potash starvation and be forced to yield to its dictation. This challenge was met in America by the prompt development of practically all of the sources of potash already surveyed by governmental agencies and the establishment of potash manufactories which made America, for the time being, independent of all foreign potash. The effect on the outcome of this world-wide imbroglio of this show of spirited aggressiveness on the part of America cannot be determined, as its value is inestimable.

Naturally the success of the different undertakings varied with various conditions, such as the nature, the richness and the ease of access to the raw material, and on the nearness of the factory to its market. The outstanding successes were those of the U. S. Industrial Alcohol Company, using the process of M. C. Whitaker; the Santa Cruz Portland Cement Company, using the Krarup process; the sugar companies, using the Steffens process; and the American Trona Company, working the brine of Searles Lake, California. The last-named plant is the largest single potash producer that has resulted from American efforts to establish a domestic potash industry. It was one of forty-four plants engaged primarily in the production of potash, and the only one to survive under peace-time conditions. Dr. Turrentine remarks of this:

The American Trona Corporation, the company that had devoted the most time and effort to fundamental chemical research, was the one that was enabled to continue in operation. The continued development of its processes, cheapening its manufacturing costs and improving the quality of its products, has enabled it to survive successfully the post-war period characterized by exceedingly severe economic conditions.

The researches, through which this brilliant result was achieved, were planned and directed by John E. Teeple, the very efficient Treasurer of our Society.²

Gas, Illuminating and Heating

This legend embraces both manufactured and natural gas. The former, as an industry, began in April, 1812, with the granting

¹ Turrentine, J. W., "Potash. A Review, Estimate and Forecast," John Wiley & Sons, N. Y., 1926.

 $^{^2}$ Teeple, John E., "Research: Its Position in the Making of an Industry," J. Ind. Eng. Chem., 14, 904 (1922).

of a royal charter to the Chartered Gas, Light, and Coke Company of London, England. It may be recalled that, at its Washington meeting in 1911, the American Chemical Society set on foot the celebration of the centenary of this event, that in consequence ioint meetings were held April 18 and 19, 1912, at the Franklin Institute, with that institution, the American Philosophical Society, and the American Gas Institute. The record of this event, with all its attending circumstances, was published in the Journal of the Franklin Institute for that year and by the American Gas Institute as a separate volume. This was followed by the enormous and profusely illustrated "Gas Jahrhundert Nummer" of the Leipziger Illustrirte Zeitung; a gas exposition at Antwerp; and finally, a brochure of 92 pages, beautifully gotten up under the direction of Sir Corbet Woodall, governor of the company, entitled "The Gas Light and Coke Company 1812-1912." The industry began to supply coal gas in this country with the chartering of a gas company in Baltimore in 1816. A marked change came about in the seventh decade of the century through the combining of the cupola retort system of Tessie du Motay with the generator-superheater system of T. S. C. Lowe for the manufacture of carbureted water gas, and especially in having available, at low cost, an abundant supply of petroleum distillates and residues for use as carburetors. At about the time our Society was formed this industry had attained a secure foothold and since then cognizance has had to be taken of water gas, carbureted water gas, and mixed coal and water gas. In the meantime, with the introduction of the by-product coke ovens, the richer gas from these devices, as well as that from retorts, has been sent out in the public service mains. Following Willson's development of the electrothermic method for the production of calcium carbide, acetylene became available as an illuminant, at first for individual and isolated installations, but later for distribution in small communities.

With the introduction of the incandescent electric lamp in 1879, the use of coal and water gas as an illuminant was seriously jeopardized. Fortunately, however, Edison's development was closely followed by the results of Auer von Welsbach's application of his discovery of the remarkable behavior of the oxides of the rare-earth metals with flames, through which he invented the incandescent gas mantle and made it possible to obtain, with low candle power, manufactured coal and water gas, and with natural gas, illuminating effects comparable with those from electric lamps. As a result of this, and of the greatly extended use of

gas for heat and power, the criterion for gas has been very properly changed from candle power to thermal units. In the establishment of the mantle industry in this country and the solution of the many chemical and other problems, which arose in creating such an undertaking, credit is due Waldron Shapleigh, Harlan S. Miner, and M. C. Whitaker, while E. G. Love and W. H. Fulweiler have been most active in the chemical investigations of gas.

The industrial progress may, to a degree, be shown from the records of the census in that in 1876 the value of the products of "gas, manufactured" was about 40 million dollars, while in 1923 it was over 450 million dollars. These figures included not only gas but the by-products also. A special feature of the development of the half-century has been the perfecting of methods for the recovery and utilization of the by-products.

In making a study of the situation in 1909¹ I canvassed all available sources of gas in the United States and found the following quantities produced:

	Thousand-Cubic Feet
Gas industry	163,744,531
By-product coke industry	65,885,778
Natural gas	480,706,174
Producer gas	100,000,000
Blast furnace gas	2,900,000,000
Total	3,710,336,483

The Bureau of Mines reports the "natural gas consumed" in 1924 to amount to 1,141,482 million-cubic feet. It is not probable that the increase in the other items of the above table has been of the same order but for each it has been great. An interesting item in the Bureau's report is that, of the 1924 natural gas produced, 156,514 million-cubic feet were used in the manufacture of carbon black—a development with which the name of Samuel Cabot has been closely associated. Before the war the stripping of the cyclic hydrocarbons from the coke-oven gas of metallurgical works, in order that these hydrocarbons might be used in enriching gas served elsewhere for domestic purposes, had become established practice. During the war this practice was extended to domestic gas supplies to obtain the toluene and xylenes required for military purposes. The Society's representation on the Toluol Committee consisted of A. Bender, F. E. Dodge, W. H. Fulweiler, J. B. Hill, F. W. Sperr, Jr., and C. C. Tutweiler.² The stripping of natural gas to obtain the homologs

 $^{^1}$ Munroe, Charles E., ''The Gas Industry of the United States, 1909,'' $Progressive\ Age,$ 30, 232–34, 274–77, 322–27, 368–73 (1912).

² "Methods for Testing to Be Used in Toluol Plant Operation," Ordinance Dept., U. S. A., 1918. The Toluol Committee was appointed by the War Department.

of methane has now become common, such hydrocarbons being chlorinated and many subsequently hydrolyzed to produce alcohols which, again, form the parent substances for other chemical products. This industry is growing so fast that natural gas, used as a source of chlorinated compounds and alcohols, may soon become a separate item in our enumerations. In the cracking of petroleum in the water-gas carburetor, or elsewhere, unsaturated, as well as saturated, hydrocarbons are produced, and these form other starting points for chemical manufacture.

By-Product Coke

This industry is practically an imported one. The first known mention of the utilization of by-products from coking in the United States is the statement in the census reports of 1880 that the Consolidated Gas Company of Pittsburgh collected the gas from beehive ovens and distributed it for lighting purposes. The first plant of modern by-product ovens built in the United States was a battery of twelve Semet-Solvay ovens erected at Syracuse, New York, in 1892. This installation demonstrated the value of by-product coking, and the number of ovens increased to such an extent that the total value of their output for the year 1904 was returned as \$53,455,108, of which over \$3,150,000 was the value of the by-products. In reviewing these returns I made² an estimate of the gain which would have resulted if all the coal which was coked during the census year had been treated in by-product ovens (assuming, of course, similar yields and unit values for the beehive coal coked, which naturally might not hold true) and found it to amount to over \$37,000,000.

The total value of the products of the coke industry for the year 1923 was \$516,922,898, of which \$153,100,896 was for the by-products. Of the 19,640,798 short tons of coke produced in 1899, 4.6 per cent was generated in by-product ovens; of the 25,143,288 tons of coke produced in 1904, 2,422,796 tons, or 9.6 per cent, were made in by-product ovens; whereas of the 56,017,325 short tons of coke produced in 1923, 36,637,455 tons, or 65.4 per cent, were the output of by-product ovens.

Since the Semet-Solvay ovens were introduced they have been greatly improved and many other forms, having special advantages, have been used. Notable among these are the Otto Hoffmann, the Koppers, and the Becker ovens. The products of the byproduct coke industry are similar in kind to those of the gas

¹ Kirkpatrick, S. D., "Commercial Production of Isopropyl Alcohol," Chem. Met. Eng., **33**, 402-3 (1926).

² Munroe, Charles E., "Coke," Census of Manufactures, 1905; Bull. 65 (1907).

industry. Today each of those from the coke industry exceeds in amount the same kind of product from the gas industry. For instance, the quantity of ammonia (in all states of combination) produced in the coke industry in 1923 was 287,681,592 pounds, while that produced in the gas industry was only 22,749,950. Among those prominent in this development may be noted J. D. Pennock, F. W. Sperr, Jr., and William Hutton Blauvelt.

It is recognized that the character and yield of products from the carbonization of coal depend not only on the character of the coal treated but also on the conditions under which it is thermolyzed. In recent years much study has been given to low-temperature carbonization and among others, engaged in this investigation, S. W. Parr has been most prominent.

Petroleum Refining

It may well be pointed out that the splendid petroleum industry of the United States (as well as those of other countries modeled on it) was initiated through the researches of an American chemist, Benjamin Silliman, Jr., who, under date of April 18, 1855, rendered his "Report on the Rock Oil, or Petroleum, from Venango County, Pa.," giving the results of his investigation of the chemical and physical properties of this petroleum. Boverton Redwood, the English authority, says:

The first to undertake the systematic examination of petroleum, and some of the commercial products obtained from it, was Prof. B. Silliman, Junr. *** He fractionated the crude oil by distillation, and on examining the distillates, he came to the conclusion that certain of the bodies which they contained were products of distillation, and were not present in the crude oil. Professor Silliman studied the action of various reagents on the fractions, the behavior of the distillates when cooled, the value of the different oils as illuminating agents and lubricants, and their suitability for employment as a source of gas.

A graduate of Yale, Silliman was appointed professor of applied chemistry there in 1846. He was one of the founders of the Sheffield Scientific School in 1847 and professor of medical chemistry and toxicology at the University of Louisville 1849–1854. He was in charge of the departments of chemistry, mineralogy, and geology at the World's Fair in New York in 1853, and in 1854 he succeeded his father as professor of chemistry at Yale, which position he held until his death in 1885.

Silliman's researches, the results of which were embodied in the above-mentioned report, were made on seepage material. Accounts differ as to his relation to the actual search for the oil deposits. It is stated that a company, styled the Pennsylvania Rock Oil Company, was formed with Dr. Silliman as president, that it acquired rights over a considerable area in Venango County, but that it was unsuccessful in its attempts to locate oil. That, later, the "New Haven stockholders" in this company formed the Seneca Oil Company, obtained access to a portion of the territory of the Pennsylvania Rock Oil Company, and employed E. L. Drake to sink wells for them. That he conceived the idea of driving an iron pipe to overcome the obstacles encountered, and that on August 28, 1859, he struck oil on Watson's Flats, near Titusville, Pennsylvania.

The growth of the industry of petroleum refining, largely because of the information furnished by Silliman, was rapid, and many chemists became engaged in the study of petroleum and its products. Notable among them was Cyrus M. Warren, for a time professor at the Massachusetts Institute of Technology, who devised much apparatus and many methods for the study of fractional and destructive distillation, and the products of these processes. At first alone, and then in collaboration with F. H. Storer, he published extensively on the "Volatile Hydrocarbons." Contemporary with Warren was S. F. Peckham, for a while professor at the University of Minnesota. He had entered the Army following his graduation from Brown and, in 1866, was chemist to the California Petroleum Company. He then began his studies of petroleum and bitumens, which he continued throughout his life. He was the author of that stupendous Report on Petroleum in the United States Census of 1880 which has proved a mine of information for Redwood and all subsequent writers on the subject. These researches on the constitution of petroleum were continued in a most able manner by Charles F. Mabery, of the Case School of Applied Science. It is of interest that this early work in this field was aided by allotments from the C. M. Warren fund of the American Academy of Arts and Sciences.

Older members will recall the active controversy that "lit up" the pages of The Journal for a considerable period between Peckham and Clifford Richardson (to whom the world owes much in the development of asphalt pavements), over the constitution of bitumens. Both men were positive, forceful characters with very different outlooks. It did not tend to soften the asperities that there was a marked disparity of age and that Peckham had addressed the National Academy of Science on bitumens nearly a decade before Richardson's graduation from Harvard. Moreover, a commercial element appeared in that



Koehne-Williams

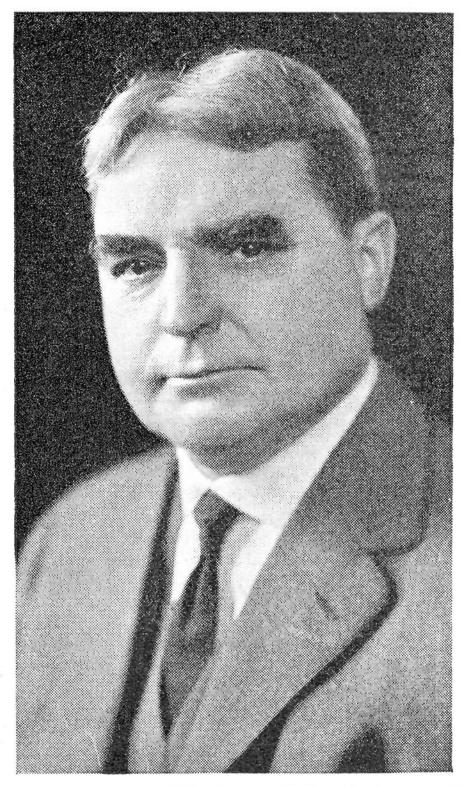
JOHN J. MILLER

(1887—)

Editor, Chemical Abstracts 1914



Evan J. Crane (1889–) Editor, Chemical Abstracts 1915–

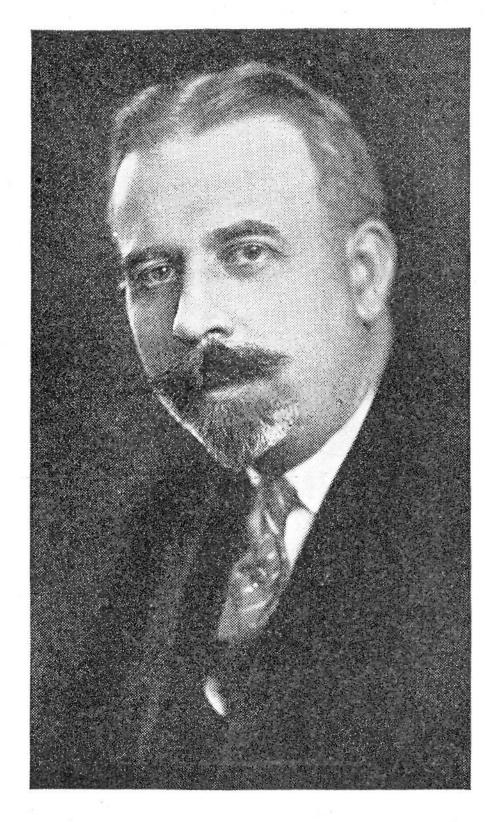


Underwood & Underwood

MILTON C. WHITAKER

(1870-)

Editor, Industrial & Engineering Chemistry 1911-1916



HARRISON E. HOWE (1881-) Editor, Industrial & Engineer-Chemistry 1922-

Richardson represented the manufacturer and contractor, while Peckham now was advisor to the City of New York and perhaps other municipalities.

It was but a short time after petroleum refining began that kerosene practically displaced whale oil, camphene, and other illuminants in use, except coal gas in communities of sufficiently dense population to permit its being distributed at a profit. It is true, "gasoline and naphtha" were burned to a slight extent in "sponge" lamps and used as solvents, as vehicles in paints, and for other purposes, but as kerosene commanded the higher price and was more readily sold there was a constant temptation to run the more volatile hydrocarbons into the kerosene "cut," thus producing low flashing-point oil. The result was that fires and explosions from the use of kerosene lamps were appallingly frequent until C. F. Chandler began his trenchant, and successful, campaign for the regulation by law of kerosene. He was aided by the development of gasoline-gas generators; by the growth of the water-gas industry, in which petroleum crudes and side products were used as carburetors; and particularly, by the automobile with the Selden engine becoming, in 1894, an accomplished fact.

The use of gasoline and of lubricants for automobiles, motor boats, and later for farm machinery, airplanes, and dirigibles, created not only an enormous demand for these substances but also for crudes for their production. Among extensive deposits of oil located and tapped were some, like that at Lima, Ohio, and in Canada and California, so high in sulfur content as not to be amenable to established methods of refining. Herman Frasch devised an operative means for the removal of this sulfur, and thus made such crudes available.

The normal gasoline yields, even aided by such cracking as the stills then in use permitted, not being enough to meet the demands, resort was had to the recovery of casing-head gasoline and then to stripping natural gas, W. O. Snelling and C. A. Burrell being pioneers in this art. The demand still growing, processes were developed for cracking under high temperatures and pressures, the Rittmann process being a type of the treatment of the petroleum in the vapor phase, and the Burton, Dubbs, and others of that in the liquid phase. The latter appears to be in successful operation.

In gasoline engines it is desired to obtain a high rate of combustion of the mixture in the cylinder, but when the rate of reaction passes from that of combustion to that of detonation knocking occurs and efficiency is impaired. In a model investigation, Thomas Midgley, Jr., and his associates found quite a number of substances which, when introduced into the mixture, prevented this change of rate. Among these they selected tetraethyl lead as the most efficient and practicable antiknock substance. This has been used successfully on an extended scale, but unfortunately, being very poisonous, it gave rise to fatal accidents during manufacture, which caused its withdrawal from the market and an investigation of the circumstances by a committee of experts acting under the United States Public Health Service. This committee has found that the handlers and users can now be properly safeguarded and "Ethyl Gas" has again come into use.

The magnitude which this industry has attained since 1859 is enormous. In 1925 the world's production of petroleum was over 1,060,000,000 barrels, of which the United States produced 764,000,000 barrels. There were refined in the United States 740,000,000 barrels, of which 41,338,000 barrels were imported. The output of gasoline was 10,886,127,000 gallons, of which about one-fifth was produced by cracking processes and one-tenth was natural gas gasoline. The quantity of kerosene produced was 2,510,334,000 gallons, or but about one-fifth that of gasoline. In 1880 the output of kerosene was about twenty times the volume of the gasoline. The consumption of our petroleum is advancing so rapidly that other sources of liquid fuel must soon be sought. One immediate source of supply is indicated in the oil shales¹ which were investigated by Charles Baskerville and W. A. Hamor in 1909.

Explosives

High explosives, in the person of nitroglycerol, first appeared in the census of 1870, six years prior to the founding of this Society. For some five hundred years prior to that time man's demands for propellants and blasting agents had been met by black powder mixtures (gunpowders and blasting powders). Dr. Smith, in his Northumberland address, also mentions guncotton, but the manufacture of military guncotton began in this country at a later date and never rose to any considerable magnitude. In 1870 the value of black powder manufactured was \$4,011,839, and of nitroglycerol \$225,700, or a total of \$4,237,539. In 1923 the total value of the products of this industry was over \$75,000,000. The total quantity of explosives made in 1923 was

¹ See also the work, "Shale Oil," by Ralph H. McKee of the American Chemical Society Monographs.

577,245,570 pounds: of these 262,290,012 pounds were dynamites; 67,334,759 permissibles; 2,695,780 nitroglycerol used directly as an explosive; 8,433,986 (25-pound) kegs of blasting powder; 2,779,422 pounds of black gunpowder; 5,150,825 of smokeless powder; 2,724,300 of fuse powder; and 23,420,822 pounds of "all other explosives." The peak of production for black powder was reached in 1907, when some 287,000,000 pounds were manufactured.

Russell S. Penniman made a most important contribution to the industry in 1885 when he introduced the coating of ammonium nitrate, to check its hygroscopic action, for use in explosives, ammonia dynamites, and ammonia-gelatin dynamites being now quite widely used. A large amount of weak nitric acid recovered from spent acids and other sources is utilized in making ammonium nitrate. In 1925 over 71,000,000 pounds of ammonium nitrate were used as an ingredient of explosives.

Permissible explosives are such as have passed the chemical and physical tests prescribed by the United States Bureau of Mines to determine their suitability for use in coal mines, where explosive atmospheres of gas, or dust, or both, with air may occur. They originated from the investigations of the "causes of mine explosion" authorized by the Congress in 1908. Among those most active in these investigations are Clarence Hall, W. O. Snelling, C. G. Storm, S. P. Howell, J. E. Crawshaw, G. St. J. Perrott, and C. A. Taylor. The chemical researches of E. J. Hoffman and W. H. Rinkenbach are of especial value. The writer has had close association with this work from its inception.

The success of a manufacturing enterprise depends, among other factors, upon its freedom from accidents that interrupt its operations and destroy its property. The explosives industry is obviously exposed to many hazards and especially in transportation. On the advice of Charles B. Dudley, chief chemist of the Pennsylvania Railroad Company, the American Railway Association in 1905 appointed a committee consisting of Charles E. Munroe, chairman, Henry S. Drinker, and Charles F. McKenna to investigate and report on the regulation of transportation by rail so as to reduce liability of accidental explosions. Following the rendering of the committee's report, the Bureau for the Safe Transportation of Explosives and Other Dangerous Articles was established and Beverly W. Dunn was appointed chief inspector. So efficiently have the duties of this office been performed that in his annual report, March, 1926, he was able

¹ Am. Ry. Assoc. Circ. **615**, 13-15 (September 21, 1905).

to say that although over 500,000,000 pounds of explosives were transported by the railroads of the United States and Canada during the calendar year 1925, but twenty-six accidents, causing a property loss of \$11,702, occurred, and no casualties whatever resulted. In fact, a distinguishing feature of the past fifty years has been the safeguarding of operations and operators, and chemists have been leaders in the safety campaign.

Prominent among the many who have been active in the development of explosives are George M. Mowbray, Walter N. Hill, Lammot du Pont, Charles L. Reese, G. C. Hale, Fred Olsen, A. M. Comey, and Tenny L. Davis. The full story is to appear shortly in a work prepared under the auspices of the Institute of Makers of Explosives.¹

This review would be incomplete without reference to the abnormal activities of the explosives industry during the World War when fifty-three new plants, involving an expenditure of more than 350 million dollars, were constructed and put into operation in eighteen months. Production of TNT, amatol, picric acid, explosive D, tetryl, TNA, and smokeless powder was conducted on a previously unheard-of scale, but this and other achievements, in the applications of industrial chemistry to warfare, have already been most fully recorded.² Conspicuous in this war development was the large-scale production of poisonous gases under the efficient efforts of W. H. Walker and in which W. L. Lewis rendered distinguished services. The story of the development of this industry and of the organization of the Chemical Warfare Service as a unit of the Army has been told by Fries and West.3 Speaking of the latter, the authors say, "This holds the distinction of being the first recognition of chemistry as a separate branch of the Military Service in any country or in any war."

Plastics

The discovery of the colloidal solution called "collodion" was made by Maynard, of Boston, in 1847. It was in 1874 that L. S. and J. W. Hyatt reduced to practice the method employed in the manufacture of that pyroxylin plastic which they styled "celluloid." Chemical progress in this industry was due largely to J. H. Stevens. Another important development was the single base smokeless powder in which use was made of May-

 $^{^1\,\}mathrm{Van}$ Gelder, A. P., and Schlatter, Hugo, "History of the Explosives Industry in America."

² Clarkson, Grosvenor B., "Industrial America in the World War," and Crowell, Benedict J., "America's Munitions."

Fries, Amos A., and West, Clarence J., "Chemical Warfare."

nard's ether-alcohol mixture, though in different proportions, for the production of the pyroxylin colloid. In both the manufacture of collodion and of smokeless powder the cellulose nitrates employed are carefully chosen and are of a definite nitrogen content and viscosity-producing capacity. Much of the success in the development of this smokeless powder manufacture is due to Charles F. Burnside.

Another advance is in the gelatinization of cellulose nitrates of medium nitrogen content by nitroglycerol, or other nitric esters, to form explosive gelatin, from which, by admixture with wood pulp, sodium nitrate and other "dopes," gelatin dynamites result. Still another application was Chardonnet's squirting of this collodion into threads, the denitration of these threads, and their conversion into artificial silk. Again we have Archer flowing glass plates with this collodion for use in the wet plate process of photography, and within the last fifty years the Kodak Company, the Celluloid Company, and others forming from collodions containing acetone, and various other solvents, long continuous films for use in modern photography. We owe much of the chemical advancements in the photographic art to H. Carey Lea and C. E. K. Mees. Yet another development has been the production of collodion-like products from cellulose nitrates, with a wide variety of solvents, known as lacquers, or, when admixed with pigments, as enamels.

Plastics have come into commerce produced from casein, gelatin, fibrin, caoutchouc, gluten, resins, and other substances. The most modern and important are the phenol-aldehyde condensates, of which bakelite, invented by Leo H. Baekeland, is the most important. It will be recalled that he also invented the very valuable Velox paper printing process.

The statistics of the substances classified as plastics are subject to variation, yet some measure of growth may be gained by noting that in 1880, the first census in which these substances appeared, the value returned was \$1,261,540; in 1900 it was \$2,864,044; and in 1923 it had increased to \$102,229,807.

Rayon

Attention has been called to Chardonnet's process for the production of artificial silk from cellulose through cellulose nitrates. In Germany this adaptation of cellulose was effected by the use of cupric ammonium compounds, whereas in England, Cross and Bevan effected the transformation through the formation of cellulose xanthate, inventing what is known as viscose.

All of these methods of producing artificial silk, now by requirement of the Federal Trade Commission called "Rayon," are in active operation in this country. The establishment of the viscose manufacture on a firm foundation is largely due to the investigations and supervision of our eloquent former President A. D. Little. Brought to public attention at the Paris Exhibition of 1889, this is now a firmly established industry. The output for 1925 was 197,000,000 pounds, of which 50,000,000 pounds were produced in the United States, which is now the leading producer. According to William J. Baxter, speaking for the United States, "we have this new industry returning more profits during 1926 than the entire cotton industry." This is a marvelous achievement of industrial chemistry.

During the World War, to meet the demands for smokeless powder, successful investigations were made into the production of cellulose from wood. These results are at the disposal of rayon manufacturers, and the progress is such that wood may drive cotton from the market. This would be most deplorable for the resources of our forests are already overtaxed. The source of the cellulose should be found in annuals.

Paints and Varnishes

This industry is a very old one. At the census of 1850 the value of its products was placed at \$5,466,052; from the average of the returns in 1870 and 1880 the value of its products fifty years ago was about \$26,000,000. At the census of 1923 the value returned was \$440,564,618. Among the novelties in the development of this industry are "ready mixed paints," with a value in 1923 of \$147,000,000; zinc oxide, \$23,471,098; lithopone, \$13,001,506; and pyroxylin lacquers and enamels, \$6,944,306. The production of the latter is growing more rapidly than perhaps any other member of the paint and varnish class. The automotive industry is a large consumer of lacquers, and the railroads are now testing them out on their rolling stock. They possess the advantage that they may be readily applied with the air brush or spray gun. The walls and wood work of the Book-Cadillac Hotel, at Detroit, containing one thousand two hundred guest rooms besides dining, ball, and lounge rooms and lobbies, have been sprayed with pyroxylin lacquer. Certain iron oxides, titanium oxide, and lead oxysulfates have come forward as pigments.

Among those responsible for advances in this industry are

¹ Baxter, William J., "The American Industry Settles Down," Manchester Guardian, Commercial (April 15, 1926).

sturdy A. H. Sabin, Maximilian Toch, Victor Bloede, and Peter Fireman. The late Senator E. F. Ladd played an important part in fixing standards, while the researches of C. B. Dudley and F. N. Pease, of the Pennsylvania Railroad, revealed the useful parts played by barytes and other supposed make-weights. H. A. Gardner, in presenting the results of his researches on behalf of the Paint Manufacturers Association, is perhaps the most voluminous writer in this field.

Rubber

The rubber industry of today is a native development, beginning with the invention of vulcanization by Charles Goodyear in 1839. It is true that shoes of raw rubber had been imported or manufactured prior to that date, and their sale continued while Goodyear's invention was being commercially developed. I remember wearing such shoes, when I was quite small. They were heavy, clumsy, and resilient. We were truly bouncing boys on the days when we wore these rubber shoes. I remember, too, how these unvulcanized rubbers became soft and sticky in summer. The industry has improved to the extent that competent chemists and chemical engineers have been put in control of plantation and factory processes, and have been given an opportunity to conduct researches into the constitution and behavior of rubber. Caoutchouc being a terpene, all researches on terpenes have contributed to the advancement of this industry.

Rubber was brought from Para, in Brazil, to Salem, Massachusetts. The method of recovering the rubber from the latex, followed in Brazil (by gathering it on a stick and smoking it over a fire) reminds me in its crudity of the method I found in use in the art for pickling copper sheets while I was investigating the corrosion of the copper sheathing of the U. S. S. Juniata. This consisted in scrubbing the sheets with the fermented urine collected from the operatives. I have learned of other gross, unscientific, and filthy practices transmitted through long periods in the empiric arts.

With the establishment of plantations the chemist was called upon for aid, with the result that the methods of separating the rubber from the latex practiced on the plantations are cleaner and better, and the product reaches the manufacturer of rubber articles in a purer condition. Kelly says: "Today more than 75 per cent of the world's rubber supply is prepared under the scientific control of the chemist."

¹ Proc. U. S. Naval Inst., 12, 319-417 (1886).

² Kelly, W. J., Chemistry in the Rubber Industry, "Chemistry in Industry," Vol. I, 1924, pp. 340-56.

Not long after the vulcanized rubber industry became established, Clapp started a plant for reclaiming rubber at Hanover, Massachusetts. In 1900 the quantity of rubber reclaimed for re-use amounted to 40 million pounds. It is believed that this is one of the earliest instances of recovering waste in manufacture outside of the obvious one of remelting old metals.

Much investigation has been given to vulcanizers; to the use of sulfur chlorides, through which the "cold" as well as the "hot cure" has been developed; to the effect of a variety of substances as "dopes" or fillers; and, of recent years, to accelerators. Time, upon which interest fattens and through which output and turnover are impeded, is the essence of manufacture and merchandizing. The chemist has speeded operations so that, by the addition of 1-1.5 per cent of an accelerator to a mixture, the vulcanization may be speeded up from three hours to as many minutes for its completion. Accelerators are found among complex organic substances, such as aniline derivatives or substituted ureas. Among recent achievements is the decoagulation of coagulated rubber by William Beach Pratt, who has also been successful in effecting rubber dispersions. Among those who have contributed to the advancement of this industry, by their researches, are H. C. Pearson, W. C. Geer, and J. B. Tuttle. The value returned for rubber products at the census of 1923— \$958,518,000—gives but a partial view of the consequences of Goodyear's comprehension of the meaning of his "cut and try methods," for the industry has attained enormous proportions in many foreign countries. It is well to note that the automobile industry rests on rubber.

Essential Oils and Perfumes

These are of natural origin, like the oil of peppermint, or artificial, like heliotropin. Many of them contain esters, but aldehydes and ketones are frequently present. They are used as perfumes, in flavoring, and as therapeutic agents. The industry is, in the monetary value of its products, a minor one, but it plays an important role in the life of man. The total value of its products in 1899 was \$434,451. In 1923 this had risen to \$3,393,720. This industry is indebted in many directions to F. B. Power, distinguished for his researches on chaulmoogra oil; also to Edward Kremers, Clemens Kleber, and E. K. Nelson, who have investigated the character of the oils from many natural sources; and to Alfred Springer, who has mastered synthetic flavors. None who have heard or read it can forget M. T. Bo-

gert's masterly address on perfumes. A leader in the field of peppermint oils was A. M. Todd, a former active member of this Society, and for some time a member of Congress.

Fine Chemicals

This is a class which one finds particularly difficult to define and delimit. Evidently pure, and especially synthetic, "essential oils" might be gathered here. Bulletin 210 of the Census of 1900 says:

Under this classification are grouped the chemically pure chemicals manufactured for sale, the chemical substances which are made for use in laboratories and in pharmacy, and those in which, like the salts of silver and of gold, the price of the unit of measure is relatively very high.

Dr. McMurtrie rather shook my foundations when, as chief chemist of the Royal Baking Powder Co., he said, with glistening eyes, "We are now turning out cream-of-tartar 99.95 fine regularly in tonnage lots." Similar progress has been made by others in the manufacture of some "General Chemical" on a large scale of a high degree of purity. Dr. Herty has recently written a charming article1 covering many substances in this class. In this group also are included organic solvents which, in recent years, not only have increased largely in volume but also have multiplied in number. These solvents not only are of immense importance in effecting analytical separations so that each new solvent possesses much potential power in solving problems, as indicated by the researches of Victor Lenher with tellurium and selenium, but they also enter into a multitude of industries, such as in the separation of alkaloids from their natural occurrences; as vehicles in paints, varnishes, lacquers, and enamels; for use in the production of colloids and colloidal solutions; and for a great variety of other purposes.

This subject has been recently developed by D. B. Keyes.² He very properly places ethyl alcohol first for, with the exception of water, no solvent is so widely used. It is also an important parent substance in farther manufacture. It was long recognized that an important factor in giving Germany dominance in many of the chemical industries, and more especially those producing organic chemicals, was that her government had made alcohol tax-free for use in the arts, while our Government and others had not done so. Finally, our legislators awakened to the gravity of the situation. In 1906, being summoned before the com-

¹ Herty, Charles H., "The Future of the Synthetic Organic Chemical Industry in America," J. Chem. Education, 2, 519-32 (1925).

 $^{^2}$ Keyes, D. B., Alcohol and Some Other Solvents, "Chemistry in Industry," Vol. I, 1924, pp. 34-57.

mittee of our Congress dealing with tax-free alcohol for use in the arts, I well recall Mr. Volstead's earnest advocacy of enacting legislation to that effect, and in 1907, being appointed superintendent of the Special Alcohol Exhibit at the Jamestown Exposition, designed to promote the purposes of the Act of Congress of June 7, 1906, and subsequent legislation of this kind, I have naturally followed succeeding events with special interest. I believe I express the feeling of all who have the welfare of the chemical industries, and the people they serve, at heart in saying that it is much to be regretted that so wise and beneficent a piece of legislation should be greatly nullified by bureaucratic regulations.

An important development in this field was the large-scale production of furfural, from corn cobs, oat hulls, and similar waste materials, which resulted from the investigations of F. B. LaForge and his associates in the United States Department of Agriculture. A marked novelty was the fitting out of the "S. S. Ethyl" as a factory in which to extract bromine from the sea water in which the vessel floats. Another novelty is the large-scale production of absolute alcohol; also that of synthetic ethylene glycol, which is displacing glycerol in the explosives industry.

This country owes much to E. R. Squibb, J. Uri Lloyd, G. D. Rosengarten, Eli Lilly, G. P. Adamson, and many others for developing this industry and keeping abreast of progress but, as pointed out, largely because of special privilege, before the World War our manufacturers were unable to compete in the market for a large line of these products. When the war broke out in Europe and we were deprived of many essential chemicals of this class, C. G. Derick inaugurated a small-scale plant at the University of Illinois, which has been continued by Roger Adams, that alleviated the situation. Actual manufacture in this field was begun by the Eastman Kodak Company in 1918, followed by the Heyl Laboratories, Special Chemical Company, and the Synthetic Laboratories. In 1923 the Eastman Company listed over 1300 different fine chemicals, and probably more than 2000 are now available.

In the census of 1900 the products in this class were valued at \$4,216,744. This classification does not appear in the report for 1923, but on assembling the separate items from the records I find the value to be over \$81,000,000.

Other Industries

Limitations of space compel but brief mention of other industries such as fertilizers, whose production in 1914 was valued ¹ Clarke, H. T., "Rare Organic Chemicals," J. Ind. Eng. Chem., 14, 836-37 (1922).

at \$153,196,000, and in 1923 at \$183,089,000; tanning materials and natural dyestuffs at \$20,620,000 and \$35,972,000, respectively; soap at \$39,075,000 and \$102,857,000; and wood distillation and charcoal manufacture at \$10,284,000 and \$29,695,000. Coal-tar products have fluctuated greatly, but for 1923 the value returned was \$143,783,985.

Dr. J. Lawrence Smith in his 1874 address devoted considerable space to "Stearinery," including soap, stearic acid, glycerol, and related material. It is pointed out that the glycerol industry owes much to the researches of R. A. Tilghman, of Philadelphia. More recently Ernst Twitchell has reduced to practice a catalytic fat-splitting process for the production of fatty acids and glycerol. During the war John B. Eoff, W. V. Linder, and G. F. Beyer, chemists in the Internal Revenue Bureau under chief chemist A. B. Adams, developed a successful process for producing glycerol from black strap molasses, using preferably as the fermenting organism S. Ellipsoideus (var. Steinberg). W. O. Snelling sought to obtain glycerol from trichloropropane, prepared from the propane of natural gas, but this had not been reduced to practice when the war ended.

The researches of William McMurtrie, H. W. Wiley, F. K. Cameron, and the chemists at many of the agricultural experiment stations and colleges contributed much to the fertilizer industry. It is to be regretted that records of Dr. Wiley's early extensive researches in this field at the Bureau of Chemistry were withheld from publication.

Food products is another large industry which, in recent years, has been greatly promoted by the researches of chemists. Notable in this field are H. W. Wiley, C. L. Alsberg, and C. A. Browne. This industry offers in the Research Laboratories of the National Canners Association, organized in 1913 under W. D. Bigelow, an admirable example of the benefit of coöperative research under competent and judicious direction.

Among the many ramifications of the food products industry is that of dairy products, which is much indebted to S. M. Babcock, of the University of Wisconsin. In his memorial notice of E. N. Horsford, inventor of phosphate baking powder, of an emergency ration for troops in the Civil War, and sometime professor of chemistry at Harvard, C. L. Jackson¹ says that Horsford invented condensed milk, which he worked out for use in Dr. Kane's Arctic Expedition that sailed in 1853. Gail Borden appears to have been investigating this field at about

¹ Proc. Am. Acad. Arts Sci., 20, (N. S.), 340-61 (1893).

the same time. Whatever be the truth as to priority, it appears evident that the industry of condensed milk originated in this country. Evaporated milk was first packed in this country on a commercial scale in 1885, and this was followed by spray drying to produce powdered milk.

Another American industry is that of cottonseed oil, which started in a small way in Columbia, South Carolina, prior to 1826. Refining by caustic soda was introduced into the refineries in New Orleans between 1860–1870. The use of fuller's earth was worked out by William B. Albright and Henry Eckstein in 1880. In 1893 Eckstein accomplished deodorization by heating the oil to a high temperature and passing steam through it, while David Wesson put in operation at Savannah, in 1900, deodorization in a vacuum. Wesson¹ says:

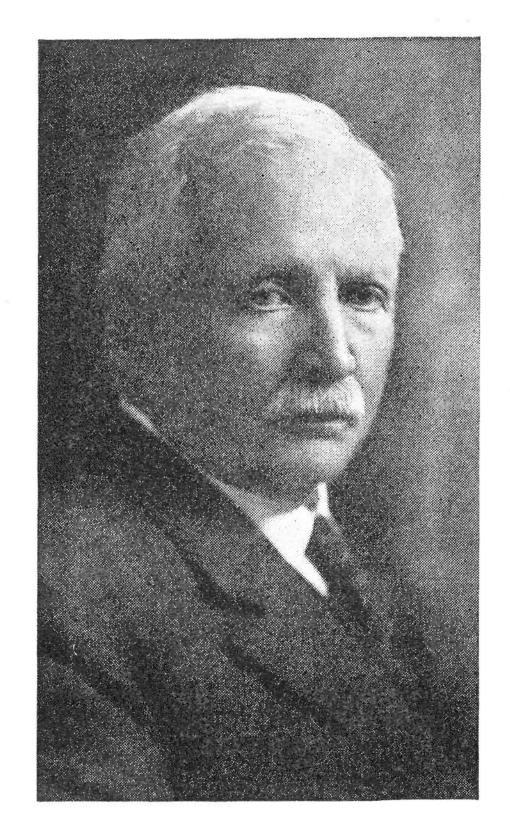
Chemistry has had the industry in hand since 1890. In consequence, refining methods have been improved greatly, losses have been prevented, and new products have been evolved. The process of hydrogenation has been particularly active in expanding the industry to its present great dimensions, The chemist has been the means of putting about \$125,000,000 every year in the accounts of the farmer; in other words, he has added ten to twelve dollars to the value of the crop for every bale of cotton grown.

A similar tale might be written for the corn products industry in which Arno Behr won his spurs.

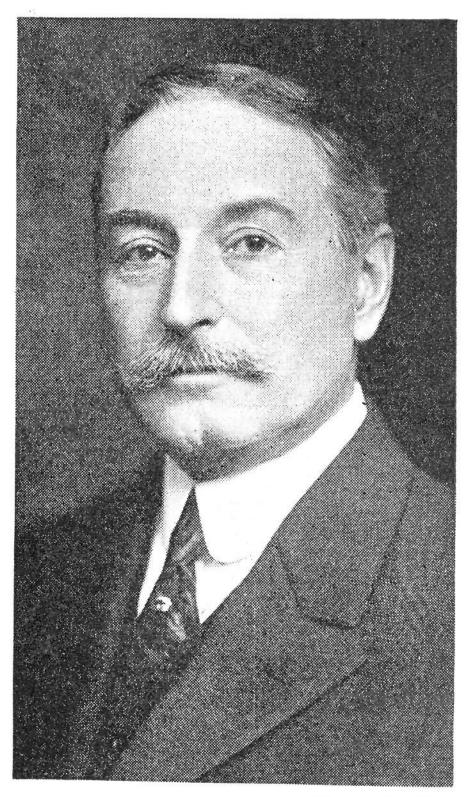
Forestry, Vegetable, Animal and Other Agricultural Industries

Little attention can be given to wood products, though they play an important part in many chemical industries, either directly as pulp in the manufacture of paper, dynamite, and other substances, or as a source of chemical substances like turpentine, rosin, many dyestuffs, tanning materials, and exudates such as balata, gutta-percha, caoutchouc, and gums for chewing and for varnishes. Large as are the number of known products from vegetable sources, the interesting production of mucic acid from the wood of the larch by S. F. Acree indicates that this mine is by no means exhausted. In fact, I am of the opinion that there are many more most valuable substances yet to be recovered commercially. The unexpected usefulness of the chemist in the forest products industry is illustrated in Charles H. Herty's invention of a cup for gathering turpentine from the long-leaf pine, which has greatly improved this wasting industry. H. O. Chute and M. G. Donk have been prominent in devising methods for the better utilization of the stumpage and improvement in distillation process by which a larger number of useful products

¹ J. Ind. Eng. Chem., 7, 277 (1915).



Henry E. Niese (1848–) Charter Member



Alman & Co.

J. B. Francis Herreshoff
(1850–)
Charter Member



Alman & Co.

SAMUEL A. GOLDSCHMIDT

(1848)

Member for Fifty Years



ADOLPH KUTTROFF (1846-) Member for Fifty Years

S. A. Goldschmidt attended the Priestley Centennial in 1874.

have been obtained. The chemists of the Hercules Powder Company, under the leadership of George M. Norman, have been especially successful in putting new life into the utilization of southern yellow pine waste for naval stores. An important factor in promoting the improvements in commercial turpentine and rosin has been the work of F. P. Veitch and his co-workers of the United States Department of Agriculture, which led to the passage of the federal naval stores act in 1923.

The paper industry has particularly benefited because of the intimate knowledge of this industry possessed by A. D. Little, the ingenuity and indomitable perseverance of Hugh K. Moore, and the organizing ability of Robert B. Wolf. It is of interest that two of the important processes for paper making are of American origin—the sulfite process, invented by B. L. Tilghman in 1867, and the soda process, invented by Watt and Burgess in 1853. Of a somewhat analogous character is the utilization of sugar cane bagasse in the manufacture of artificial lumber to replace for certain uses white pine and other soft woods that are so rapidly disappearing. With the art reduced to practice by T. B. Munroe and C. G. Muench some six years ago, there are now produced over 17 million square feet of lumber per month. The application of chemistry and physics to the protection of the users of paper was first suggested and undertaken in this country at the Bureau of Chemistry. As a result of this, the Congressional Joint Committee on Printing has since 1912 purchased all paper for the Public Printing and Binding on carefully prepared specifications.

The federal Department of Agriculture, during the last half-century, has also made generous provision for the advancement of animal and plant industries through the chemical investigation of their special problems. Notable among these may be mentioned the researches of E. A. de Schweinitz and Marion Dorset through which the deadly hog-cholera was conquered. The researches of J. K. Haywood, C. C. McDonnell, H. H. Custis, J. N. Taylor, and other chemists of the department upon insecticides, and of V. K. Chesnut and J. F. Couch upon poisonous plants also deserve to be mentioned in this connection.

The great packinghouse industry, which is dependent upon agriculture, is of American origin and involves almost innumerable applications of chemistry in the solution of its problems. W. L. Lewis, Arthur Lowenstein, W. D. Richardson, Paul Rudnick, and L. M. Tolman are among the more prominent workers in this field.

The Chemist in Sanitation

Water is probably more important and quite as valuable as the product of any of the industries cited. The chemist has been most active in investigating potable water and water for industrial, manufacturing, and therapeutic purposes. Public service waters are brought into proper condition for sale by coagulation, sterilization, and softening. In 1875 there were 275 water works in the United States, whereas in 1926 there were over 9000. The most novel development was that of sterilization worked out at Chicago, Illinois, and Boonton, New Jersey, in 1908 with hypochlorite of lime and in 1910 with chlorine. Among those active in this field have been W. R. Nichols, W. D. Collins, J. W. Mallet, C. R. Darnell, A. M. Buswell, E. M. Chamot, F. R. Georgia, R. S. Weston, W. P. Mason, Edward Bartow, W. W. Skinner, and J. W. Ellms. Mrs Ellen H. Richards' chlorine surveys were especially ingenious and useful. C. F. Chandler's reports on the Saratoga waters were valuable contributions to knowledge. C. B. Dudley showed the value of the chemical supervision and treatment of waters, both for potability and steam generation, to railroads. W. P. Mason, Edward Bartow, L. P. Kinnicutt, and E. B. Phelps have also devoted attention to the chemistry of sewage, a closely related subject.

Another topic to which chemistry has contributed to a continually increasing extent, and especially since the introduction of water heaters and automobiles, is ventilation, more particularly with a view to the prevention of poisoning with carbon monoxide. Among examples of this are the studies of vehicular tunnels, and especially of the one projected under the Hudson River, by A. C. Fieldner, and of the New York subways by C. F. Chandler.

Research

A marked feature in the development of industrial chemistry during the last fifty years is the employment of educated chemists, at first in inspection and control work, and later in research work. Realizing what this meant to the industries, an inquiry as to the number of chemists employed was made, at the census of 1900, of each establishment reporting on "Chemicals and Allied Products." The total number reported as employed was but 276. An analysis, made by Secretary C. L. Parsons, of the membership of this Society, under date of October, 1924, discloses 2697 engaged in technical direction; 1236 in chemical development as research chemists; and 1167 in chemical control

as works and laboratory chemists. It is not disclosed how many of the 1004 serving as executives, or of the 2423 in the managerial class, are trained chemists, but the number is large.

Much aid in industrial development has come from the professional chemist upon whom the manufacturer, in the early days, relied to get him out of trouble. The oldest of existing practitioners is probably the firm of Booth, Garrett, and Blair, founded in 1836 by J. C. Booth, the first man to be thrice elected President of this Society. His career has been set forth by Edgar F. Smith. Space does not permit the naming of all practitioners but Rickett and Banks of New York, Mariner and Hoskins of Chicago, Arthur D. Little, Inc., of Boston, Pittsburgh Testing Laboratories, John E. Teeple of New York, S. P. Sadtler and Son, Inc., of Philadelphia, and the Industrial Research Laboratories, Washington, D. C., are among those well known to have engaged in development work. But the most outstanding feature of the latter part of the half-century is the inauguration of well-equipped research plants by manufacturers, such as the Hercules and du Pont explosives corporations, the General Electric Company, New Jersey Zinc Company, Eastman Kodak Company, and all corporations that desire to continue to do business. There are many instances in which industries as a whole have engaged in coöperative research, and this broad policy has commended them to those they serve.

The federal Government has contributed to this first, in the establishment of the Department of Agriculture with its widely known and most efficient Bureau of Chemistry and chemical laboratories in the Bureau of Soils and many other divisions, followed by the colleges of agriculture and agricultural experiment stations to each of which a corps of skilled chemists is attached. In fact agriculture, in its many ramifications, has received the aid of government chemists to a much larger extent than any other industry. Agriculture and other industries have also been served by the chemical staffs of the United States Bureau of Standards, Bureau of Mines, and Geological Survey.

A most beneficent outcome of the World War is the National Research Council which was created to organize, promote, and coördinate researches. Through the successive services of E. W. Washburn, W. D. Bancroft, F. G. Cottrell, J. E. Zanetti, J. F. Norris, and W. J. Hale, as chairmen of the Division of Chemistry and Chemical Technology, research in American chemical in-

¹ Smith, Edgar F., "James Curtis Booth, Chemist 1810-1888," pamphlet, 1922, 17 pp.

dustries has been greatly advanced. A recent example of the progress being made in this direction is the allotment of \$100,000 per year for five years for research upon petroleum, the program of which was arranged by the National Research Council.

Conclusion

As I review the foregoing I realize how much important material I have been compelled, through exigencies of time and space, to omit. The thrilling story of our synthetic dyestuffs industry, leather, glass, refractories, sugar, cement, iron and steel, and all the metallurgical industries, which are founded on and controlled by chemistry, have had to be passed by with many others.

In reviewing the phenomenal growth of industrial chemistry in America during the past fifty years it is natural to speculate upon the outlook for the future. Will the curve of accomplishment continue to rise at its present ascending rate or will it gradually flatten out in a horizontal direction? The peak of production with regard to certain important resources, that have played such an important part in the development of American chemical industries during the past fifty years, has already been passed. The supplies of natural gas, formerly regarded as almost unlimited and so lavishly wasted, are already approaching the point of depletion; one of the large sulfur wells of Louisiana has been exhausted; the annual yield of petroleum in the United States is diminishing and the untouched stores of anthracite coal are apparently nearing an end. The gradual exhaustion of these and other natural resources will tend to retard the development of our chemical industries with respect to certain of their present phases. With the depletion of our reserves we may look, however, to far greater improvements and economies in their chemical utilization. The resources of bituminous coal in the United States are still sufficient for many centuries and the utilization of these extensive deposits, not only for the generation of power and gas, but also as raw materials for the production of liquid hydrocarbons and other organic chemicals, will receive increasing attention during the next fifty years. There will also be a much greater utilization of water power as a source of electricity for chemical purposes, the recent developments at Muscle Shoals serving as a conspicuous example. Whatever the future may hold in store the American industrial chemist may be depended upon to render even more conspicuous accomplishments than those which have been so briefly reviewed in the present paper.

^{1 &}quot;Proposed Research regarding Petroleum," Mining and Metallurgy, 7, 347-49 (1926).