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Contents

Editorials 762–763

Pittsburgh as a Chemical Research Center. William Allen Hamor. 764
Pittsburgh as an Industrial Center. J. H. James and W. F. Rittman. 772
The Paint Industry. A. H. Sabin 775
Pittsburgh as a Center of Chemical Education. E. H. McClelland. 776
The Foundation for Chemical Development. W. A. Noyes 779
Progress in the Chemistry of Naval Stores, 1920–1921. F. P. Veitch and V. E. Grotlisch 781
A Department Store Laboratory. E. B. Millard 785
Potash in America—Two Years' Progress. John E. Teeple 787
The Fertilizer Industry. Wm. H. Waggaman 789
Developments in Nitrogen Fixation. J. M. Braham 791
Progress in the Canning Industry in the Last Ten Years. W. D. Bigelow 793
A Boom Needed. H. W. Jordan 794
Recent Chemical and Technological Advances in Our Knowledge of Gelatin and Glue. Robert Herman Bogue 795
Progress on Emulsions. Leon W. Parsons 797
Vegetable Glue. C. K. Reiman 799
Colloid Chemistry. Jerome Alexander 800
The Chemistry of Intermediates. M. L. Crossley 802
Science in the Textile Industry. E. D. Walen 806
Heat Treatment Progress during 1921. A. E. White 807
Heat Transmission and Evaporation. W. L. Badger 808
The Vegetable Oil Industry. David Wesson 809
Solvent Extraction of Vegetable Oils. C. F. Eddy 810
Local Anesthetics. Henry Gilman 812
Pharmaceutical Chemistry. Frank R. Eldred 814
Chemistry as an Aid to the Tobacco Industry. A. L. Chesley 817
Recent Contributions of Chemistry to Photography. S. E. Sheppard. 820
Glass Technology. George W. Morey 823
Review of Analytical Work Applicable to Leather and Tanning, 1920–1921. F. P. Veitch and R. W. Frey 825
Vegetable Tanning. Arthur W. Thomas 829
Mineral Tannages. F. L. Seymour-Jones 832
The Preparation of Skin for Tanning. John Arthur Wilson 834
Rare Organic Chemicals. H. T. Clarke 836
Organic Catalysis. E. Emmet Reid 838
Chemistry of Sanitation. A. M. Buswell 840
Activated Sludge. Edward Bartow and Gerald C. Baker 842
By-product Coking. F. W. Sperr, Jr. 844
Shale Oil. Ralph H. McKee 847
The Application of Chemistry to the Conservation of Motor Fuels. Thomas Midgley, Jr., and T. A. Boyd 849
Scientific Method in Rubber Compounding. C. O. North 851
Physics of Rubber, 1920–1921. W. B. Wiegand 854
The Chemistry of Rubber Vulcanization and Acceleration. C. W. Bedford 856
Recent Advances in Pulp and Paper. Clarence J. West 858
Hardwood Distillation. Harry C. Merriam 860
The Ferro-Alloy Industry. B. D. Saklatwalla 862
Recent Progress in Magnesium Alloys. John A. Gann 864
Nonferrous Alloy Progress in 1921. H. W. Gillett 865
Physical Chemistry as Applied to Foods. Carl L. Alsberg 867
An Outline of the History of Chemistry Symbolically Represented in a Rookwood Fountain. Harry Shipley Fry 868
National Exposition of Chemical Industries 872

Washington Notes 873

Miscellaneous:

Research in Wood Finishing 775
A Metric Dozen 786
Commercial Methods of Making Carbon Black 786
Desulfurizing Coke 792
Help Kazan 794
Inventions by British Government Workers 798
Industrial Films 805
The Trend of Prices 811
Platinum Theft 811
Buy Chemicals in Metric Units 824
The Chief Chemist Remarks 831
Oil-Cracking Patent Application of 1913 Just Granted 839
Meeting of the American Electrochemical Society 853
Fatal Explosion at Harvard College 855
D. H. Killeffer Succeeds R. T. Stokes 857
Meeting of Chemists at Utrecht 857
Publicity for Chemistry 863
Chemical Equipment Manufacturers Petition Congress 863

Book Reviews 874

Current Publications 876

Market Report 878

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EDITORIALS

Our Progress Number

THIS ISSUE is something of an innovation for *The Journal of Industrial and Engineering Chemistry*. It is an effort to meet numerous requests from our readers for authoritative summaries which will enable those interested but not specializing in a given field to gain some knowledge of progress therein. These reviews are intended not as short cuts to information but as a stimulus, especially to our younger chemists, to read more thoroughly beyond their own specialty or even to engage upon new investigations. It is also an attempt to acquaint our younger chemists with some of those whose work is recognized as authoritative. Several articles received too late for this issue will appear in early numbers.

If you like our idea, your thanks are due not only to those who have prepared these special articles, but also to our regular contributors who have been willing to have the publication of their articles delayed in order to give precedence to these summaries. If you have any comments or criticisms to make, please write the editor, for similar numbers may appear from time to time and suggestions are wanted.

Our policy is to do whatever we can to advance the cause of chemistry, to further the interests of chemists individually and as a profession, and to assist in the establishment and development of the chemical industry. You have a part in the achievement of these purposes, and your opinions serve to guide us.

A Type of National Service

THERE ARE a number of altruistic organizations in America in a position to investigate impartially and advise the Government on programs in special fields. Officials frequently call into conference an individual from this, that, or the other part of the country, but the instances where these national groups are called upon for particular service are disappointingly few and far between. Is the fault with the Government or with the organizations?

In times of emergency, as in the Civil War when the National Academy of Sciences was chartered, the Government feels the need of every available bit of information and experience, but in times of peace actions of far-reaching importance are often taken without paying the slightest notice to those in a position to render well-considered, sound opinions.

As a rule, scientific organizations take little part in affairs which may have a political aspect, and indeed some of them refrain from participating if an industrial aspect is possible. It is another phase of the aloofness of scientific men from public affairs. They do little to command their rightful place, yet they complain at the lack of attention given them.

We do not favor scientific organizations participating in all sorts of political and industrial arguments. That would only weaken their position. But when conditions arise in which an expression of their opinion would do much to clarify the situation and to guide our public servants, it should be given. When such conditions arise we believe that bodies like the National Academy of Sciences and the National Research Council should not wait to be called upon. Experience has shown that such calls are seldom made. The fact that they are not asked does not relieve them of their duty and responsibility. They should make an independent investigation of the facts and frankly state their findings. This is particularly true where questions of public welfare, fundamental research, and the progress of science are directly or indirectly involved. The Federated American Engineering Societies, the American Institute of Chemical Engineers, the American Chemical Society, and others who are in the habit of expressing opinions after careful deliberation have lost nothing of prestige or influence by so doing.

Time and again we hear of the importance of scientific work in the life of the republic, and then too many of us go cold when we are asked to take a decisive stand in public affairs where science is involved. We need to develop an organization consciousness as well as an individual conscience.

A Commendable Experiment

THE General Electric Company has entrusted to F. M. Dorsey an experiment which is highly commendable and unique. It is an effort to promote the mutually profitable exchange of research problems and products with men in educational institutions and with other industries.

Forward-looking industrialists have pointed to the desirability of engendering more confidential relationships between the industries and our universities. Too often in our country the college man has seen nothing but a grasping spirit in industry, while industry has regarded the college professor as a somewhat irresponsible individual with little regard for business principles. Fortunately, academic men now have a greater appreciation for the work of their colleagues in industry, which has been brought about largely by the fundamental work of such industrial laboratories as the one under W. R. Whitney at Schenectady, and that directed by C. E. K. Mees at Rochester. The results of these researches have been presented through monographs, the scientific press, and publications such as the new volume of Abridged Scientific Publications of the Eastman Kodak Company.

There has developed abroad between the industrial chemist, the chemical engineer, and the pure scientist, a close relationship with financiers and executives which has contributed largely to commercial success. Many of us would like to see a similar condition brought about in America.

The AMERICAN CHEMICAL SOCIETY, through its committee on Coöperation between Industries and Universities, is contributing toward the ultimate solution of this problem.

This new plan of the General Electric Company seems to be a step in the right direction. This company has already made a name for itself in both pure and applied research. It proposes to take the researches of university men, carry them through the development stage, and determine their commercial possibilities. It also plans to suggest to these research men the problems in which it is interested and to give them many by-products from its own industrial research. A further step is an exchange of the products of research, between this company and other great industrial groups, which would appear to be an encouraging beginning in casting off the old trade secret idea. Finally, coöperative research is contemplated.

No group of scientists will watch this experiment with greater interest than the chemists; and that it may have a fair trial we owe it our sympathetic coöperation.

Determine America's Foreign Economic Policy

MANY AMERICANS probably feel that the Genoa Conference failed because the United States declined to take part in it. Others undoubtedly think we did well to stay away, although a large number believe that by our aloofness we failed in our duty as the strongest nation.

Mr. Vanderlip, who has devoted most of his time during the last two or three years to this greatest of all economic problems, has been writing on the subject for various American newspapers. He has urged action of one sort or another, pointing out the danger to America of this threatened collapse. Other individuals and groups have also studied the question. For instance, the special committee appointed by the Chicago Association of Commerce to study this question has prepared an excellent report, "What Shall Our Foreign Policy Be?," which has recently been published by that Association. We commend it to your careful consideration.

The unrelated efforts of individuals and groups indicate a pressing need. America would not go to Genoa or to The Hague. Very well. Let America consult herself. It is greatly to be regretted that Congress and other government officials have as yet been unable to offer any solution that meets with popular support. President Harding's plan for concentrating the best minds of the country upon national problems could not be better applied than here. But we believe in this case it would be better to let the best minds take the initiative.

Our idea is that interested Americans representing every industry should get together in a national convention or conference and submit their answers to the question "What shall be our foreign economic policy?" Chemists and the chemical industry have a very important interest in the question and are particularly well organized to sit in at such a meeting. In the American Chemical Society, the American Institute of Chemical Engineers, the Manufacturing Chemists Association, the Synthetic Organic Chemical Manufacturers Association, and the Chemical Equipment Association, chemists have an excellent means for the expression of their views. Other scientific societies are similarly organized—particularly the engineers. The trade bodies, such as the National Automobile Chamber of Commerce, and such associations as the National Grange and the American Farm Bureau Federation are in a position to consider this great question in orderly manner and should be represented in this conference.

The method of procedure would be as easy to work out as was that by which the recent Conference for the Limitation of Armaments was conducted. The idea is simply this: Let America, in orderly manner, get to the task of making up her mind. Let her settle upon a program of action or non-action, as the case may be, in Europe's sadly tangled affairs.

There is only one way to do such a thing, however: If committees are appointed to consider certain questions, let their findings—both of the majority and the minority—be made public. One of the most disappointing things about the Conference for the Limitation of Armaments was the failure to follow such a policy.

Unquestionably, the reëstablishment of strong governments, balanced budgets, and work devoted to the creation of new wealth would be worth much to America, and would earn for Europe the sympathetic coöperation otherwise impossible. Such a conference could not only be the means of conveying this idea to Europe, but could make suggestions and possibly aid in the work of such reëstablishment.

Productive Chemistry

IT WOULD be interesting to know how many manufacturers still look upon the chemical laboratory as nonproductive overhead. We know of one instance where the laboratory director was indignant when he learned that his department was classed in its entirety as nonproductive and was cited as one reason why such a large percentage had to be added to production costs to cover the overhead of doing business.

It is easily understood how in times of industrial depression the departments considered to be nonproductive are the first to be discontinued or curtailed. We believe that chemists and particularly the younger men should have before them the question of whether their work is really productive.

There has been a decided change in this direction during the last generation. The graduate formerly looked forward to becoming a unit in some industrial laboratory or to taking up the dignified work of a teacher. A little later, with the coming of chemical engineering courses, laboratories of applied chemistry and the like, he looked forward to taking an active part in construction and in the perfection of factory processes began to go beyond mere control. The next stage is now upon us, in which the well-trained chemist realizes that he has an excellent opportunity to become an executive, whether as superintendent of the plant, manager of the sales department, or president of the company.

What with analysis, synthesis, research, control, and consultation, chemists are beginning to recognize that they are something more than a bearded luxury or a spare tire. Nowadays, to "get by" a chemist must be a producer, or better, a productive man. Most of them are beginning to realize that they are an important part of the money-making forces in the world's work, and not wholly the spenders, and they are feeling a commensurate responsibility. If they are productive men, they must know their depths and if weakness lies therein, be ready to correct it.

International Chemistry

THE OFFICERS of our SOCIETY were empowered by a Council vote, 138 to 7, to arrange for the continuation of the *Journal of Physical Chemistry* as a joint project with our English colleagues. Upon a better understanding of the issue, dissent has disappeared and it now seems certain that the Council at Pittsburgh will unanimously approve the new venture which has already received the hearty approval of the committee of the Chemical Society (London).

Too much cannot be said in praise of the fine spirit shown by that society, whose officers met with our representative, Charles L. Parsons, on June 23, 1922, to discuss various details. Arrangements for the appointment of a joint editorial board, the election of an editor, and agreements with respect to various policies were made. The continuation of this journal of research is to be without financial liability to either society. All details will come before the Council for final confirmation.

The plan does not run counter to any of our policies regarding *The Journal of the American Chemical Society*, and the editor, A. B. Lamb, has expressed his full approval of the final plan. The editor of the *Journal of the Chemical Society* (London) is also in full accord. We are about to take an important step, not only in the publication of scientific research in the English Language, but in establishing still another bond of friendship and coöperation with our colleagues in Great Britain. It is a joint undertaking in which the AMERICAN CHEMICAL SOCIETY has a new responsibility.

Pittsburgh as a Chemical Research Center

By William Allen Hamor

Assistant Director, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

THE HISTORY of chemical research in the Pittsburgh district is an informative demonstration of the material value of chemistry. In fact, the science has been the industrial searchlight which illumines dark corners of manufacturing and enables technologists to see, sometimes in dim outline, but usually plainly, much that would remain hidden if they were denied its aid. And the light once used has been applied wherever necessary.

William A Hamor

There has been a live interest in chemistry in Pittsburgh ever since the days when it was a frontier town. In 1811, F. Aigster, an honorary member of the Columbian Chemical Society, of Philadelphia, delivered a series of lectures on the application of chemistry to industry, and two years later the Pittsburgh Chemical and Physiological Society, the third chemical society in the United States, was formed under the presidency of B. Troost, a well-known early scientist. A chemical firm of those days, Trevor, Pettigrew and Troost, manufactured alcohol, ether, sweet spirits of niter, nitric acid, hydrochloric acid, calomel, and "chemical preparations generally," thus implying experimental confidence and equipment.

Indeed, chemical research carried out in the Pittsburgh district has given new industries of economic importance, as several illustrations will show.

In the first place, it is of interest to mention that the manufacture of bromine was begun in the United States in 1845 by David Alter, of Freeport, Pa., in partnership with Edward and James Gillespie. Alter was a physician of investigational resourcefulness who also conducted original research in spectroscopy and devised a commercially successful process for the destructive distillation of bituminous minerals. In 1866 works for producing bromine were erected at Tarentum, Pa., and in the following year Alter secured patent protection for his retort and process of obtaining bromine and iodine from bittern. In 1887 Francis C. Phillips, then professor of chemistry in the Western University of Pennsylvania, effected technically valuable improvements in manufacturing bromine and iodine, and his process was adopted by a company operating in Allegheny.

The pioneer work of S. M. Kier, a pharmacist of Pittsburgh, in distilling crude petroleum also deserves brief notice here. Kier began about 1855 to "refine" crude oil from a Tarentum brine well, using a still which he constructed. The "light, wine-colored" distillate which first came over was found useful for illuminating purposes as "carbon oil," while the heavier product was sold for cleaning wools. Kier adopted the Downer process of refining in 1860, obtaining more satisfactory results. Unlike Silliman's classical investigation of crude petroleum, Kier's independent work was not systematic, but it gave some information on the economic value of crude oil. In 1859 there were six "coal oil" plants near Pittsburgh, but most of them were converted into petroleum refineries soon after Drake demonstrated that petroleum could be secured by drilling.

The bringing of aluminium into the rank of the cheaper metals is looked upon generally as one of the foremost metallurgical achievements of the nineteenth century, and the historian of technology classes the industrial production of aluminium alongside the invention of Bessemer steel. Charles M. Hall, a chemist, took a metallic rarity and made out of it a common metal, and made the entire human race his debtor. The commercial development of the Hall process was begun in 1888 on Smallman St., Pittsburgh, and the manufacture of aluminium became a business success at New Kensington, Pa. Since then the progress has been wonderful, and chemistry has been the pathfinder.

Another example is the discovery of silicon carbide by E. G. Acheson. Acheson first produced carborundum in March 1891, at Monongahela City, Pa., and began its manufacture in a small way. For the first six months his production amounted to about one-fourth pound per day; but the preliminary manufacturing experimentation proving encouraging, a company was organized, and in 1894 industrial operations were transferred to Niagara Falls.

And then there is radium, Pittsburgh's great gift to American medicine. The commercial production of radium preparations was begun in the United States by the Standard Chemical Co., of Pittsburgh, in 1913. This company, organized by the late J. M. Flannery, an enthusiastic supporter of scientific research, has depended upon the radiochemical ingenuity of Charles H. Viol since the inception of its activities in 1912.

Certain nationally important industries have also been richly benefited by chemical research conducted in the Pittsburgh district. It is, for example, quite difficult to recall a more far-reaching invention than that of the dry air-blast for the manufacture of iron, devised by James Gayley, a metallurgical chemist. This discovery effected a reduction of from $0.50 to $1.00 per ton in the cost of producing pig iron, besides making it possible for the ironmaster to produce, in all weathers, a metal of uniform quality. The dry air-blast was developed by Gayley between 1885 and 1904 at the Edgar Thomson and Isabella furnaces in Pittsburgh, and between 1894 and 1911 he received no less than fifteen successive patents in this country.

In the following sections of this paper the important bearing of chemical research upon the industrial and civic welfare of Pittsburgh will be considered at some length. Special attention will be given to the application of scientific investigation in specific industries.

THE IRON AND STEEL INDUSTRIES

The Pittsburgh district produces nearly 40 per cent of the country's iron and steel. In fact, the capital invested in Pittsburgh in mills, blast furnaces, and foundries amounts to over a billion dollars, and 90,000 men are employed in its steel mills.

The technically important contributions of chemistry to the iron and steel industries began with the introduction of the great pneumatic process of steel-making. The Bessemer process and the Siemens-Martin open-hearth process produced a revolution in the iron industry that afforded the chemist his first real opportunity. Prior to the days of steel, iron-making was largely an empirical art, and no manufacturer considered the estimation or control of the impurities which generally accompany the metallurgy of iron to be a vitally important matter. Of course, it was known through the operation of the puddling and crucible processes that certain elements imparted hardness and toughness, but the very important quantitative roles in the metallurgy of iron played by carbon, manganese, sulfur, phosphorus, and silicon were not understood. Original chemical researches into the methods for determining and controlling these so-called impurities forced the essentiality of chemistry upon ferrous metallurgists. Indeed, the iron blast-furnace is but the chemist's crucible on a gigantic scale, operated on chemical principles; and the application of chemistry to iron smelting has effected such wonderful transformations that to-day the chemist occupies the foreground in directing the operations in the industry. Not only has inorganic chemistry in its analytical and physical branches played a highly important part in the steel industry, but organic chemistry has also entered the field in the by-product coking of coal. Thermochemistry, electrochemistry, and metallography are the divisions of physical chemistry which have been most active in promoting the scientific development of the metallurgy of steel. Ceramics has also been of essential aid in providing information respecting refractories.

In describing the many difficulties encountered during the early operation of the Lucy furnace at 51st St., Pittsburgh, Andrew Carnegie, the great ironmaster, says in his autobiography that the undertaking "would have been postponed if we had realized its magnitude." Little furnaces could be run by rule-of-thumb and guess, but not such a monster as the Lucy. Finally he employed Fricke, a chemist, to assist the manager, and straightway "Lucy furnace became the most profitable branch of our business, because we had almost the entire monopoly of scientific management. It was years after we had taken chemistry to guide us that it was said by the proprietors of some other furnaces that they could not afford to employ a chemist. Had they known the truth then, they would have known that they could not afford to be without one."

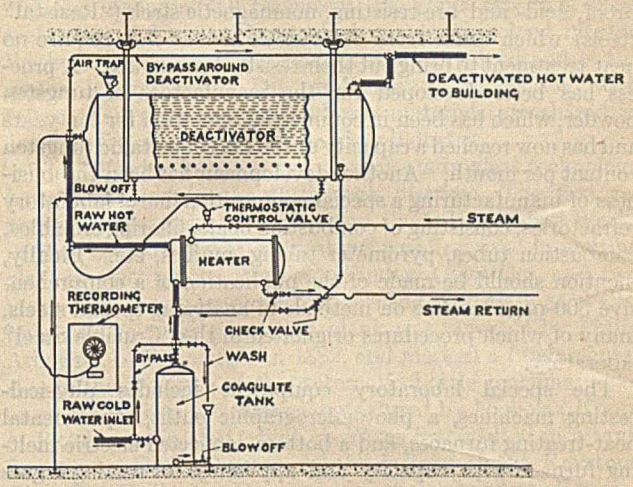
Research on Iron and Steel Products

The Carnegie Steel Company has modern analytical and control laboratories in all its plants, but it does not operate a special research laboratory. All investigations of the Central Research Bureau are carried out at the works of the company, with the facilities of the plants and the assistance of their chemical personnel. To illustrate, the laboratory of the Edgar Thomson Works is at the present time giving special research attention to refractories.

The Jones and Laughlin Steel Company follows a similar plan. This organization does not maintain a research laboratory, but chemists are detailed from the analytical laboratories of the South Side and Aliquippa Works to handle the relatively simple problems which arise in the plants from time to time.

The A. M. Byers Company's laboratory, which is located at Sixth and Bingham Sts., Pittsburgh, is engaged in the study of corrosion problems and problems incidental to the improvement of the quality of wrought iron, and in the development of processes for increased production of wrought iron, wrought-iron welded pipe being the product of manufacture. In addition to general equipment for chemical and metallographic work and for physical testing, the laboratory has special apparatus for the study of corrosion and an electric furnace and accessories for research on the production of special grades of wrought iron.

Steel tubes and pipe, seamless and welded high-pressure cylinders, and trolley poles are the principal products of manufacture of the National Tube Company, and accordingly its McKeesport laboratory is concerned especially with research on protective coatings and the control of corrosion in water where unprotected pipe is used, although mill materials and the improvement of products also receive attention. Among the accomplishments of this laboratory are a new method of finishing welded pipe without scale and with a smooth finish, non-galling steel couplings for pipe, special slow-corroding steel for pipe, and methods for the "deactivation" of water by removal of free oxygen, originally developed in 1908 and now coming into general use for the protection of pipe in hot-water lines. The laboratory has a torsion machine and a large tensile machine (600-ton) which will take a piece 30 ft. long.



HOT WATER DEACTIVATOR WITHOUT FILTER

HEAVY LINES INDICATE COURSE OF WATER THROUGH SYSTEM
LIGHT LINES INDICATE BY-PASSES AND OTHER NECESSARY CONNECTIONS

The research laboratory of the American Sheet and Tin Plate Co., 210 Semple St., Pittsburgh, carries out investigations of chemical engineering problems in the manufacture of sheet steel, tin plate and galvanized sheets, and studies in the metallurgy and metallography of steel, tin, and zinc, and their alloys, in pyrometry and its applications, and in the recovery of by-products. This laboratory is particularly well equipped, including precision instruments for physical testing, electric furnaces, and metallographic and pyrometric apparatus.

Vanadium, Tungsten, and Molybdenum

Vanadium, tungsten, and molybdenum and their alloys are manufactured at Bridgeville, Pa., by the Vanadium Corporation of America. Research has had and is enacting a most essential role in the success of this firm, among the accomplishments of its laboratory being a new system of electric furnace control, a process of reducing vanadium

oxides by carbon in the electric furnace, producing low-carbon alloy, and the recovery of vanadium alloys from waste materials, such as slag, containing low percentages of vanadium.

The investigational work in progress includes the concentration of rare-metal ores, the electrothermal reduction of rare-metal ores, the metallography of alloy steels, and the improvement of electric-furnace regulation-control mechanisms.

Tool Steels

Research looking toward improvements in the composition and manufacture of tool and cutlery steels, and the development of better processes of heat treatment, is under way in several laboratories in the district. The Firth Sterling Steel Co., McKeesport, Pa., has a laboratory provided with experimental melting and heat-treating furnaces, testing machines, and metallographic equipment. The Vanadium-Alloys Steel Co., Latrobe, Pa., also supports a research laboratory. The Latrobe Electric Steel Company is not conducting research, although it has a works laboratory for control work.

The research achievements in the laboratory of the Crucible Steel Company of America (30th and Smallman Sts., Pittsburgh) constitute important additions to ferrous metallurgy. A number of special steels have been patented. Two more patents have been granted on a new-composition group of stain-proof, mine-water and sea-water proof, rust-proof, acid- and fire-resisting, nonmagnetic steels ("Rezistal" steels) which differ from other steels in that they require no heat treatment to bring out their resistant properties. A process has been developed for the manufacture of tungsten powder, which has been in commercial operation for ten years and has now reached a capacity of 100 tons of metallic tungsten content per month. Another development has been the business of manufacturing a special composition line of laboratory refractories, consisting of combustion boats, filtering crucibles, combustion tubes, pyrometer tubing, muffles, etc. Finally, mention should be made of the publication of a comprehensive 500-page treatise on methods of analyzing special steels, many of which procedures originated in the "Crucible Steel" laboratory.

The special laboratory equipment includes physical-testing machines, a photomicrographic outfit, experimental heat-treating furnaces, and a bottom-connected electric melting furnace with capacity and appliances for casting ingots of special alloy steels up to 400 pounds in weight.

The Crucible Steel Company of America manufactures open-hearth, crucible and electric steels, both plain carbon and alloy steels of all kinds, tungsten and molybdenum metals, plumbago crucibles, and laboratory refractories.

RADIOCHEMICAL RESEARCH

The Standard Chemical Co., of Pittsburgh, was the first commercial producer of radium in the United States (1913) and is now the world's largest producer (over 87 g. of radium element to May 1922). It also manufactures phosphorescent zinc sulfide, luminous compounds, oxides and salts of uranium and vanadium, ferro-uranium, and ferro-vanadium.

In 1920 the Standard Chemical Company produced 18.2 g. of radium element, breaking the previous record of 13.6 g. established by itself in 1918. It required 575 men working one year to accomplish this, the quantity of ore treated amounted to 9100 tons, and the value of the finished product was $2,184,000. Seventeen grams of radium element constituted the 1921 production.

All the processes in use by this organization are the result of scientific inquiries carried out in the Vanadium Building laboratory, where improvements in methods for the extraction of radium, uranium, and vanadium from carnotite, and in the procedures for preparing radium for therapeutic and other purposes are being sought; the metallurgical applications of uranium are also receiving study. This notable laboratory has apparatus for the analytical determination of radium and for the refining of radium salts, and photomicrographic apparatus for metallographic work.

Crystallizing Radium-Barium Chlorides in the Refining of Radium Salt, Research Laboratory of the Standard Chemical Co., Pittsburgh, Pa.

RESEARCH IN THE COKE INDUSTRY

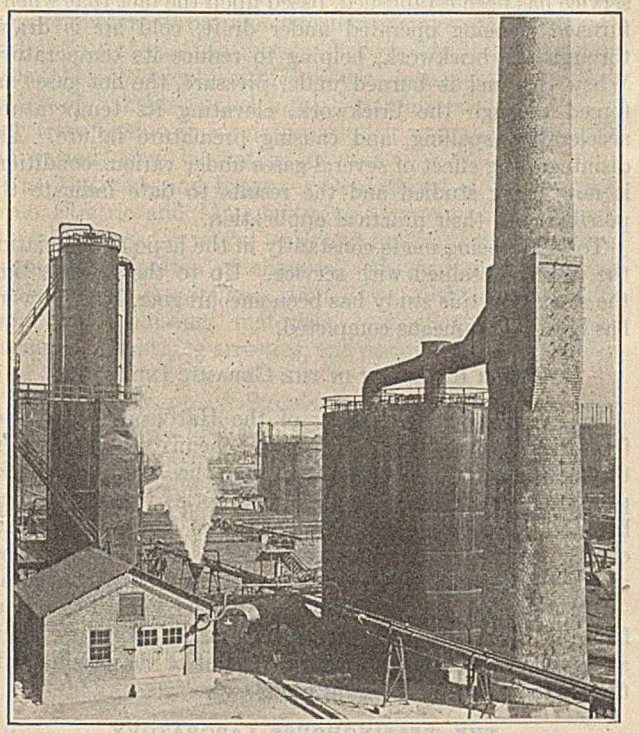
Pittsburgh is surrounded by the richest bituminous coal section of the United States and it is the cheapness of fuel which has attracted so many industries to the district. Within a radius of a few miles are more than 350 coal mines, which are capable of turning out 100,000,000 tons a year. Normally, Pittsburgh produces three-fourths of the bituminous coal in Pennsylvania and over 40 per cent of the country's output, while Connellsville, heart of the coking region and an integral part of the Pittsburgh district, alone supplies the country with 25 per cent of its coke. Fifty per cent of all the coke in the United States comes from the Pittsburgh district.

The development of the by-product oven industry in the United States was begun by the Solvay Process Co., which, in 1891, started the construction of 12 Semet-Solvay ovens in Syracuse, N. Y. The design of this type of oven had already been well established in Europe. An initial plant of Otto-Hoffmann ovens was built at Johnstown, Pa., in 1895, and began making coke in 1896. By the close of 1900 the number of completed ovens included 345 Semet-Solvay, 680 Otto-Hoffmann, and 60 Newton chambers, the latter being a modified type of beehive oven adapted with apparatus for by-product recovery, which, like all similar hybrid designs, did not long survive. Of utmost importance in the development of the by-product oven was the use of silica brick, which was first introduced in the Johnstown plant in 1899. This material was indispensable for the high temperatures, rapid coking, and high plant yields that were subsequently attained. An important improvement in by-product recovery was the system of gas separation introduced by F. Schniewind in 1899 in the plant of Otto-Hoffmann ovens at Everett, Mass.

For a number of years the progress of by-product coke making was slow, being retarded by imperfections of construction, difficulties of operation, and finally by the deep-rooted prejudice of blast-furnace men against by-product coke. In 1908, however, the industry received a marked impetus as the result of the activities of the U. S. Steel Corporation,

which, after an exhaustive study of various European types of ovens and by-product apparatus, selected the Koppers design and built a 280-oven plant of this type in Joliet, Ill. This plant, which had the old indirect system of ammonia recovery, was successful beyond all expectations, and was rapidly followed by the construction of large plants using the Koppers direct process, at Gary, Ind., Fairfield, Ala., and Duluth, Minn. The European war caused an enormous increase in the construction of by-product ovens, and at present it would seem that at the close of another decade little should remain of beehive coke manufacture.

The Koppers Company designs, manufactures, and instals plants and apparatus for by-product coke and gas manufacture, concentrating ammonia liquor, ammonium sulfate recovery, benzol recovery, gasoline absorption and recovery, tar distillation, water-gas and producer-gas manufacture, and gas purification (liquid process). Its research laboratory in the Mellon Institute is excellently equipped with apparatus for coal carbonization at high and low temperatures, coal washing, coke research, gas purification by dry and liquid processes, furnaces for the investigation of refractory materials at high temperatures, laboratories and experimental plant fully equipped for semicommercial tests, and plants available for large-scale tests in relation to coke and gas manufacture and by-product recovery. Among the



Apparatus for Gas Purification by Liquid Process (Treating 25,000,000 Cu. Ft. of Gas per Day) Developed by the Koppers Company Laboratories

research accomplishments are the recovery of benzene and toluene from carburetted water-gas, the manufacture of coumarone and other resins, motor fuels, and improved blueprint, purification of ammonia-still waste, improved methods of gas purification, recovery of hydrogen sulfide, and special methods of coke investigation. Members of this organization have about 60 United States patents issued or favorably acted upon. The lines of research at present in progress are as follows: coal carbonization, gas production and purification, by-product recovery, secondary treatment of various by-products, general fuel research, refractories, pyrometry, and coal properties.

RESEARCH IN THE GLASS INDUSTRY

The glass industry is one of the most important in the Pittsburgh district, 62 factories producing window glass, plate glass, lighting glass, and numerous other forms of glassware. The total capital investment exceeds a quarter-billion dollars, and normally there are employed more than 25,000 workmen at a total annual payroll of over $20,000,000.

Though American contributions to the advance of the glass industry have been largely from the engineering standpoint, it is not to be supposed that the chemist and the physicist have entirely neglected this great field. In fact, the part of these scientists has been of greater importance than is usually acknowledged. Little has been written of the chemist's accomplishments, except, perhaps, in connection with the development of optical glass during the past few years. As Tillotson has indicated, chemical contributions have been isolated, sporadic, and, unfortunately, dimmed in the shadow of a general policy of secrecy which has resulted partly from tradition and partly from fear of legal complications. Such conditions do not make for real scientific progress in this or any other industry; but it is believed that the present is a period of transition, and it is certain that great opportunities exist for the chemist and that his work in the future, in conjunction with that of the physicist and engineer, will transform the whole aspect of glass technology. The problems which are to be solved include the basic principles of all the operations involved and of the materials employed. The problems in connection with refractories, furnaces, fuel and raw materials are shared in common by all branches of the glass industry.

The following important developments in glass technology have originated in the Pittsburgh district: The first regenerative pot furnace was built at the O'Hara Glass Works in 1865 by J. B. Lyon; natural gas was first used in melting glass in 1882 by the Bradford Window Glass Co., and two years later it was employed for melting flint glass at Wellsburg, W. Va.; the prepressed blank was invented by Philip Arbogast, of Pittsburgh, in 1882, and marked a fundamental step in the evolution of the automatic bottle machine; selenium ruby glass was first manufactured by Nicholas Kopp, of Pittsburgh, in 1894; flint glass was first melted in a tank furnace by C. H. Runyon, in the factory of the Keystone Glass Co., Rochester, Pa.; machine-drawn window glass was first made in 1900 in the Arnold, Pa., plant of the American Window Glass Co., by the machine invented by J. J. Lubbers; and machine-drawn sheet glass was first produced successfully at Franklin, Pa., by the invention of I. W. Colburn (now the Libbey-Owens sheet-glass machine).

Chemical Research Laboratories in the Glass Industry

The Pittsburgh Plate Glass Co., whose products of manufacture include polished plate, window, optical, and black and white Carrara glass, and also refractories, has a research laboratory at Creighton, Pa.

The American Window Glass Company is not operating a research laboratory at the present time, although experimental work is in progress at Arnold, Pa., on pots and tank blocks.

The Hazel-Atlas Glass Co., of Wheeling, W. Va., manufacturer of glassware for packers' use, olive and vinegar bottles, ink containers, fruit jars, jelly glasses, hotel tumblers, amber ware, and blue and opal ointment jars, has research laboratories at Washington, Pa., and Clarksburg, W. Va., where research is centered on the improvement of the

physical and chemical properties of glass and on the development of technical control. Raw materials are now purchased entirely by specifications, and control tests of operation are almost entirely under technical supervision. Among other accomplishments of this laboratory may be mentioned the production of some economical glasses and the improvement of the physical properties of glass for specific purposes. It is equipped with apparatus for the physicochemical study of glass and for the control of furnace operation.

The Macbeth-Evans Glass Company maintains a research laboratory at its Charleroi, Pa., factory. This company produces lighting, marine, railway, and laboratory glassware.

The H. C. Fry Glass Company and the Beaver Valley Glass Co., of Rochester, Pa., have derived many benefits from chemical research, but the outstanding accomplishment of their laboratory is the development of a translucent oven glass for baking purposes and other uses where heat-resisting glass is required. Other products of these related concerns are blanks for the cut-glass trade, cut glass, parabola and motion-picture lenses, plate and needle etchings, stemware, table tumblers, and cylinders for gasoline pumps. The laboratory has a glass furnace and small tank, and attention is being given at present to the application of glasses to the useful arts.

THE BRICK AND FIRE-CLAY PRODUCTS INDUSTRIES

Pittsburgh occupies a dominant position in the manufacture of face brick, refractories, and similar ceramic products. The monthly capacity of the plants in this section has been estimated to be approximately 20,000,000 nine-inch bricks; but at present the production is about 70 per cent of this figure, or a monthly tonnage of 49,000. The bulk of ordinary and special brick production in western Pennsylvania has an annual value of $15,648,000; this, taken together with other products manufactured from fire clay, gives a total ceramic products output of about $20,000,000 a year.

Research on Refractories

The Refractories Manufacturers' Association, an organization of 98 companies, has been conducting research in coöperation with the Mellon Institute of Industrial Research for a period of five years. The problems studied may be divided into three distinct classes, dealing with the manufacture, use, and testing of refractories. Among the manufacturing problems that of properly classifying the raw materials is perhaps the most important. It is necessary to study each deposit, either at the working faces or by means of drill cores, in order to obtain accurate information regarding the physical and chemical properties of the various sections. Slight variations in color, hardness or texture have been found to be indicative of a change in refractoriness, plasticity, or burning property. Investigations of this kind may result in the use of certain clays that have been rejected, in the rejection of clays that have been accepted, or in the separation of certain portions for special purposes.

After having determined the refractoriness of the various clays, it has been found essential to study their burning properties. Certain flint clays have little or no tendency to shrink, others have an inclination to vitrify, and plastic clays usually have a tendency to burn dense but attain their maximum density at different temperatures. When these tendencies are known, it is possible to devise mixes that have dense, open, or medium burning characteristics. Having these, the product will possess either high resistance to abrasion, high resistance to spalling, or properties that recommend it for general use.

Each step in the process of manufacture exerts a controlling influence upon the properties of the finished product. Even the amount of water used in developing plasticity affects the structure of the burned brick. Insufficient water gives an open product, as does an excess; an intermediate quantity gives a product of maximum density. Density is also influenced by the texture, molding pressure, and burn of the product.

Several problems pertaining to the use of refractories have been or are being studied. While it is often difficult to apply the results because of lack of information regarding the operation of most furnaces, this objection is disappearing rapidly with the development of recording devices.

A great many failures may be traced to furnace design, especially where brickwork is heated throughout, where the radiating surface is small as compared with the heating surface, or where the bricks are heated under pressure. Others may be traced to the mortar which has been used in laying up the brickwork. Certain mortars contain high percentages of basic fluxes. When fire clay is used, the brickmason often adds lime or portland cement to produce a cold set, little realizing the effect of these additions upon refractoriness. A reduction in refractoriness of 1000° F. is easily possible from this cause; as a result the mortar runs from the joints, leaves the brickwork exposed, and gives the appearance of high shrinkage.

Quite recently a relationship between furnace pressure and service has been established, based upon the fact that when a furnace is being operated under draft, cold air is drawn through the brickwork, helping to reduce its temperature. When the fuel is burned under pressure, the hot gases are forced through the brickwork, elevating its temperature, accelerating spalling, and causing premature failure. The disintegrating effect of several gases under various conditions is now being studied and the results to date indicate the possibility of their practical application.

Tests are being made constantly in the hope of associating the results obtained with service. Up to the present time the success of this study has been encouraging, but the work has been by no means completed.

Other Research in the Ceramic Industry

In the research laboratory of the Harbison-Walker Refractories Co., at Hays, Pa., several chemists are engaged in the development of refractories and the study of special problems pertaining to uses of refractories (fire clay, silica, bauxite, magnesite, and chrome). The special equipment of this laboratory embraces test kilns, load test, spalling-test and melting-point furnaces, and a Riehle crushing machine.

The Beaver Falls Art Tile Co., of Beaver Falls, Pa., manufacturer of glazed wall tile, maintains a laboratory where attention is given to the improvement of the product and the minimization of losses in plant operation.

THE WESTINGHOUSE LABORATORY

Year by year the annual value of electrical equipment manufactured in the district has increased, until in 1920 the total reached $165,000,000. Besides electrical utensils for the household, there are produced electrical machinery, dynamos, transformers, motors, and turbine engines; while in the new branch of radio-equipment manufacture a leading position is held, mainly because of the researchful attitude of the Westinghouse Electric and Manufacturing Company. This organization occupies more than 100 acres of floor space and employs 35,000 people.

The Research Department of the Westinghouse Electric and Manufacturing Company is located on Ardmore Boulevard, near East Pittsburgh, where problems under investigation pertain to the manufacture of electrical apparatus of all classes

OTHER INDUSTRIAL RESEARCH LABORATORIES

Company	Products of Manufacture	Location of Research Laboratory	Important Accomplishments
Aluminum Company of America	Aluminium, including ingot, sheet, wire, foil, and other fabricated forms; bronze powder and collapsible tubes	New Kensington, Pa. (main laboratory)	Chemical research has been vital in the welfare of this organization, but no information is available respecting definite achievements of the present laboratory. The fundamental work of C. M. Hall has been described
Armstrong Cork Company	Cork products, cork compositions, linoleum and other floor coverings, and insulation	Pittsburgh, Beaver Falls, and Lancaster, Pa.	Perfection of high-temperature insulating brick and a material for cabinet-safe insulation; improved method for baking low-temperature, cork-board insulation; improved method of washing and bleaching cork stoppers; and new cork compositions
Duquesne Reduction Company	Copper and nonferrous alloys, made from secondary metals	Gross and Yew Sts., Pittsburgh	.....
Electrolabs Company	Oxygen and hydrogen generating plants; acetylene apparatus	2635 Penn Ave., Pittsburgh	Levin cell; synthesis of precious stones in the corundum family; and methods for the detection of cotton in asbestos
Philadelphia Company	Manufactured (and natural) gas	Appliance laboratory, 553 Seventh Ave., Pittsburgh; gas manufacture laboratory, Elrama, Pa.	.....
Rodman Chemical Company	Carburizing materials and special carbons	Verona, Pa.	"Patents issued as the result of work done in this laboratory dominate the manufacture of carburizing materials in this country"
Vulcan Detinning Company	Tetrachloride and bichloride of tin, tin crystals, fused caustic soda, and detinned steel scrap	Neville Island, Pa.	Development of "secret processes" in use by the company
Waverly Oil Works Company	Petroleum products	54th St. and A. V. R. R., Pittsburgh	Development of "thin-thick" oil or compound for internal-combustion engines

for power generation, distribution, and utilization. The department lists as its prominent achievements steel for magnetic work, effect of gases in metals, disk-pipe lightning arresters, radio tubes, electrical ceramic products, iron plating, standardization of bakelite, novel insulating materials, the study of heat transmission in insulators, sludging of transformer oils, and various new laboratory devices.

The Materials and Processes Department of the Westinghouse Electric and Manufacturing Company has a million-volt laboratory for power work and much special equipment for the investigation of chemical, physical, and electrical problems. Among its important accomplishments are radio apparatus, insulating materials, new alloys, high-tension phenomena, lightning arresters, and design data in many electrical lines.

The Department of Standards of the same company is also of interest, although strictly electrical in nature of work. It is concerned with standards, the standardization of meters, and the use of meters in all kinds of electrical measurements. There is considerable development work in progress, but all real research is done in the first-mentioned department.

The research laboratory of the Union Switch and Signal Company is engaged entirely in the study of physical and engineering problems.

RESEARCH IN OTHER PITTSBURGH INDUSTRIES

While the production of coal and coke, the manufacture of iron and steel, their products, electrical and railroad equipment, glass and glassware, and brick and fire-clay products, constitute the real strength of the high industrial position of the Pittsburgh district, there are many other branches of manufacture which have attained national prominence. Some of these industries have sprung directly from chemical research, while others of them have been and are being nurtured by it.

The Chamber of Commerce of Pittsburgh has reported that there are 300 lines of manufacture in and about Pittsburgh, most of them of a ferro-metallurgical character, but many being uniquely different. The production of radium has been mentioned. It may be noted here that the district leads the world in the production of finished aluminium, has the largest pickling and preserving plant in the world, and the greatest cork products manufacturing plant.

It has been estimated that the annual production value of the Pittsburgh industrial area is nearly $3,000,000,000 and that the yearly value of the products of the purely diversified industries amounts to $200,000,000.

Several other important industrial organizations having plants in the Pittsburgh district maintain research laboratories elsewhere. The American Zinc and Chemical Co., Langeloth, Pa., manufacturer of spelter, sulfuric acid, zinc oxide pigments, and zinc sulfate, has its investigational work carried out in the laboratory of the parent company, the American Metal Company, Ltd., in New York, N. Y. The Pittsburgh refinery of the Atlantic Refining Co., manufacturer of petroleum products, does no appreciable amount of research, laboratories for this purpose being operated at the Philadelphia plant. The Pennsylvania Salt Manufacturing Co., which has a works at Natrona, Pa., has its research laboratory at Greenwich Point, Philadelphia, where seven chemists are engaged in the study of processes for manufacturing heavy chemicals. Finally, the Gulf Refining Co., which has its general offices in Pittsburgh, maintains a large petroleum research laboratory at Port Arthur, Texas.

CONSULTING RESEARCH LABORATORIES

The R. H. Brownlee Laboratory, Inc., occupies the nineteenth floor of the Benedum-Trees Building, 223 Fourth Ave., Pittsburgh. This laboratory is specializing in petroleum refining, the design and installation of special refinery equipment, the preparation of utilizable products from natural gas, and rubber technology. It is equipped especially for investigational work in hydrocarbon and rubber chemistry. The R. H. Brownlee Laboratory has developed a new mixture of gases for use in metal-cutting and welding, a process for the production of gasoline, a new lubricating oil for airplane and automobile motors, and an improved process for making carbon black.

The Pittsburgh Testing Laboratory, 616 Grant St., is engaged in research on refractories, glass, and enamels, and on general chemical and metallurgical problems. The special equipment includes furnaces for the manufacture and testing of refractories, a metallographic outfit, apparatus

for coal testing and research, and complete facilities for work in analytical chemistry.

The Pittsburgh Testing Laboratory has perfected improvements in the manufacture of glass, dolomite refractories, and enamels for cast iron. The metallurgical researches of J. O. Handy have been technically important, his investigation of copper-bearing steel being particularly noteworthy.

THE PITTSBURGH EXPERIMENT STATION OF THE BUREAU OF MINES

The Pittsburgh Experiment Station of the Bureau of Mines, located at 4800 Forbes St., carries out, on an elaborate scale, research pertaining to safety and efficiency in the mining and metallurgical industries. Its laboratories are splendidly equipped with apparatus for the chemical and physical testing of explosives, furnaces for studying the combustion and inflammability of gases and dusts, and apparatus for research in hydrocarbon chemistry. There is a constant-temperature room, in which humidity, temperature, and air movement can be accurately controlled for making studies of the physical effects of these factors in connection with ventilation problems; and a gas chamber for investigations on gas masks and breathing apparatus.

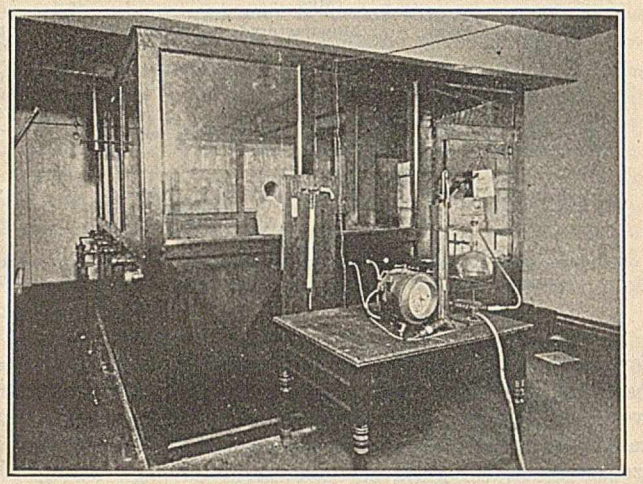
The research accomplishments of this station are numerous. Among the outstanding achievements are the following: Solution of the problem of ventilating vehicular tunnels, such as the one under the Hudson River; determination of the effects of carbon monoxide in tunnels and mines and in the industries; effects of low concentrations and repeated exposures to carbon monoxide, etc.; development of new methods for determining the percentage of carbon monoxide in blood; determination of forms in which sulfur occurs in coal, coke, and gas, and reactions which it undergoes during carbonization, thus providing fundamental data for the desulfurization of coke; identification of the gum-forming constituents in manufactured gas, with a view to the elimination of gum deposits in meters and gas-distribution systems; determination of the solubility of trinitrotoluene, tetryl, and other explosives in various organic solvents; use of silica gel and other absorbents in removing sulfur and gum-forming constituents from coke-oven light oil; development of gas indicators for use in coal mines; and development of gas masks for industrial use.

CHEMICAL RESEARCH IN EDUCATIONAL INSTITUTIONS

The University of Pittsburgh

Chemistry in the University of Pittsburgh was placed on a high plane by the late Francis C. Phillips, distinguished generally for his investigations on natural gas, petroleum, and iron and steel, and the present staff of the Department of Chemistry has been able to enlarge the facilities for research and to elevate the standards in accordance with the best practice in chemical pedagogy. The departmental laboratories, while small, are well equipped for research in organic and physical chemistry and in glass.

The Departments of Chemistry and Chemical Engineering of the University have several advantageous coöperative arrangements with the Mellon Institute of Industrial Research, also a part of the University. The Mellon Institute provides lecturers on special technochemical topics, thus affording direct contact between the students and specialists who are engaged in studying important problems of industry. The facilities offered by the Mellon Institute for systematic training in research methodology have led to the establishment of another coöperative relationship, which is even more valuable from a practical standpoint. Reference is had to the provision of temporary assistantships on certain of the Industrial Fellowships of the Institute. According to this arrangement, properly qualified students in the Department of Chemical Engineering are placed in salaried assistantships during the periods when regular coöperative work is required. This plan carries the proviso that the student's thesis work is to be done under the direct supervision of the Industrial Fellow under whom the student has temporary employment. This system of temporary assistantships furnishes opportunities for the well-trained student to carry out technically important research and thus come to the notice of the manufacturer supporting the Fellowship on which he is employed. The outstanding importance of the arrangement, however, is that it gives opportunities for an intimate acquaintance with specific industries and their problems, as well as providing intensive training in scientific order in the application of research procedure.



Gas Chamber Used for Experimental Purposes, Pittsburgh Experiment Station, Bureau of Mines

Notable Investigations Conducted at Mellon Institute

Investigations	Industrial Fellows	Years
Physical properties of glass	E. W. Tillotson, Jr.	1911– ..
Bread technology	H. A. Kohman and others	1911– ..
Citrus products	F. A. McDermott	1912–1913
Electrical precipitation	W. W. Strong	1912–1913
Smoke investigation	R. C. Benner, John O'Connor, Jr., and others	1912–1914
Pressed glassware	S. R. Scholes	1912–1916
Chemistry of petroleum	R. F. Bacon, B. T. Brooks, W. F. Faragher, and others	1912– ..
Manufacture of carbon dioxide, carbon monoxide, hydrogen and nitrogen	R. H. Brownlee and R. H. Uhlinger	1913–1915
Composition flooring	R. R. Shively	1914–1916
Fractional distillation	M. A. Rosanoff and others	1914–1919
Hydrometallurgy of copper	R. F. Bacon, E. R. Weidlein, G. A. Bragg, and others	1914–1920
Olefin gases	G. O. Curme and others	1914– ..
Flotation of ores	H. P. Corliss, C. L. Perkins, and R. E. Sayre	1915–1921
Dental cements	C. C. Vogt	1915–1921
Chemistry of laundering	H. G. Elledge, A. F. Shupp, and others	1915– ..
Natural gas	J. B. Garner	1915– ..
Refractories	R. M. Howe and others	1916– ..
By-product coking	F. W. Sperr and others	1916– ..
Fiber container	J. D. Malcolmson	1917–1921
Heat insulation	G. D. Bagley and R. H. Heilman	1917– ..
Glue	R. H. Bogue	1917– ..
Insecticides	O. F. Hedenburg	1917– ..
Food and beverage flavors	M. DeGroote	1918– ..
Inks	F. F. Rupert	1918– ..
Protected metals	J. H. Young	1918– ..
Sulfur	H. S. Davis	1919–1921
Galvanizing	W. G. Imhoff	1920– ..

The present status of the Industrial Fellowship System of the Mellon Institute is presented in Director E. R. Weidlein's *Ninth Annual Report*, an abstract of which appeared in the preceding number of This Journal. The Institute

is a center for technical investigation in chemistry and allied subjects. Its purpose is to promote industrial success through scientific research; in other words, to find new materials and new processes for industrial development and to advance manufacturing through the application of scientific methods to industry. At the present time there are 51 Industrial Fellowships, or distinct lines of research, in operation, on which 88 chemists and engineers are engaged.

Of 200 technochemical inventions by Industrial Fellows of the Institute, the following are considered the outstanding ones from an economic viewpoint:

Inventions	Inventors	Dates of Patents
Synthetic resins ("redmanol")	L. V. Redman	1914
"Arkady" yeast food	H. A. Kohman, Charles Hoffman, T. M. Godfrey, and A. E. Blake	1915
Glass-making receptacle	S. R. Scholes	1916
Hydrometallurgy of copper	E. R. Weidlein	1916
Flotation of minerals	H. P. Corliss	1917
Shortening composition	H. A. Kohman, T. M. Godfrey, and L. H. Ashe	1917 and 1919
Flotation of minerals	C. L. Perkins	1917–1921
Absorbent material	J. B. Garner	1918
Manufacture of enameled ware	R. D. Cooke	1919
Synthetic acetylene	G. O. Curme	1919
Acetaldehyde, acetic acid, and acetone preparation	G. O. Curme	1919
Ethylene preparation	G. O. Curme	1919
Recovery of butane and propane	J. B. Garner	1919
Contact sulfuric acid process	H. H. Meyers	1919
Paint or varnish manufacture	F. W. Sperr and Marc Darrin	1919
Dental cement	C. C. Vogt	1919
Gasoline from natural gas	J. B. Garner	1920
Dry lime-sulfur product	O. F. Hedenburg	1920
Arsenate of lead	O. F. Hedenburg and D. S. Pratt	1920
Coating materials	J. H. Young	1920
Adhesive	J. D. Malcolmson	1921
Flotation of minerals	R. E. Sayre	1921
Liquid glue	D. K. Tressler	1921
Protected metal articles	J. H. Young	1921

The Carnegie Institute of Technology

The Carnegie Institute of Technology, located at Schenley Park, Pittsburgh, maintains a Division of Coöperative Research, the function of which is to encourage research throughout the institution and to establish research connections with industrial concerns. The Chemical Research Section has laboratories in each of three of the colleges of the Institute. Chief of these are the laboratories of chemistry and chemical engineering. These laboratories, located in the Science Building of the Engineering College, are at present occupied primarily with research on petroleum derivatives, and also the use of electrolytic methods in investigating certain nonaqueous solvents, colloids, and new alloys.

In the teaching laboratory of the Department of Industrial Chemistry, College of Industries, research is being conducted on the constitution of commercial products such as clay-jointing compounds, steel castings, and alloys. In the chemical laboratory of the Margaret Morrison Carnegie College for Women, analyses of soaps and of waters from many water systems are being made, and the effects of soaps and laundering processes on various fabrics determined.

The most important recent accomplishments in chemical research at Carnegie Institute of Technology are described in the article on "Some New Petroleum Products" by J. H. James, published in the February 1922 number of *Chemical and Metallurgical Engineering*.

The special equipment of the chemical laboratories of the College of Engineering includes: double-effect evaporator, Lummus extraction apparatus, Lummus diffusion apparatus, autoclaves, large hydrocarbon oxidizing apparatus, Cook compressor, motor generator, International oxygen-hydrogen cell, and fractional distillation outfit.

Related laboratories for research in pure and applied science are maintained by the departments of physics, metallurgy, mining, mechanical engineering, machine design, electrical engineering, and civil engineering. The problems studied are characteristic of Pittsburgh industries. The physics laboratories are engaged on problems of glass manufacture, such as the effects of varying compositions of borosilicates on the optical properties of glass. The metallurgical laboratories work largely on problems in iron and steel. Special equipment for metallurgical research includes apparatus for measuring fatigue-resisting properties of steels in drill pipe, drill rod, etc. The geology laboratory is studying Pennsylvanian shales and coals, and the faculty of the Department of Coal Mining has the coöperation of the staff of the Pittsburgh Experiment Station of the Bureau of Mines, in directing several researches on problems of engineering in bituminous coal mining. The Mechanical Engineering Department has concentrated chiefly on problems of lubrication, thermodynamics, governors, and steam-engine design. This department has detailed plans for an experimental rolling-mill, the erection of which is, however, awaiting the provision of additional funds. Such a mill is essential for the scientific study of roll-pass design and of the effects of varying pressures and speeds on the properties of the rolled steel.

Allied with these researches is the program of the departments of commercial engineering and industrial economics, which are at present engaged in a comprehensive study of the natural resources, power, transportation, labor and finances of the Pittsburgh district; while problems of marketing, sales-organization and industrial personnel administration are studied by the Bureau of Personnel Research. The cost of these researches is financed in large part by coöperating commercial and industrial concerns.

The Carnegie Institute of Technology aims to foster scientific research, because a research atmosphere is an aid to efficient instruction and because the institution recognizes its obligation to utilize to the full its facilities, both of brains and of equipment, in the service of the industrial community.

HOSPITAL RESEARCH LABORATORIES

Research in biochemistry is being carried out in several hospital laboratories, in addition to the Department of Physiological Chemistry of the School of Medicine of the University of Pittsburgh.

The William H. Singer Memorial Research Laboratory of Allegheny General Hospital, Sandusky Street and Park Way, N. S., Pittsburgh, is concerned principally with the study of medical problems, but several of the researches completed therein are of chemical interest. Reference is had to the work on the pathology of trinitrotoluene poisoning and on the bactericidal action of arsenical compounds on experimentally produced *Streptococcus septicaemia*.

The Magee Pathological Institute of Mercy Hospital is located on Stevenson St., Pittsburgh. Among its contributions to biochemical literature have been the following: Basal metabolic rate in constitutionally inferior children, rate of nitrogen elimination, a micromethod for blood sugar determination, and bacteriology of human cystic bile.

The new chemical laboratory of the St. Francis Hospital, 45th St., Pittsburgh, has begun research in biochemistry, although to date it has been engaged mainly in equipping the laboratory and standardizing technic for clinical use.

The laboratory of West Penn Hospital, 4800 Friendship Ave., Pittsburgh, is well equipped for pathological, bacteriological, and biochemical research. It has just completed an important investigation of the value of certain dried foods in the prevention of scurvy.

Pittsburgh as an Industrial Center[1]

By J. H. James and W. F. Rittman

Carnegie Institute of Technology, Pittsburgh, Pa.

IT WOULD be interesting if some writer in the field of industrial economics would trace the history of each of the industrial cities of our country, giving reasons, geographical and otherwise, that led to its specialization in manufacturing. These reasons in some cases have no connection with any strategic situation of the city in its transportation facilities, or its proximity to raw materials, but depend upon the accidental location in that place in its early days of a strong individual with the enthusiasm and the vision to work out the development of an industry that later dominated the district.

W. F. Rittman

Location and Transportation Facilities

Pittsburgh, the ninth city with its population of 600,000, is the hub of the fifth metropolitan district of the country, which immediate district has a population in excess of 1,200,000. Within the radius of a night's trainride there is a population of over 60,000,000, more than one-half the people of the country.

The geographical position of Pittsburgh alone is sufficient to have brought about the development of a great city. At the junction of the Monongahela and Allegheny Rivers, with the great Ohio stretching away to the southwestward, and being in water communication with all the valleys of the great Mississippi Basin, it holds a strategic position for distribution.

Pittsburgh is the central radiating point for six major railroads of the country, and thereby offers transportation facilities second to none. The tonnage originating in the Pittsburgh District is larger than the combined tonnage of New York and Boston, and is far in excess of that of any European port. The Monongahela River alone in 1920 floated 24,000,000 tons of freight, an amount equal to the combined tonnage of the Suez, Panama, and Kiel Canals.

Natural Resources

Remarkable as the factor of location has been in Pittsburgh's military and political history, this city would never have been anything but a distributing point for the great Middle West, had it not also had easy access to a most wonderful group of natural resources. These natural resources, coupled with the location and the indomitable spirit of the people, make her to-day "The Workshop of the World," and from the earliest days of the young republic we find here the utilization of these natural resources that are of prime importance to the industrial chemist.

For any manufacturing we must have, of course, first of all, a cheap and abundant fuel. Pittsburgh is in the heart of the northern half of the great Appalachian bituminous coal field. The "Pittsburgh Seam" is known the world over, and it is a satisfaction to Pittsburghers to know that at a lower level, and not yet mined to any great extent, we have the "Freeport Seam," insuring the supremacy of this district for years to come. The annual production from the Pittsburgh Seam alone is over 100,000,000 tons, approximately one-fifth of the country's bituminous coal output. The importance of this abundant fuel supply, with its resultant cheap power supply, is in itself a major influence and of primary importance to the industrial man, and more particularly to the chemical industry requiring power or fuel in a variety of forms.

The natural gas of the district is being sold at about one-fifth the cost of manufactured gas, when considered on a heat or B. t. u. basis. It is because of this natural gas supply that Pittsburgh is of primary importance as a glass manufacturing center.

Industrial Development

It appears pretty well settled that as early as 1795 there was established a window-glass factory of eight pots on the west side of the Monongahela River, and that General O'Hara erected his window-glass plant in the summer of 1797. At this time the population of Pittsburgh was 1565.

Glass manufacture gradually increased in volume. We find that the glass factories in 1804 turned out products to the value of $12,500, including window glass, bottles, jars, blue glass, and decanters. In 1807 the O'Hara works alone turned out $18,000 worth of products. In 1831 it is reported[2] that there were four window-glass houses and four flint-glass houses, employing 102 hands, using 7000 cords of wood, 150,000 bu. of coal, and turning out products to the extent of $500,000. Without spending time to trace the glass manufacturing development through the nineteenth century, it is sufficient to note that there was a steady and at times a phenomenal growth in this industry in Pittsburgh. For example, in 1886 we find that the use of natural gas had begun, and the operators were congratulating themselves on the more brilliant product obtained, particularly in the case of tableware and lamp chimneys.

J. H. James

While Pittsburgh cannot boast of such a scientific development of glass production as we have seen at Jena, yet there have been engineering improvements that represent equally

[1] Composite of addresses by the authors to be presented at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 9, 1922.

[2] Thurston's "Pittsburgh's Progress," 1886.

as much in another direction—the writers refer to the machine production of glass bottles, etc., and the wonderful window-glass machine. Pittsburgh capital and Pittsburgh technologists have been closely connected with these developments, and from the modest beginning in the early part of the nineteenth century, to-day the industry musters 62 factories with over 3000 pots, an employment of 25,000 workers in normal times, and an annual payroll of over $20,000,000.

Although glass manufacture preceded that of iron in Pittsburgh, it was not long before the iron ores of the district were smelted and a thriving business developed, particularly in making iron for castings. The rapidly growing country to the westward absorbed the products of these early furnaces and foundries.

It sounds strange in this day of beehive coke and by-product coke to hear that the first iron ores in this district were smelted with charcoal. George H. Thurston, writing in 1857, notes that the first "coke metal" was of inferior quality, but that later experience both at the blast furnace and the puddling furnace had obviated this difficulty.

In any discussion of Pittsburgh's iron and steel development it should be emphasized that the real inventor of the well-known Bessemer process was Kelly, a Pittsburgher.

Three important events took place in the latter half of the nineteenth century which placed the United States in the lead as a steel-producing country.

The first of these was the development of the Kelly-Bessemer process, and the second was the entrance of Mr. Andrew Carnegie into the steel business. Although Mr. Carnegie had already embarked in a small way in iron and steel manufacture, he at first opposed the adoption by his firm of the Bessemer process. The story goes that a little later he stood in an English steel plant watching a Bessemer converter in full blast. The spectacle of 30,000 lbs. of pig iron converted into steel in a few minutes changed Mr. Carnegie from a somewhat aimless investor and speculator into a steel enthusiast. It is still further related that this rapid and cheap production of steel opened up for him the vision of replacing all the wooden bridges of the Pennsylvania Railroad with steel structures, an accomplishment to which his firm later contributed largely.

The third great factor in the development of steel manufacture was the opening of the great Superior ore properties. The hard ore mines, opened in the seventies and eighties, and followed by the Mesaba in the early nineties, placed the United States ahead of any other steel-producing country in the world, and Pittsburgh, because of the fact that it was already an iron center, became the leading steel center of the United States and of the world.

The Bessemer ores, which served in the earlier part of the period outlined, have begun to decline, and we have had a gradual increase in the basic open-hearth process. Pittsburgh's natural gas has contributed in a remarkable manner to the cheap manufacture of steel from the Superior ores. With the present rapid decline in the natural gas supply, producer gas from bituminous coal is taking an important position in the steel industry.

The steel man is primarily interested in metallurgical coke, and as a result the by-product coke industry has been wedded to the steel industry. We have had a great deal of loose talk in this country about the belated development of by-product coke.

It should be pointed out that the steel industry is probably one of the most sensitive in the country to the fluctuations of business. The steel manufacturer would hesitate about the installation of an expensive by-product coke plant which he might have to close down within a year or so. Assuming a ready market at all times for all the by-products except the gas, he would be compelled to stock coke in a time of depression with no market for the gas. A market for gas means usually a contract with a local public utility corporation. Gas would be demanded for domestic purposes in dull times and in good times, but the steel man can use the gas in his own plants in good times.

All these objections, however, diminish when we see how by-product coke manufacture is handled by the United States Steel Corporation at its local Carnegie plants. At Clairton is now the largest by-product plant in the world, and work has already begun on an addition that will double its present capacity. The Clairton plant ran all through the recent business depression; this plant sends the gas to the steel mills at Duquesne, Edgar Thomson, and Homestead. By transferring business from other parts of the country to these plants, the Clairton by-product plant was kept in operation.

It seems certain, therefore, that as far as metallurgical coke is concerned, the by-product development will succeed best with the largest corporations.

It is but logical that along with the growth of "tonnage" steel manufacture we should have the manufacture of alloy steels. Crucible steel manufacture is an important factor in Pittsburgh's steel activities. At this point we should pay our tribute to the man whose vision and enthusiasm as a capitalist made possible the realization of the dreams of a chemist; the capitalist, the late Mr. Jos. M. Flannery, and the chemist, Mr. J. Kent Smith, worked over immense obstacles to the successful production of vanadium alloys. To-day, the company which they founded is the greatest producer of vanadium in the world, and a monument to these pioneers in a difficult field of metallurgical development.

The growth of iron manufacturing in Pittsburgh gradually attracted other industries which might be called iron subsidiaries: these include iron galvanizing, tin plate, sulfuric and hydrochloric acids, and in late years we have seen the interesting development of zinc and sulfuric acid manufacture here, as well as many other chemical industries (see table). The reasons, freight rates, markets, etc., which prompted capitalists to locate the latter industries in Pittsburgh, make an interesting study for the industrial chemist.

Although aluminium manufacture is now centered elsewhere, it should be remembered that Hall made his early experiments here, and that Pittsburgh capital supported him. The headquarters of the successor company is still in Pittsburgh, and one of the largest aluminium rolling mills is located near the site of Hall's early experiments.

Pittsburgh is becoming known as the "Electric City," because of its efficient means for changing coal into electricity. The district is served by two major utility companies, which are able to sell power on such favorable terms that most manufacturers, and particularly the smaller ones, prefer to purchase power in the form of electricity. The city has the largest steam power central station in America. The new Colfax plant has one operating unit of 80,000-h. p. capacity, with a second 80,000-h. p. unit now under construction. Ultimately, as the power demands increase, this one plant will have six turbines of 80,000-h. p. capacity, a total power development of 480,000-h. p. capacity. The combined electrical horse power of the two public utility companies serving in the Pittsburgh District will be about 1,000,000 h. p. The power generating plants are located directly adjacent and in direct open communication to the coal mines, making power as cheap, if not cheaper, than in any other locality in America.

The story of petroleum reads as much like a romance as the story of steel, and the discovery of petroleum and its ultimate utilization was the work of Pittsburghers. It seems

well authenticated that Mr. George H. Bissell and Dr. F. B. Brewer of Pittsburgh were the prime movers in the formation of a company called the "Pennsylvania Rock Oil Company," which included some New Haven capitalists and Prof. B. Silliman, Jr., who was president. It was this company that employed Colonel Drake of New Haven to sink an artesian well. Work on this well was begun early in 1859 and oil was struck on August 28, 1859; the production was ten barrels a day, without pumping, and the oil sold for fifty cents per gallon.

The rapid growth of oil refining is shown by the following figures: in Pittsburgh, one year after the opening of the Drake well, seven refineries had been erected, bringing oil into "use as an illuminator and a lubricator," as one of the local historians records it; in 1861, 17 new refineries were added; in 1862, 9 new ones, and in 1863, 15 additional were constructed. By the year 1867, the Pittsburgh district had 58 refineries and supplied over 60 per cent of the whole foreign exportation of petroleum.

While the later centralization of petroleum refining and the development of pipe-line transportation of the crude have changed the aspect of oil refining from what it was when Pittsburgh boasted of 58 refineries, this city is still a factor in the petroleum industry. The headquarters of many of the large oil firms are located here, and Pittsburgh's capital and technical skill are now going to all the oil countries of the world.

It may seem like an anomaly that, in a district dedicated to the element iron which has determined our engineering and material development, we should have the first large-scale development of the element radium, whose study has revolutionized chemical thought.

In 1911, Joseph M. Flannery of Pittsburgh with his associates organized the Standard Chemical Company, securing carnotite ore claims in southwestern Colorado and Utah, and having in mind the production from carnotite of radium and the associated values, uranium and vanadium. After large investments and discouragements that would have led an ordinary man to give up, the first production of radium on a commercial scale in America was made by this company in 1913. The chemical treatment of the ore is made at Canonsburgh, 21 miles southwest of Pittsburgh, and the final purification of the radium is made at the laboratory at Forbes Street and Meyran Ave., Pittsburgh. The production of radium was rapidly increased, owing to the demand for this material in Europe just prior to the outbreak of the war, the production in 1914 amounting to 9.6 g. of radium element. The company founded by Mr. Flannery is now the strongest concern engaged in refining carnotite ore, having produced 90 g. of radium since 1913, and possessing ore reserves capable of producing, on the lowest estimate, over 1000 g. of radium element in the finished product.

In speaking of Pittsburgh, one may refer to the corporate city, the county, or the metropolitan Pittsburgh District. The following table gives a list of Pittsburgh industries, with the number of plants located in each of these sections.

A study of this table shows that the metal and metal products industries hold first place. With 391 of these industries in Pittsburgh, 119 in Allegheny County outside of Pittsburgh, and a total of 694 in the Pittsburgh District, most of which are fabricating iron and steel and their products, it is apparent why Pittsburgh is called the Steel City and the Pittsburgh District is a steel center. These comprise 32 per cent of the industries of the district.

As might be expected, the next largest industrial activity, measured by the number of industries in the district, is that of mines and quarries, principally coal, and numbering 519 in the district. The groups of industries ranking next are: paper and printing, 297; textile and textile products, 193; clay, stone and glass products, 169; chemicals and allied products, 165; lumber and its re-manufacture, 96.

INDUSTRIES OF PITTSBURGH, ALLEGHENY COUNTY, AND THE PITTSBURGH DISTRICT

	Pittsburgh	[1]Alleg. County	Ptsb. Dist.
Aluminium and Its Products	2	3	8
Automobiles and Parts	35	41	46
Axles	3	4	5
Bars—Iron and Steel	13	22	32
Billets—Blooms and Slabs	8	12	19
Bolts—Nuts and Rivets	17	22	27
Brass and Bronze Products	23	32	39
Bricks	22	37	67
Canned and Preserved Goods	28	31	35
Cars and Parts	8	9	16
Castings—Iron and Steel	44	64	97
Cement	1	2	2
Chemicals	12	16	20
Cheroots and Stogies	23	23	27
Chocolate and Cocoa Products	1	1	1
Cigars	16	22	28
Clay	5	8	15
Coke—By-product and Beehive	10	12	52
Coal—Bituminous	142	207	479
Cork	3	3	4
Forgings—Iron and Steel	25	34	42
Gasoline	35	44	60
Glass Bottles	7	11	21
Glass—Lamp and Chimneys	0	6	9
Glass—Plate	4	8	10
Glass—Tableware	2	6	16
Glass—Window	2	2	6
Glue and Gelatin	0	1	1
Hoops, Bands and Iron Ties	7	11	14
Ingots—Iron and Steel	9	15	24
Iron—Pig	9	15	20
Lead	4	4	4
Machinery and Parts	47	55	72
Men's Clothing	32	32	33
Meters	2	3	4
Motors, Dynamos, Generators, Etc.	6	8	8
Oils—Crude	31	33	51
Oils and Greases	17	22	25
Oil Well Supplies	1	1	11
Paper—Printing and Wrapping	4	5	6
Pipes and Tubing	17	20	28
Planing Mill Products	39	57	90
Plates—Iron and Steel	4	7	9
Printing and Publishing	167	205	291
Pumps and Valves	8	8	13
Radium	1	1	1
Rails—Iron and Steel	1	2	2
Railroad Supplies	9	11	13
Refrigerators and Ice Boxes	3	3	5
Repair Shops	5	7	11
Sand and Gravel	14	17	25
Shafting—Cold Rolled, Drawn, and Turned	3	4	8
Shapes—Structural	13	16	19
Sheets—Iron and Steel	4	7	11
Ships and Boat Building	8	10	10
Slaughtering and Meat Packing	15	18	21
Sole Leather	1	1	1
Soap and Soap Powder	8	8	8
Springs	9	12	14
Supplies—Electrical	22	23	32
Stoves, Heaters and Ranges	14	14	21
Terra Cotta and Fire-Clay Products	11	14	38
Tin and Terne Plates	6	8	12
Toys and Games	3	4	6
Ware—Galvanized and Enameled	6	7	12
Washing Machines and Wringers	1	1	1
Wire Products	12	16	22
Woolen and Worsted Yarns	0	2	1
TOTAL	1064	1388	2180

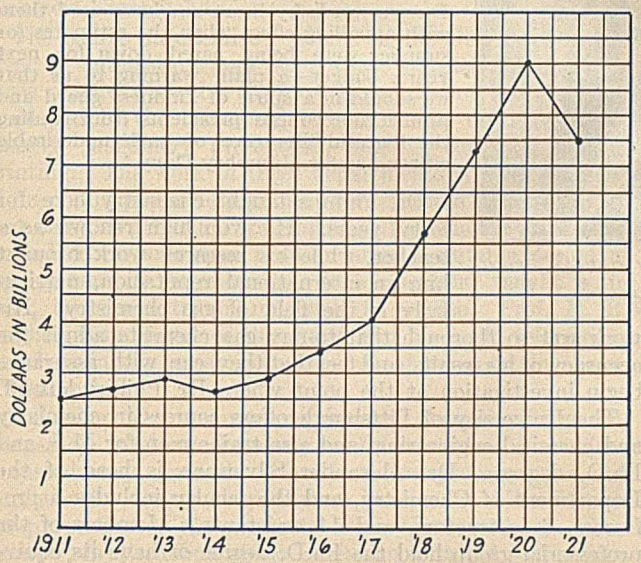
[1] Includes Pittsburgh.

FINANCIAL FACILITIES

Despite the generally accepted axiom that, given time, finance follows industry, the element of the credit and financial facilities of any community is important to the industrial leader, more particularly when the pioneer's facilities are such that he cannot wait on the "time" element. In making the financial appraisal of a community with a view of establishing an industry, the controlling elements are three: facilities for credit information, facilities for marketing commercial paper on a national scale, and availability of New

York finance. Through the evolution of various credit information bureaus, Pittsburgh to-day has facilities in this direction second to none in the country. Of the fifteen commercial paper houses in America to-day, four are located in Pittsburgh. This means, that should money be cheaper in San Francisco, or in any other community in America, than in Pittsburgh, by means of these commercial paper houses, the Pittsburgh manufacturer can get the benefits of that market.

In the element of finances, it is to be noted that the authors refer to availability to New York finances. This is a direct recognition of New York as the center of all major financing. Many cities attempt to show themselves as major elements in national financing projects, but a consideration of the transactions of their local stock markets and their achievements in financing large new industries as compared with New York, shows such claims to be without foundation. The effort of Pittsburgh financial leaders in dealing with national financial problems has not been one of financial competition with New York, but instead the effort and the result has been that Pittsburgh financial institutions to-day are able to offer their clients all the advantages of New York, Boston, and Philadelphia, as well as of Pittsburgh, either for the purposes of home manufacture or foreign trade.



PITTSBURGH BANK CLEARINGS, 1911–1921

Regardless of this, Pittsburgh as a financial community is in the forefront of American cities. With bank clearings in 1911 of about $2,500,000,000 these have grown to more than three times that much during the past decade. Pittsburgh has 78 banks and trust companies, with a capital of $63,000,000 and a surplus of $95,000,000, and with savings deposits of $323,000,000. One institution alone has a combined capital and surplus of $39,000,000, a figure which compares favorably with any financial institution in the world. The assessed valuation of Allegheny County's property is $1,800,000,000, an amount greater than any one of 34 states of the United States.

Such is a brief account of the industrial development of Pittsburgh. Enough has been given to show that the people who settled in this district have risen to the occasion in the development of their resources, and have met every challenge imposed by the city with reference to the developing valleys to the westward. To-day, Pittsburgh stands one of the industrial giants of the world, having satisfaction for work well done, and seeing even greater promise for future development.

The Paint Industry

By A. H. Sabin

CONSULTING CHEMIST, NATIONAL LEAD CO., NEW YORK, N. Y.

RELATIVELY little can be said of progress in the paint industry. During 1921 titanium oxide became important enough commercially to be recognized by the paint trade. It is produced by a single company; is obtained from a deposit of ilmenite (double oxide of titanium and iron) found in Florida associated with zircon, rutile, garnet, monazite, etc., from which it is separated by milling and concentrating; and then shipped to Niagara Falls, where it is treated in an electric furnace, and then leached with dilute sulfuric acid to make a crude titanium oxide. This is dissolved in strong sulfuric acid, and is then partly diluted with water. Barium sulfate (blanc fixe) is added, more water, and then treated until hydrated titanium oxide precipitates in intimate mixture with the barium sulfate. It is dewatered, calcined, and pulverized. The finished product contains 75 per cent of barium sulfate and 25 per cent of titanium oxide and is sold under the trade name of Titanox. As in the case of lithopone, the opacity of the final product is nearly as great as that of its opaque ingredient. Hydrofluoric is the only common acid which attacks it. It makes a soft film with oil, and is mixed with 25 to 40 per cent of zinc oxide to harden it.

A. H. SABIN

The makers of lithopone claim that they are progressing in making it less liable to change by the action of light, and this seems to be generally conceded. It is said to be due not so much to any new discovery as to increased care and knowledge of the processes involved. Lithopone is used to some extent in outside paints, but two of the foremost makers express doubt as to its value for this use.

There appears to be nothing new in the paint vehicles. Perilla oil seems to have secured a permanent place, so much so that all offerings are taken, usually at a price above that of linseed oil; it is chiefly used in the varnish industry.

Research in Wood Finishing

Dr. A. H. Sabin, working in coöperation with the Forest Products Laboratory, the Engineering Foundation, and the National Research Council, is largely responsible for the organization of a committee which is going forward with the organization of research in wood finishing.

We have groups of men who are well versed in the characteristics of different woods and others who through research and experience have important data on finishing materials, but the two groups have not combined their knowledge on the solution of the problem of making articles of wood more enduring. There is much research still to be done, but the first work of the committee is the assembling of data in the literature, the reports of experienced painters and finishers, and in general the collection of what is known of the present state of the art. The initial work is being underwritten by industries concerned in the use of wood finishers and the work of research is being initiated at the Forest Products Laboratory, Madison, Wis.

Pittsburgh as a Center of Chemical Education

By E. H. McClelland

Technology Librarian, Carnegie Library of Pittsburgh, Pittsburgh, Pa.

PITTSBURGH, by reason of its industrial supremacy, has long been characterized as "The Workshop of the World." The city has won wide fame also as a center of engineering activity. There is an old but unverifiable tradition that one in five of the engineers in this country spends some part of his life in Pittsburgh, and monuments to the ability of Pittsburgh engineers exist in the form of important engineering achievements in all parts of the world.

Despite the recognition of Pittsburgh's preëminence in industrial and engineering lines, there has been little general realization of her importance as a center of chemical work and chemical training. This may be, in part, because the chemist's work, however important, is not spectacular and the results are not conspicuous, and because the layman does not understand the nature of chemical work and thus the public in general remains uninformed regarding the true significance of the chemist's achievements.

It has been said that 60 per cent of manufacturing is chemistry. This statement applies with particular force in the Pittsburgh region where the manufacture of the more important products, such as steel, glass, and coke, is under chemical control.

W. O. Breckon Studios

E. H. McClelland

As a matter of fact, Pittsburgh is an important center of chemical industry, as will be competently set forth elsewhere in this issue of the Journal. In the scientific control of this industry, as well as in chemical consultation and research, Pittsburgh employs thousands of chemists, and she is in very large measure training them to meet the demand.

From a recent survey of "Investment in Chemical Education in the United States, 1920–1921"[1] considering all the larger colleges and universities, it appears that Pennsylvania leads in the number of institutions reporting (33), is fourth in valuation of buildings and equipment ($1,854,852), and fifth in total investment in chemical education ($2,404,521). A considerable part of these totals, of course, represents institutions in the eastern part of the state, but there is a large number of colleges in western Pennsylvania, outside of Pittsburgh but within what is generally recognized as the "Pittsburgh District," and in Pittsburgh alone the total college enrollment is approximately 14,000.

Academic Education

University of Pittsburgh—The University of Pittsburgh, formerly the Western University of Pennsylvania, first organized classes in engineering 80 years ago, and was the first institution west of the Allegheny mountains to grant engineering degrees. Of the older graduates, half of those now living are in executive positions, and approximately one-third are engaged in the steel industry.[2]

The teaching of chemistry was inaugurated at an early date, but the records are very scanty. A catalog of 1822 lists Rev. Robert Bruce as "Professor of Natural Philosophy, Chemistry, Mathematics, etc."[3] The first laboratory courses were introduced by John W. Langley (a brother of Samuel Pierpont Langley), professor of chemistry, mineralogy, and geology, in 1872–1873. Francis C. Phillips took charge of the work in chemistry in 1875. He says:

> In my early teaching the complete lack of equipment proved a serious obstacle. In answer to my earnest appeal for apparatus and chemicals the Chancellor was able to quote Sir Humphry Davy, who had publicly declared that a chemist needed only a few tobacco pipes and teacups in order to perform the most varied experiments. Assuredly this wicked and thoughtless remark of Davy's has done more to obstruct the progress of academic chemistry than did all his discoveries to advance it: because University presidents have made it a practice to know Davy's words by heart and have used them with appalling effect when the estimates for supplies were being pared down for next year's budget—a plain warning to us that we should in a spirit of kindness guard and protect our college presidents from reading the harmful literature of such undesirable citizens as Sir Humphry Davy.[4]

Dr. Phillips taught chemistry here for forty years. He won high renown as a teacher, while his research work brought him an international reputation, particularly in the field of gas chemistry. His work was so thorough that to-day gas chemists admit the accuracy of his results, and feel that they can with assurance begin investigation at the point where Dr. Phillips left off.

The University of Pittsburgh offers courses in chemistry and chemical engineering, and also trains men for M.S. and Ph.D. degrees. Dr. Alexander Silverman is head of the Department of Chemistry, and the faculty includes 5 professors, 6 instructors, and 14 assistants. Members of the professorial group hold the Ph.D. degree or have its equivalent in experience, while most of the remaining members of the faculty have the master's degree.

The Department of Chemistry offers 14 undergraduate and 22 graduate courses and certain special courses are offered by senior fellows in the Mellon Institute of Industrial Research. The courses for chemists and chemical engineers devote two years to each of the fundamental subjects—inorganic, organic, analytical, and physical chemistry—and include courses in sanitary chemistry, fuels, and industrial chemistry. One requirement of these courses is three years' work in modern languages. About 120 students were enrolled in chemistry and chemical engineering during the college year just ended.

In the work for advanced degrees, two-thirds of the work must be done in courses and one-third in research. The research may be conducted either at the University or in certain approved industrial laboratories in the vicinity. Forty-five graduate students were enrolled in these courses last year.

[1] This Journal, **14** (1922), 237.

[2] "Facts from the Engineers of To-day to the Engineers of To-morrow." A pamphlet published by the University of Pittsburgh, June 1922.

[3] "The Western University in 1922," by Francis C. Phillips, **1919.**

[4] "The Old Western University at the Corner of Diamond and Ross Streets, Pittsburgh," **1914.**

The Department of Chemistry also provides training for undergraduates planning to enter engineering, medicine, and other fields, and the enrollment from these sources is 950. Some of the special engineering courses require considerable chemistry; for example, the course in oil and gas engineering—the pioneer course of its kind—goes pretty fully into organic chemistry and certain branches of chemical technology.

Carnegie Institute of Technology—Here courses in chemistry were taken by some 1800 students during the past college year. Sixty were registered in chemical engineering, in which an excellent course is offered under Dr. J. H. James, and a smaller number majoring in chemistry in the four-year course in science. (These figures do not include freshmen, as selection of courses is not made until the end of the first year.) Considerable attention is given to judicious guidance in the choice of these courses. In the former, encouragement is given to those whose qualifications are such that they are likely to be successful in the operating field, while the latter course is recommended to the more scholarly type of student who gives promise of developing into a research worker. The latter course naturally offers less of mechanics and engineering, and more of chemistry and physics, and in the senior year prescribes a brief research. Both courses include technical French and German.

The course on chemistry offered in the College of Industries is interesting and somewhat unusual. Instruction deals chiefly with the chemical properties of the materials employed in the three major departments of the College, namely, machinery production, building construction, and printing. The work of these departments stresses methods of economic production rather than creative design, the intent being to give such training as will enable the student to work into an executive position after a suitable period of employment in the industry. The chemistry taught is, in brief; the chemistry of materials in service. Prof. R. B. Leighou is in charge of this work, and his book, referred to elsewhere in this paper, is to some extent based on the course of instruction.

Following a foundation in general chemistry, organic, inorganic, and electrochemistry are introduced as the subject discussed may demand. Manufacturing processes are not emphasized; only such phases as have a notable effect on the properties of the products are studied in detail. For example, in discussing steels, attention is called to the fact that of two steels, one acid and the other basic open-hearth, the latter would be less suitable for castings, since it would probably be more oxidized because of the longer period in the furnace and the fact that it could not be deoxidized in the furnace on account of the phosphorus-bearing slag. In the accompanying laboratory work, for example, the permeability of paint films is determined; iron castings are examined for segregation of sulfides by making sulfur prints; and polished samples of steel are sealed up in air-free water to show that the steel will not corrode in the absence of free oxygen, thus indicating the effect on the metal in closed heating systems as compared with those in which the water is frequently changed.

In the Margaret Morrison Carnegie School for Women, chemistry is in charge of Prof. Charles Watkins. In addition to chemistry the young woman who is graduated from the Department of General Science has also had three years of training in biology, including bacteriology. Her training admits her to the best medical colleges and to the graduate schools of universities, and fits her for commercial work or for teaching. Many graduates now hold positions in hospital, industrial, and research laboratories.

The Carnegie Institute of Technology has just announced two fellowships in mining research, and two in teaching and research in coöperation with the Pittsburgh Experiment Station of the United States Bureau of Mines. The fellowships are open to graduates, and it is evident that chemistry will play an important part in the work, since the list of investigations announced includes such subjects as by-product coking and acid mine waters.[5]

Other Institutions—Pittsburgh has two other institutions of collegiate rank, Duquesne University and the Pennsylvania College for Women, and the curricula of both institutions include courses in chemistry.

The teaching of chemistry in Pittsburgh's secondary schools must not be overlooked. One of the recent high-school buildings, "Schenley High," cost the city nearly $1,500,000. It ranks among the first ten high schools in the United States, and its equipment for science teaching is vastly superior to that of many colleges and universities. Evidence of the thorough instruction in chemistry may be found in the character of the material in Pugh and Miller's "Problem Course in Chemistry"—a text which two of the instructors have prepared for their courses there.

Corporation Training

Concise but definite and systematic instruction in chemistry and metallurgy now forms a part of the required training of many salesmen and other nontechnical employees of the large steel companies. The pioneer development of these courses was the work of a Pittsburgh chemist, and the instruction now given here goes far to increase the competency of many employees who will never engage directly in chemistry or metallurgy.

Practical Training

Pittsburgh's contribution to chemical education is by no means confined to academic education. The industries of the Pittsburgh region maintain a very large number of chemical laboratories and each of these is a center of chemical training. The chief chemist of every industrial laboratory is a graduate teacher of the young college-trained chemist and, to an even greater extent, the instructor of the untrained practical chemist.

The staff of a large steel works laboratory may number 50 employees, many of whom enter with no training but with the well-defined purpose of becoming chemists. The training is intensive and the textbooks in many cases are the "Standard Methods" of the United States Steel Corporation. The number of entrants is very large and many of the ablest survive and pass on to positions of considerable responsibility. One who has been long acquainted with the steel laboratories can point to many men who, beginning as "carbon boys," are now assistant chemists, assistants preparing special solutions, etc.; and to a lesser number who have become able chief chemists or successful furnace superintendents. Though this practical work cannot be recommended as a substitute for theoretical training, it remains a highly important element in the education of chemists in industrial regions such as Pittsburgh.

Writing of Books

The creation of authoritative textbooks and reference books is an important factor in chemical education, and the service of good textbooks is by no means limited to their use in schools and colleges. Probably few Pittsburghers realize the extent to which the literature of science and technology has been enriched by the contributions of local authors. Several hundred such books and monographs are catalogued in the Carnegie Library of Pittsburgh and many of these are concerned with chemistry and allied subjects. A mere list of these would in itself afford worthy evidence of

[5] *Science*, **55** (1922), 553.

Pittsburgh's influence on chemical education.[6] Obviously complete enumeration cannot be undertaken here, but a few works may be mentioned as illustrative.

The widely read books of the late Robert Kennedy Duncan have been a source of instruction and inspiration to chemists and laymen, and by reason of their popular appeal have doubtless been instrumental in bringing many new disciples to the shrine of chemistry. "Chemical German," by the late Francis C. Phillips, has been adopted as a textbook in 28 educational institutions, and thousands of copies have been sold. "Technical Examination of Crude Petroleum," by W. A. Hamor and F. W. Padgett, has been adopted in seven institutions and has a large sale abroad. R. B. Leighou's "Chemistry of Materials of the Machine and Building Industries" is a valuable book, which in scope and treatment is not paralleled by any other American work. C. M. Johnson's "Rapid Methods for the Chemical Analysis of Special Steels" is the standard work in its field. H. P. Tiemann's "Iron and Steel" is without a rival as a concise encyclopedic dictionary of terminology and processes in ferrous metallurgy. S. L. Goodale's "Chronology of Iron and Steel" is unique in its field and constitutes a valuable reference work. "The Making, Shaping and Treating of Iron and Steel," by J. M. Camp and C. M. Francis, is the best existing work on American steel-mill practice. Privately published, and with no attempt at direct publicity, some 12,000 copies have been sold since the appearance of the first edition in 1919. Its high value in educational work is evinced by the fact that it has been adopted in more than 20 colleges, some of which have ordered well above 300 copies. The senior author, formerly chief chemist of one of the largest steel works in the Pittsburgh district, is also chairman of the Chemists' Committee of the United States Steel Corporation, and is thus in charge of editing the standard methods of analysis issued by the Corporation. These "Methods" have appeared in 8 pamphlets, some of which have reached a circulation of nearly 3000 copies.

Able specialists at the Pittsburgh Experiment Station of the United States Bureau of Mines are continually adding to their already valuable contribution to chemical literature, and among the forthcoming books by other Pittsburgh authors are important works on fuels, glue, glass, and metallurgical heating furnaces, on most of which subjects there are now few satisfactory books in the English language.

Lectures and Society Meetings

Public lectures constitute an important, if unsystematic, means of education. When delivered by men of culture and experience, they have a broadening influence, very efficacious in redeeming the prosaic life of the individual overburdened by routine. Pittsburgh is fortunate in having a wealth of this service concerned more or less directly with chemistry.

Most of the important national societies have regular section meetings in the city, and in addition there are several local organizations. The Engineers' Society of Western Pennsylvania, one of the strongest local engineering societies in the country, has many addresses on metallurgy and other subjects of interest to the industrial chemist. Fifty Pittsburgh women chemists, the largest group in any city of the United States who have completed regular courses in chemistry and are making it their life profession, have applied for an Iota Sigma Pi charter and expect as a feature of the coming September convention of the American Chemical Society to be installed as a regular chemical society of women, of which there are relatively few in the United States.

The United States Bureau of Mines contributes generously to education by means of its motion-picture films (concerned largely with chemical technology) and its mine-safety lectures and demonstrations (based in part on chemistry). These activities are nation-wide in service but both are entirely in charge of the Pittsburgh Experiment Station of the Bureau. The station is also responsible for numerous public lectures which in many cases are on chemical subjects.

The Mellon Institute of Industrial Research is a prominent feature in any survey of Pittsburgh's resources in the field of chemical education. The activities of the Institute will not be elaborated here, since elsewhere in this issue of the Journal this subject will be ably presented. Aside from the systematic research work of the Institute, however, during the past season the public were admitted to some 30 technical lectures by staff specialists, and to a series of 12 lectures on "Scientific Method" by Dr. Walter Libby, one of the highest authorities on the history of science.

Library Resources

Chemical education, in the fullest sense, is broader than instruction in colleges and training in laboratories. In a very recent paper on "Aims and Means in College Education," Dr. Vladimir Karapetoff[7] says, "Every item of our knowledge is, or will be, contained in books and magazines," and indicates that the student's future success will depend very largely on his having learned how to use the resources available in literature.

Mr. Charles L. Reese, in discussing the work of the Research Information Service, in Washington, says:[8]

> If the scientific and technological literature of the world were regularly and systematically abstracted and listed, and if all this condensed information were available *** it is reasonable to anticipate that from 70 to 90 per cent of all requests could be answered directly and with reasonable satisfactoriness from this single master-key.

Any city, therefore, which is to acquire and retain high prestige as a center of chemical education and scholarly chemical work, must have adequate library facilities to enable its workers to get effectively in touch with the rich resources in the literature.

Pittsburgh is fortunate in having exceptional library advantages in the field of chemistry. The various research activities of the region (discussed elsewhere in this issue) in many cases include libraries. The Mellon Institute of Industrial Research, the Aluminum Company of America, the United States Bureau of Mines, the Pittsburgh Testing Laboratory, and other laboratories have well equipped library collections in their special fields.

The most important reference collection, however, is that of the Technology Department of the Carnegie Library of Pittsburgh, which was the first public library to establish a department devoted solely to scientific and technical literature. Something of what this library offers the chemist is set forth in an earlier paper[9] and only a brief review can be attempted here. Though this department is concerned with all branches of pure and applied science, it is especially strong in chemistry and metallurgy. Evidence of its strength in current chemical periodicals is shown by the fact that it contains approximately 80 per cent of the material abstracted in *Chemical Abstracts*. The greatest weakness is probably in medical and biological chemistry, but this gap is to some extent filled by the two local medical libraries (in the Pittsburgh Academy of Medicine and the Medical School of the University of Pittsburgh), and as the Technology Department of the Carnegie Library maintains a "union" card catalog of current scientific and technical periodicals in other

[6] A partial list of books on chemistry and metallurgy by Pittsburgh authors appears in the *Monthly Bulletin* of the Carnegie Library of Pittsburgh for July 1922.

[7] *Engineering Education*, **12** (1922), 398.

[8] This Journal, **14** (1922), 368.

[9] *Ibid.*, **11** (1919), 578.

local libraries, it is enabled to put patrons promptly in touch with this supplementary material.

In the selection of books the Carnegie Library of Pittsburgh probably makes more use of book reviews than does any other library, and in connection with this work the Technology Department publishes a quarterly "Technical Book Review Index," which is the only publication in the world devoted to recording reviews of new scientific and technical books.

The Carnegie Library of Pittsburgh is the only large library that regularly publishes a classified catalog in book form. The sections of this catalog dealing with scientific and technical books may be purchased separately, the latest series including books added to the collection during the years 1912–1916, inclusive. This catalog is brought up to date by a "Monthly Bulletin," which is annually provided with a subject index. These publications enable patrons at some distance from this library to keep much more closely in touch with the resources and growth of the book collection than is possible with most libraries.

The Technology Department has compiled and published many bibliographies on special technical topics. Among the subjects included are Lampblack; By-product Coking; Sewage Disposal; Mica; Sand; and Refuse and Garbage Disposal. A list of nearly 600 references on water-glass is now in press. The Technology Librarian compiles annual lists of new books on iron and steel and on the coal industry. These lists are published in local trade journals, and, through the courtesy of the editors, reprinted and distributed by the library. This department makes use of a "classified" card catalog—a type found in only two other large technical libraries, but which affords better service than the card catalogs generally found in libraries.

That the Technology Department is of some definite value to the chemists in the community is evidenced by the attitude of the local membership of the American Chemical Society. In 1921, a general reduction of municipal appropriations affected the library to some extent. Realizing that the funds available for technical literature were insufficient to maintain the service which this community deserves and rightfully expects, the Pittsburgh Section organized a Library Committee which, under the able leadership of Mr. J. O. Handy, raised among the local industries a fund of $2500 for supplementing the resources of the technology department, thus making possible the purchase of some important reference material. This fund was drawn upon also to finance an undertaking which enables this library to offer a special service not available elsewhere. A list has been made of the actual numbers identifying all patents in 48 complete classes of the U. S. Patent Office classification. These classes comprise approximately 200,000 patents, covering, in general, the entire field of chemistry and metallurgy. This is a field of great local importance and within its limits users of the library are now enabled to make a complete patent search by subjects—a service not possible with the printed indexes issued by the Patent Office.

So far as is known to the writer of this article, this work of the Pittsburgh Section is unprecedented in the history of any public library in America. Such action is a source of great gratification and encouragement to the library staff, and such constructive coöperation will go far to improve the library service in the community.

Conclusion

The character of the instruction in Pittsburgh's educational institutions, the close contact with her basic industries, and the superiority of her resources in chemical literature combine to make Pittsburgh an exceptionally favorable field for chemical education, while the nature and extent of her industries afford an important outlet for the product of this education. In confirmation of this statement, one interesting bit of evidence is found in the fact that many thoughtful technical students, after a year in contact with Pittsburgh conditions, change to courses in chemistry.

The Foundation for Chemical Development

By W. A. Noyes

University of Illinois, Urbana, Illinois

In 1918, in the midst of the Great War, a society for chemical industry was organized in France. In one of the early numbers of the journal published by the society an estimate was given of the number of chemists in the leading countries before the war. According to this estimate there were 30,000 chemists in Germany, 5000 in England, 2500 in France, and about 16,000 in America. These numbers indicate very clearly that if America will use her opportunity she may soon hold the position of preëminent importance in chemistry held by Germany before the war. At such a time we should inquire on what foundation we must build if we are to seize the chance which surely lies within our grasp.

W. A. Noyes

Almost exactly one hundred years ago a young German of nineteen took his doctor's degree at Erlangen in Germany. After that he went to Paris to study with Gay-Lussac, for chemistry was at a very low ebb in Germany in those days and he chose to work with one of the greatest chemists of his time. There is such a thing as scientific heredity. It differs from physical heredity in that a man may choose his own father. And so Liebig chose Gay-Lussac, just as Wöhler, his intimate friend of later years, chose Berzelius, the Swedish chemist—the greatest chemist of that time. It is worth our while to remember, too, that it was only six years after the close of the Napoleonic wars, when France and Germany had been bitter enemies—but Liebig went to Paris to study chemistry. Two years later he returned home and at the age of twenty-one he was made assistant professor in Giessen, and in another year he was appointed full professor.

There in Giessen he founded a new school of chemistry. It was not so much a place where students were taught what was known of their science, as a workshop where students and teacher worked side by side in the endeavor to add something to the world's knowledge. To that laboratory men came from all over the world and from that laboratory went out influences that touch every chemist and, it might almost be said, every individual in the world to-day.

One of the students in Liebig's laboratory, A. W. Hoffman, was called to London in 1845 by Prince Albert, to fill a chair in the newly founded College of Chemistry. Ten years later he had an assistant by the name of William H. Perkin, only

nineteen years of age. Young Perkin fitted up a small laboratory at home, and there he tried some experiments to convert aniline into quinine. We know now that there was not the slightest possibility of doing what he attempted. Instead he obtained a beautifully colored compound, the substance we call mauve. He tells us that at that time when chemists got a colored compound in their operations they were accustomed to throw it in the slop jar or remove it with boneblack. Perkin was struck with the beauty of the substance and he conceived the notion that it might be profitable to manufacture it for a dye.

The story of Perkin's difficulties and success is one of the romances of science and of industry. Benzene was not made by the ton then, as it is to-day. It was necessary to transform laboratory test-tube reactions into factory operations. Even when all these troubles were over and the mauve had been produced in quantity, the dyers who had been accustomed to Turkey red and fustic and indigo and other dyes of natural origin did not know how to use it, and Perkin had to go into their dyehouses and teach them.

Soon afterwards two German chemists, Graebe and Liebermann, demonstrated that anthracene is the mother substance of alizarin, the Turkey red obtained from madder root. They also succeeded in making alizarin from anthracene, but they did not succeed in establishing commercial production on the basis of their scientific discovery. Once more it was Perkin who did this in his factory, and within a few years the manufacture of alizarin from coal tar was so successful that the Dutch farmers had to give up raising madder root. Even as early as 1880 it was estimated that the alizarin which was manufactured from anthracene at a cost of $8,000,000 a year would have cost $28,000,000 if it had been prepared from madder root. It is scarcely an exaggeration to say that enough has been saved from this to pay for all the university laboratories in the world.

With such a beginning one would think that the coal-tar dye industry belonged to England. The initial great success was achieved there, and the coal tar from which the dyes were made was produced in much larger quantities in England than on the continent. But within a few years the new industry was almost completely transferred to Germany. At the beginning of the Great War the value of the product of this manufacture was estimated at about $100,000,000 annually, from two-thirds to three-fourths of the whole amount being made in Germany. We used in America dyes to the value of about $17,000,000, but manufactured only about $3,000,000 worth ourselves. Why should Germany so far surpass all other countries in this industry? The chief reason undoubtedly was that Germany had a larger number of chemists trained in methods of research in the spirit of Liebig's laboratory. There were other reasons that we do not like so well. Over and again American manufacturers tried to make aniline and other substances called "intermediates" which are used for the preparation of various dyes. In every case German manufacturers took care that the price of the article made was put so low that the American manufacturer was forced out of the business.

A few years ago our sailors were in danger of going to meet the submarines, blind, because we could not manufacture the optical glass needed to make the necessary instruments. In such an emergency to whom did we turn for help? To the manufacturers of glass? No, we appealed instead to men trained by many years of research at the Bureau of Standards and at the Geophysical Laboratory in Washington, where they had been studying silicates, not for the purpose of making glass, but in order to discover how the rocks have been formed. These men were able to attack the problem, and with the aid of a manufacturer they were ready to furnish six different kinds of glass within a few months. Then a seventh different glass was called for. Meanwhile, they had worked out the so-called triaxial diagram for silica, potash, and litharge, by means of which they could predict the relation between the composition of a glass made from these ingredients and its index of refraction and dispersion. They located on this diagram the composition of the glass having the desired properties, put the materials together, and it came out right the first time. Such is the difference between the old cut and dry methods of so-called practical men and a genuine scientific method.

Universities are not the only institutions where researches are prosecuted. It was at the Royal Institution of London that Sir Humphry Davy made those brilliant discoveries in electrochemistry which lie at the foundation of the great electrochemical industries of our time. There Faraday discovered the laws of electrical induction, that an electrical current could produce mechanical motion, and that mechanical motion could produce an electrical current. Those were principles which carried the germ of every machine used to generate electricity and of every electrical motor in use to-day.

Not long ago the Dean of a College of Commerce in one of our state universities made the statement that there are two ideals in vogue in these schools. One is that the students shall be trained primarily to do some specific thing—to be a stenographer, a bookkeeper, an accountant or something of that sort—in short, that the training shall be vocational. The other idea is educational, the laying of a broad, thorough foundation for future work. He spoke emphatically in favor of the second ideal. Thirty years ago many of us got the impression that the steel industry was calling for chemists who could make steel analyses just as those analyses were made in a works laboratory. That was training for a trade, not for a profession, and many young men trained in that way found that they were soon displaced by high school lads or boys of even less training, who could carry out the mechanical manipulations required as well as they. It was only those with a broader, professional training who continued successfully in work as chemists. We often tell our students that it is fully as important to secure good training in mathematics, physics, German, and French as it is to study chemistry while in college. If they are successful as chemists they will continue to study chemistry all their lives but they will probably never again find such a good opportunity to study the other things essential as a foundation for their work.

A thorough knowledge of chemistry and of related sciences is not enough. It was not knowledge of chemistry, merely, nor, indeed, chiefly, which made the men trained in Liebig's laboratory so efficient. It was not knowledge alone which made many of our chemists and physicists so efficient in the emergencies of war. The factor of far greater importance was the habit of research, the ability to attack new and strange problems and solve them quickly. Chemical knowledge was much more limited one hundred years ago than it is to-day and the young men in Liebig's laboratory were given the joy of research work after comparatively brief preliminary training. It now takes several years to gain that elementary knowledge of inorganic, analytical, organic, and physical chemistry which we think essential. Our students certainly do not get a too comprehensive knowledge of these subjects but it is a question whether we do not carry the process of cramming too far before we give them an opportunity to begin constructive work. As teachers, too, there may be a question whether we are not sometimes more anxious that they should get results of interest to us rather than that they should acquire the habit of solving difficulties for themselves with a minimum of guidance from others.

Progress in the Chemistry of Naval Stores, 1920-1921[1]

By F. P. Veitch and V. E. Grotlisch

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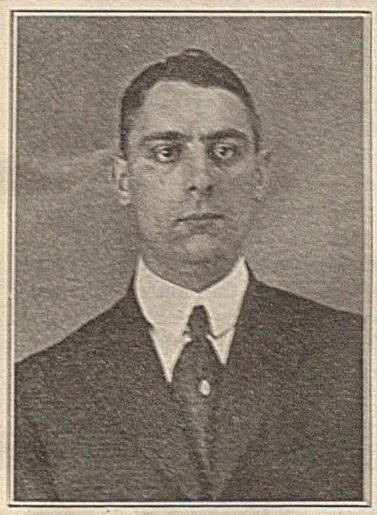
During the past two years there have been numerous contributions to our knowledge of the chemistry of naval stores, of which oil or spirits of turpentine and rosin are the most important. Probably because of its more widespread and divers uses, and also because of the fact that its composition and constitution are less well understood than is the case with turpentine, more work has been done on rosin than on turpentine. Even now the constitution and exact composition of rosin are not definitely settled. We shall consider the subject at hand under three major headings: first, the crude resin or gum; second, turpentine oil or its constituents and closely related compounds; and third, rosin and its products.

F. P. Veitch



V. E. Grotlisch

Resin and Gum

Among the less well-known sources of turpentine and rosin are the pine forests of China. There is quite an appreciable quantity of rosin exported from China, principally to Japan and Australia. Shinosaki and Ono[1,*] obtained the following results from a sample of crude Chinese resin: essential oil, 8.5 per cent; rosin, 84.35 per cent; loss, impurity, and water, 7.5 per cent. The essential oil consisted largely of *l*-α-pinene, with a trace of dipentene and about 11 per cent of a new tricyclic sesquiterpene. Heurich[2] has examined the oleoresin from the Norway pine, *P. sylvestris*, the source of turpentine in Germany, Poland, and Russia. The yield of essential oil and rosin, as well as their composition and properties, is stated to correspond to those of American turpentine and rosin, except that the oil is levorotatory, in this respect simulating French turpentine. A possible new source of naval stores in India is the tree known as *Boswellia serrata*, or Salai tree. The resinous exudation, known locally as salaigugul, is a gum-resin containing, beside essential oil and rosin, about 20 per cent of soluble gum. Fowler and Malandkar[3] have worked out a method of separating the rosin and the gum, after removal of the oil by steam distillation, in which the resin is hydrated by heating with water under pressure. The hydrated resin floats on the surface and can be removed as a solid on cooling. The gum forms a flocculent precipitate on the bottom of the vessel. It has weak adhesive power. The hydrated resin is subsequently dehydrated by heating. It differs from ordinary pine rosin principally in acid and saponification numbers, which are, respectively, 51.6 and 61.3. These low values make the rosin useless for soap making, but it may be useful for varnish making.

In a series of articles, G. Dupont[4,5,6] describes the results of his investigations on the resin of the French maritime pine. The two isomeric acid constituents, *d*- and *l*-pimaric acids, show marked difference in the stability of their rotatory power. The rotation of *d*-pimaric acid was not changed by the action of very dilute HCl, but *l*-pimaric acid showed decreasing rotatory power according to the length of time in contact with the hydrochloric acid, up to 24 hrs., after which the rotation increased again slightly. He considers the abietic acid in rosin as a mixture of isomorphous acids which he designates as pimarabietic acid, produced by the action of heat on the pimaric acids of the crude resin.

Turpentine

The terpenes, of which pinene, the principal constituent of turpentine, is probably the best known, constitute a large and complex class of compounds. Only those bearing a direct relation to turpentine and its constituents are considered in this review. Simonsen[7] has found a new bicyclic terpene, *d*-carene, and a new tricyclic sesquiterpene, which he calls longifolene, in the Indian turpentine oil obtained from the Chir pine, *P. longifolia*. The author ascribes to these two new compounds the two properties of Indian turpentine which make it inferior to the American or French product, namely, ease of oxidation and high per cent of residue on evaporation. Although not oxidized by a mixture of dichromate and sulfuric acid, *d*-carene readily absorbs oxygen from the air, as shown by the fact that one cc. of this compound, when placed in a closed vessel (dimension not stated), absorbed all the oxygen from the air in three days. Analytical constants for the new compounds are given.

The preparation of synthetic rubber and synthetic camphor has occupied the attention of chemists, more particularly in Europe, for many years. If economically successful, it would open up a wide field for the use of turpentine. In order to throw some light on the conditions governing the formation of isoprene, as well as to check up a theory advanced some years ago that limonene or dipentene gives better yields of isoprene than pinene, Mahood[8] passed the vapors of turpentine, both from gum spirits and steam-distilled wood turpentine, through heated tubes, with and without catalysts, under carefully regulated thermal conditions. His results indicated that limonene, or rather the turpentine fractions consisting largely of limonene, did not give any marked increase in the yield of isoprene, and that gum turpentine was just as good as wood turpentine. The small yields of both isoprene and toluene preclude any economic disposal

[1] Published by permission of the Department of Agriculture.

* Numbers in the text refer to Bibliography at end of paper.

of turpentine in this way. The production of synthetic camphor, however, has shown considerably more promise, from an economic point of view, than the manufacture of synthetic rubber from isoprene. Luttringer and Dubosc,[9-16] in a series of articles, have described a number of methods of treating turpentine or derivatives thereof, principally pinene hydrochloride, to obtain esters which can be easily converted into camphor. Along this same line, Wesson[17] has patented a process of converting pinene hydrochloride into isobornyl esters, based on the action of certain organic acids in the presence of zinc as a catalyst. An interesting review of the patent literature on the manufacture of synthetic camphor has been published by Witte,[18] the author going back to some of the earliest patents taken out in Germany. The practicability of some of the patents, in the light of our present knowledge on the subject, is also discussed. The Fabrique de Prod. Chim. de Thann et Mulhouse[19] has patented in England a process for obtaining optically active borneol, free from isoborneol, based on the reaction of pinene and tetrachlorophthalic acid.

Pariselle[20] has separated α- and β-pinene from a large volume of French turpentine by very careful fractionation *in vacuo*, and checked up their physical constants. By the action of hydrogen bromide both compounds gave the same two hydrobromides, one solid and the other liquid. Bromine in carbon tetrachloride solution, at low temperature, gave a complex mixture of addition and substitution products, containing both bromides and hydrobromides. A monobromide and two dibromides were isolated.

Henderson and Marsh[21] obtained three pinene dichlorohydrins, soluble in water, by the action of a dilute aqueous solution of hypochlorous acid on pinene. In one of the papers of their extended series on the chemistry of pinene, Ruzicka and Trebler[22] dispute the constitutional formula for nitrosopinene advanced by Wallach, and advance one based on their own observations.

Analysis

The analysis of turpentine is largely confined to detection and estimation of adulterants and for compliance with specifications. Hofman[23] has described a simple method of detecting adulteration of certain essential oils, among them being turpentine. These oils are relatively insoluble in alcohol at ordinary temperatures. The oil is dissolved in four volumes of alcohol by warming, the concentration of the alcohol depending upon the oil under observation. Ninety per cent alcohol is used for turpentine. If the turpentine is pure, the solution should start to become turbid, indicating separation, at about 60° C. Allina and Salvaterra[24] and Salvaterra[25] have described methods of determining mineral oil in turpentine, for which they claim greater accuracy than is shown by most of the practical methods now in use. Their methods are based on the formation of nonvolatile compounds by the absorption of bromine or iodine by the terpenes to the point of complete saturation. The volatile unchanged mineral oil is then removed by steam distillation. The application of the methods (especially Salvaterra's iodine method) is rather expensive, however, on account of the high cost of the reagents used, since turpentine absorbs over three times its weight of iodine, and considerable excess must be used to insure complete reaction.

Very few methods have been published on the determination of coal-tar oils, such as toluene, xylene, and solvent naphthas, in turpentine, probably on account of the relative infrequency of such adulteration. Grotlisch and Smith[26] have worked out a method which is not only applicable to adulteration with small percentages of coal-tar oil, but also detects the presence of mineral oil. Some of the pinene of the turpentine is removed by conversion into the solid pinene hydrochloride, and the adulterant concentrated by fractional distillation of the filtrate at reduced pressure. The distillate containing the adulterant is then sulfonated to destroy the remaining terpenes and to form sulfonic acids of the coal-tar hydrocarbons. Steam distillation of the sulfonation mixture separates any unchanged mineral oil that might be present. Finally, the sulfonic acids of the coal-tar hydrocarbons are broken up with recovery of the oils themselves, by direct heat distillation.

Specifications for turpentine have heretofore been far from uniform. Based on the results of examining a considerable number of commercial pure turpentines, the U. S. Interdepartmental Committee on Paint Specification Standardization[27] has adopted and published a set of "Recommended Specifications for Turpentine," which have been adopted by various bureaus of the Government and other agencies as standard specifications for turpentine. Instructions for sampling, analysis, preparation of reagents, and a basis of purchase, which take account of the expansion and contraction of turpentine with changes in temperature, are given. A handbook on turpentine has been published by Veitch and Grotlisch[28] containing, besides the above specifications, a review of the principal sources of turpentine throughout the world, the principal uses, process of manufacture, methods of transportation, expansion tables, simple methods of detecting adulteration, review of state laws covering the sale of turpentine, statistics on production and exports, and a method of calculating capacity and outage of tanks.

Uses of Turpentine

By far the largest proportion of turpentine is used as a thinner in paint and varnish. Several interesting new uses have recently been described. An anonymous article[29] describes the use of turpentine in a bleaching liquor said not to affect the strength of the fiber of the cloth, as chlorine often does. Several formulas for preparing the "ozonized" turpentine are given. Another interesting new use is described in a patent by Pratt.[30] A sulfur-terpene compound known as "toron," in the form of a black viscous liquid or semisolid, is prepared by heating turpentine with sulfur. It is used for waterproofing canvas, preparing rubberized cloth, and as a bond for attaching or coating metal surfaces with genuine rubber. The physiological effects of turpentine vapors when turpentine is used in quantity as an extraction medium for fats, waxes, etc., are discussed by Lewin.[31] Turpentine is classed as a narcotic type, producing depression of the nervous system, and may cause eruption of the skin and mucous membrane.

Rosin

One of the less well-known constituents of rosin is a body called retene. Virtanen[32] has attempted to throw some light on the relationship between retene and the resin acids by preparing hydrogenated retenes and studying their chemical properties. One peculiarity brought out is the stability of the hydrogenated retenes toward permanganate, although they are unsaturated bodies. Aschan and his co-workers[33,34,35] have described and investigated a new resin acid, called pinabietic acid, which they obtained from a Swedish pine oil. Its molecular weight indicates the formula $C_{20}H_{30}O_2$, thus being isomeric with abietic acid. It does not, however, show the same color reaction by the Mach† test as abietic acid. A striking peculiarity is the difference in rotation in various solvents. It is dextrorotatory in the aromatic

† *Monatsh.*, **15** (1894), 627.

hydrocarbons, and levorotatory in alcohols, ether, and chloroform. By adding absolute alcohol to the solution in benzene, the rotation can be changed from positive to negative, with a zero reading in a mixture of 92 per cent of benzene and 8 per cent of alcohol. It is nearly insoluble in petroleum ether and ligroin. A constitutional formula is given.

Aschan[36] claims to have discovered and describes a new series of acid bodies in rosin which he calls colophenic acids, with a general formula $C_nH_{2n-10}O_4$. Several methods of separating them from rosin are described. The author believes that it is owing to the presence or formation of these acids that the dark color of low-grade rosins, as well as the bitter taste, is due. The dark color of the "leim-galle," the precipitate which forms on boiling a solution of rosin size, is also supposed to be due to these bodies. They are amorphous, highly unsaturated, and instantly decolorize permanganate. Fahrion[37] has taken issue with Aschan as to the originality of the discovery of these bodies in rosin. He claims that they are identical with the so-called oxyabietic acids described by him in a previous work†† on the atmospheric autoxidation of powdered rosin. In a later article Aschan[38] refutes Fahrion's claim to priority, and shows that there is no relation between Fahrion's oxyabietic acid and the colophenic acids.

Grün,[39] on the basis of his observations, has attempted to formulate a structural formula for abietic acid to show its relation to α- and β-pinene. He discusses the possibility of the formation of abietic acid by the union of one molecule each of α- and β-pinene. Stock[40] has distilled rosin under the high vacuum of the green cathode ray, *i. e.*, practically a complete vacuum. It was possible to distil it almost completely without appreciable decomposition. The relatively small difference in temperature between the boiling liquid rosin and the vapors proves that rosin does not contain polymerized bodies of abnormally high molecular weight. He obtained crystalline acids from amorphous rosin by heating *in vacuo*, the time required to effect complete change depending on the temperature used. Among his conclusions is the following on the composition of rosin: α-abietic acid, 31 per cent; β-abietic acid, 31 per cent; γ-abietic acid, 19 per cent; resenes (or retenes) 10 per cent; essential oil and bitter principles, 0.5 per cent; impurities, 0.5 per cent.

Analysis

The detection and determination of rosin in mixtures and preparations is probably the most important phase of rosin analysis, since it is seldom bought on specification and not much subject to adulteration. Wolff[41] has described a method of detecting and approximately estimating the rosin in oil varnishes. He finds it necessary to isolate the resin acids, since boiled linseed oil, especially in the presence of manganese driers, sometimes gives a reaction with the Storch-Morawski test which closely approaches that of rosin. Neither rosin which has been heated to high temperature for some time nor rosin esters give a characteristic color test. McNicoll[42] has published a method for determining resin acids in fatty mixtures, depending on the esterification of the fatty acids by naphthalene-β-sulfonic acid, leaving the resin acids unchanged. These are titrated or separated and determined gravimetrically. More reliable results are claimed than by former methods, such as Twitchell's.

Use of Rosin

The three principal uses of rosin in order of their importance in the United States are the manufacture of soap, paper size, and varnish, soap makers using about as much as the other two industries together. A bibliography on the use of rosin in soap-making has been published by Jungkunz,[43] which also includes a discussion of the methods of determining rosin in soap. German rosins, prepared in Germany from the resin of *P. sylvestris*, seem not to have measured up to the imported American and French products, especially from the soap-makers' standpoint. Goldschmidt and Weiss[44] have examined several samples of German pine resin, from which they prepared the rosin by the use of solvents. Their analysis of these brings them to the conclusion that German rosin is not greatly inferior to American or French rosin, so far as acid and saponification values and per cent of unsaponifiable are concerned. Goldschmidt[45] found that rosin, when left in lump form, showed up better on the "stearin" method* for available rosin substance, *i. e.*, the soap-making power or value of the rosin, than powdered rosin. They conclude, from the results obtained on powdered rosin which was exposed to moist air for some time, that a water-soluble oxidation product is obtained, which is lost during the analysis by escaping solution with other resin acids in the ether.

The application of rosin to the sizing of paper has brought out a number of new ideas. Thindon[46] concludes from recently published data that the sizing property of rosin is due to free rosin which in turn is protected by a film of aluminium hydroxide or resinate. Traquair[47] states that by dissolving the size and alum in a suitable starch solution the quantity of rosin required can be reduced by about 50 per cent. Sutermeister[48] seems to think that high-grade rosins gave better sizing efficiency than low grade, but the difference between them hardly warrants the payment of any material difference in price.

Sieber[49] has investigated the behavior of a suspension of free rosin toward various electrolytes. The suspension was precipitated by $Al_2(SO_4)_3$ at a concentration of 0.00261 mols. per liter. Calcium and magnesium salts required 0.025 and 0.015 mols. per liter, respectively, to precipitate the rosin. From this he concludes that hard water does not materially affect the suspension of free rosin. Schneider[50] also discusses the bad effect of hard water on size emulsions containing a high percentage of free rosin, and further points out that a size emulsion should not get above 100° F., since aluminium resinate starts to solidify or coagulate at this temperature, losing its finely divided form. Miles[51] has taken out a patent for oxidizing rosin by agitation with H_2O_2 until it is capable of forming an ammonium compound which may be diluted indefinitely with water, thus being adapted to paper sizing.

Within the past five or six years the use of rosin in varnish-making has increased markedly, owing to the discovery that rosin could be esterified, reducing its acid value and increasing its hardness and weather resistance. Very satisfactory varnishes are now made from rosin esters and tung oil. Gardner and Coleman[52] have described a process for the esterification of rosin with glycerol and tung oil in the open varnish kettle, using hydrated lime or calcium soaps as catalysts. Formulas for several different classes of varnish are given.

Sterling, Grotlisch, and Veitch[53] have patented a process of esterifying rosin with glycerol using zinc as a catalyst, whereby very low acid values are obtained. Murray[54] has investigated the various conditions governing the esterification of rosin with glycerol. A very satisfactory product is obtained by esterifying with somewhat less than the required quantity of glycerol for complete neutralization, and completing the latter with lime. An interesting point brought out is the fact that a good rosin ester approaching kauri can be ob-

†† *Z. angew. Chem.*, **20** (1907), 356.

* Goldschmidt and Weiss, *Seifenfabr.*, **39** (1919), 49; *C. A.*, **13** (1919), 1942.

tained by esterifying a mixture of one part rosin and three parts congo copal, but the process must be carried out in an aluminium vessel instead of copper, since the latter acts in a catalytic manner, setting the mixture of resins before esterification can take place.

Jahn[55] has examined the properties of mixtures of rosin and beeswax, and found that under certain conditions solid solutions are formed, or mixtures in which the solid solution of rosin in wax is in equilibrium with pure wax. Changes taking place on storage of such mixtures are described. Gerstacker[56] has examined what he terms a "distilled rosin," the residue or product obtained by only partially breaking down rosin and volatilizing the oil formed. He gives the properties of the bodies obtained by heating the rosin at 310° to 320° C. and at 350° to 370° C. Strange to say, the latter product is the harder of the two. Neither is entirely soluble in a mixture of alcohol and chloroform.

Miscellaneous

Hübscher[57] describes a product obtained in Sweden as a by-product in the manufacture of chemical wood pulp, which is known as "tall-öl," or Swedish rosin oil or pine oil. The crude product is refined by distillation leaving a so-called "tall-öl pitch." Recipes for using the products are given.

Shippen and Griffen[58] have investigated the properties of emulsions made from pine oil and other oils obtained by the distillation of pine wood, with reference to their value as antiseptics and bactericides, along the line first pointed out by Stevenson.** They substantiate some of the earlier findings of Stevenson, notably that steam-distilled pine oil gives a more active disinfectant than the destructively distilled oils. They conclude, however, that disinfectants of this type have only a limited value, since they failed to kill *Micrococcus aureus* and *B. anthracis* in any dilution capable of emulsification. For killing *B. typhosus* in a limited time, a dilution of $^1/_{100}$, or 1 per cent, is recommended even though a $^1/_{500}$ dilution killed when in contact with the organism for a longer time.

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A Department Store Laboratory

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PERHAPS it is because the chemist has been such a poor salesman of his services, even though he is working in a productive field where he should be of great value to his employer, that so few department or retail stores have chemical laboratories of their own, or regularly seek the advice of a chemist as to the quality of the merchandise they buy. Nearly all such stores have college-trained mechanical or architectural engineers in charge of their engineering problems; all of them have specialized advertising men. Yet neither the mechanical features and attractiveness of the building and its contents nor the selling value of advertising is nearly so important as a reputation for handling *all the time* a dependable line of goods. Such a reputation depends upon the ability of the buying staff to judge merchandise; but "judging" as applied to materials is practically a matter of the "feel" of materials, a mixture of intuition and previous experience with other similar material which has given more or less satisfaction. When stocks are to be maintained steadily at certain standards, especially if this must be done by purchasing from several sources, these standards should be carefully defined in terms of measurable quantities, and deliveries of merchandise checked constantly to see that they meet the established standards. The merchant who really *knows* his goods are all wool, or all silk, fast to perspiration, and of a specified weight or strength, consults a chemist constantly. Unless facilities for testing are constantly and quickly available, it is a rare merchant who will not take his chances or accept the word of a salesman as to what he buys to sell to his customers. Yet his reputation as a dealer in reliable merchandise, the good will of his trade, is at stake on every sale he makes.

E. B. Millard

The writer has been for some years in charge of a chemical laboratory maintained in a department store as an aid to its buying staff in the selection of supplies for its own use and for sale to its customers. The testing facilities of the laboratory are available without charge to any buyer who wants them; the laboratory has no authority over any purchases on which it passes. It gives an opinion as to the percentage of wool or silk, based upon an analysis of a sample, or as to the fastness of a color, or the probable wear to be expected of a material of a given mechanical strength. The buyer may or may not be guided by this opinion. When goods of any kind are purchased from a sample, it is customary for the buyer to send a specimen of the material delivered to the laboratory, where comparative tests are made for him to see if the delivery is of the same grade as the sample. Checking of this kind has often eliminated material from stock which would not have given the service expected of it.

It should be understood by all chemists, as it is not now understood, that to the layman there is no such thing as an organic chemist, a physical chemist, or a biological chemist. He is a Chemist, and he should realize the compliment implied by the capital letter; he should be far more ready than he is now to say, "I will find out for you," and less ready to say, "That isn't in my line." A department store chemist must be in addition an informal microscopist, a physicist of a kind, something of a skilled questioner, a laundryman when need presents itself, and an ever-ready consultant of the chemical literature to find out what is wanted. More often than not the questions presented to him are vague, poorly put, or indefinite; many times they do not concern what a chemist would call chemistry at all. But the man who comes to a chemist with these questions has faith in his science or he wouldn't come with the question. If the chemist can answer the question, or partly answer it, or even appear to be answering it while the conversation brings out what the other fellow is trying to ask in the first place, he has made a friend for chemistry. If he laughs at the question, or rules it out of the field of chemistry because he is too lazy to look it up, he might better give up chemistry and turn to a trade which is content to limit itself to that which is already known.

On the day our laboratory was installed, a boy came up from the wash dresses department and asked the chemist, "Can you analyze this dress for fading?" Ask yourself as a chemist, what you would have told him? Would you have asked him to leave it for a while and tried to find out for him, or would you have ruled that problem out of chemistry? The laboratory had a wash pan, a bar of soap, and hot water; with such "apparatus" the chemist "analyzed" the dress, dried it on a piece of string, took it to the alteration room and had it pressed. The color was the same as before and the dress showed an average shrinkage of 2 or 3 per cent in the half dozen places where it had been measured before and and after. To the man who sent up the dress that was an *analysis*, but "the separation of a substance, by chemical processes, into its constituents" (Webster) would have been a catastrophe. A chemist must daily choose his words very carefully, on account of such differences as between chlorates, chlorides, chlorites, etc., but he should remember that a questioner of non-chemical training knows hardly more than that a chemist performs in his laboratory a variety of mysterious operations which the outsider doesn't hope to understand, but which he thinks of as "analysis."

The ordinary work of a department store laboratory consists largely of determinations of the wool or silk in materials, and especially the detection of artificial silks, together with tests of the fastness of dyed fabrics to perspiration, sunlight, washing or water spots. For such service it is of tremendous advantage to have the laboratory located within the store building and immediately accessible to all departments by telephone or messenger boy at all times.

Most of the tests requested of such a laboratory are "rush" tests, but the laboratory also controls the deliveries of supplies of many kinds. A daily determination of ash and moisture in the coal affords a valuable check upon the quality delivered; determination of the butter fat in the milk and cream is also effective in its own way. There is a certain pride in saying, "Our own laboratory reports so and so."

When new materials appear upon the market, or new names are attached to modifications of old materials, the store laboratory is available at once to determine the composition of these materials and their suitability for the purposes to which they are put. Salespeople are provided with this information, so that they may answer promptly the inquiry of a prospective purchaser as to whether an article is of one material or another. Such service is important to a store, even if it only serves to keep out of stock articles which are of attractive appearance, but which may not be properly dyed or properly finished for outdoor wear, or which are not well chosen for their particular class of service.

One of the most important activities of a store laboratory is in connection with adjustments of claims of unsatisfactory materials. These claims occasionally arise from the abuse of materials, often innocently, by the customer; more often they are to be traced to the wrong use of materials or dyes in the manufacture of the goods, or to the defective material being made into a garment together with good material. In service the faulty fabric soon fails or a fugitive dye spreads or comes off on other clothing. It is the aim of the laboratory to trace the fault to its proper source, as a protection for the good name of the house, and as a service to the customer. If the customer has used bleach in the colored wash, or used corrosive toilet preparations, or used stockings as a pen wiper, the laboratory saves the store an expensive adjustment claim; if the lining of a suit or coat fades or crocks off on white clothing, or an undergarment gives way on its first washing it is the laboratory's place to report the probable cause to the proper person within the store, who recommends that adjustment be arranged with the customer.

In common with almost every chemist who has tried his hand at textile matters of any kind, our laboratory has designed a wearing machine. Doubtless a mechanical engineer would not approve of the details of the design, but it has been our experience that of two pieces of similar material, the one which will wear longer on our machine will wear longer in service. The plan is very simple: a canvas belt is driven at a speed of about six feet a minute from a wide faced pulley to which a revolution counter is attached, and the specimens under test are stretched over canvas-covered weights placed on the moving canvas belt. After many comparative tests we have found that a good coat lining should not wear through before a certain number of revolutions on the driving wheel; one which wears out in half the standard number is a poor lining. Perhaps this is not chemistry, and it is not much of a test anyway. The buyer of linings will, however, be content to call this test an "analysis;" and if by doing this for him we can pick out the better linings from the poorer ones we have raised the general standard of linings in the store. It will be chemistry to him, and it is through his opinions and similar opinions from others that the laboratory is left unmolested on the roof from week to week while it does hundreds and hundreds of tests which anyone would call chemical work.

At the time our laboratory was installed, the chief executive of the store confided in the writer that he was not sure why they were having a laboratory, but they were willing to bear the expense of a small one for a year or two as an experiment to see if it would be of any benefit. Two or three items of a chemical program were outlined, but the main part of the list was left blank and for the future to develop. After four years the laboratory is handling over a thousand inquiries a month upon almost every activity of the store except the two or three in the original plan. Many of these are very informal, the kind of test one might make Saturday afternoon on a tiny piece of cloth clipped from the inside of a coat where it wouldn't show. An unspecified number of the rush tests (together with some of the more deliberate ones also, no doubt) have been incorrect, but the large majority of them have unquestionably been of benefit in the selection of materials about to be purchased, or in confirmation of the stock already on hand.

It seems probable to the writer that many retail stores will sooner or later find it to their advantage to maintain their own small laboratories, with simple equipment and two or three men, or a man and a boy, as a service to their staff and their customers. It will be many years in the experience of an active store laboratory before surprises are not of almost daily occurrence. The recent splendid improvements in the manufacture of artificial silks have made its distinction from real silk more and more difficult; the dyes used in most "novelty goods" will probably always require closer inspection than the stable colors in more common use; and the ever-increasing variety of finishing processes will unquestionably need some watching through chemical eyes.

A Metric Dozen

It has been observed that objection is being offered by many retail merchants against the metric system of packing. Contention is made that it is more convenient to buy "By the Dozen" than "By the Box of Ten" or "By the Carton." It is true that the carton does not specify any certain number, and equally true that long usage has made the dozen an easy term to think by, hence the reluctance to adopt any system that does away with such a convenient term. Those of us who would hasten the universal adoption of the metric system would undoubtedly further the cause a little by adopting some term as a standard to designate "a package containing ten articles"—a metric dozen.

The word "Dekon" is suggested as such a term. It is expressive, easily remembered, easily abbreviated as "Dk.," and if adopted and used by manufacturers now using the metric system of packing, and given notoriety through the press, would soon displace the "dozen" and score another point for "Metric," and others would no doubt soon see the wisdom of falling in line. "Methanol" was adopted almost over night, even by the laity. The Dekon could be made the standard small package, and ten Dekons, or a multiple thereof, depending upon the size of the article, a standard "case." The druggist could, with just as much ease, say "Send me down three dekons of helanthyol at once" as "three dozen" of the same article, and he would unconsciously be using the metric system. [*W. Carl Matthews*, Jacksonville, Fla.]

Commercial Methods of Making Carbon Black

In commercial practice there are four different processes of manufacturing carbon black from natural gas, states the Bureau of Mines in a recently issued bulletin. Classified according to the quantity of carbon black produced, these are: (1) Channel process; (2) small rotating disk process; (3) large-plate process; and (4) roller process. These methods differ mainly in the size and shape of the surface upon which the carbon is collected and the rate of travel of the moving devices. The channel process is probably the best method and is the one most extensively used. At present the production of carbon black by cracking or thermal decomposition methods is not extensive.

The French Senate has unanimously voted 2,000,000 francs for the observance of the hundredth anniversary of the birth of Louis Pasteur, this year. In voting the appropriation, Pasteur was described as the "symbol of French science."

Potash in America—Two Years' Progress

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Production

SUCH PROGRESS as we have to record is not in increased production. In 1915 our production was practically nothing; in 1918 it reached a maximum of 54,000 tons of K_2O; in 1919 it was 32,000; in 1920 it was 48,000; and in 1921 it amounted to about 8000 tons from less than 20 plants.

To-day, in July 1922 as I write this, only one commercial plant is in full operation making potash as a main product. This is the American Trona Corporation plant on Searles Lake in California. Incidentally, this company has probably spent more time and money on systematic and fundamental research and development work than any other, which may account for its being in operation.

John E. Teeple

The by-product plants in commercial operation include the molasses distilleries, of which the U. S. Industrial Chemical Company is probably the chief producer, the cement plants and blast furnaces, the Santa Cruz Portland Cement Company in the lead, and the sugar companies using the Steffens process. That is about the whole story of production in America to-day. Of the 128 plants reporting production in 1918, over 100 made nothing in 1921. Some few were abandoned as war babies that could not live in peace times, but many are simply standing by continuing the study of their problems and hoping for Congress to give them the temporary protection that will carry them over this distressing period and enable them to make a permanent potash industry here.

The year 1921 was the worst we expect to see in potash production. The outlook for 1922 is better. The American Trona plant alone, although it only recently reopened, should produce more in 1922 than all America did last year. It has already exceeded 50 tons of K_2O per day and in September, after some minor troubles are worked out and a third smaller unit is in operation, it should be going at a rate of 22,500 tons of K_2O per year, or over 60 tons of K_2O per day. This is equivalent to about the output of the three largest German mines, or 5 average-producing mines, or 15 to 20 small ones.

Possibilities

Mention should be made of some nonoperating plants which look promising. The Eastern potash plant to operate on New Jersey greensand has been in construction several years, represents a large amount of money, and is not yet finished. Little idea can be formed regarding its position in a permanent industry until it has an operating history back of it. The plant and the hopes of its owners have been repeatedly described.[1]

None of the plants in Nebraska are now operating commercially, but some of the companies are understood to have given careful thought to their problems in recent years. Their particular hope of success lies in recovering soda ash and other by-products. Cheap fuel is also a necessity here and an oil well is now being put down to furnish it. The Nebraska lakes have been fully described[2] and there is no doubt that they will play an important part in permanent production.

The alunite beds of Utah have been receiving a good deal of attention from both promoters and technical men. The manufacture of potash and alumina or aluminium salts from alunite is a perfectly feasible operation. When someone is willing to spend the time and money necessary to get systematic information and work out manufacturing details this should be a real part of our industry. If anyone has done this up to the present it has not become a matter of public knowledge. The prospectuses that happened to be presented to me so far have consisted of partial information and half-baked details. One large company seems to be making real progress.

The story of Wyoming leucite is much the same as that of alunite. Leucite is a proper source of potash, and one company seems to be making real headway in the solution of the problem.

The Inyo Chemical Company of Deep Springs Valley, Calif., has had a pilot plant working on a natural potash brine at that place. The method is refrigeration to remove sulfate, then concentration by evaporation. They announce that the experiments have been successful and that they are now constructing a 10-ton per day plant.[3] Other natural brines rich in potash could be worked if people would study them.

Texas potash deposits have received as much newspaper publicity as a prima donna. No doubt soluble potash is there but no one seems to know whether it exists in commercially workable quantities. There is no reason why it should not and we certainly hope it does. Under the method of taking samples with core drills outlined by the Bureau of Mines, future oil wells will serve as prospect holes for potash and in a short time we will know just what we have to expect from Texas.

Development Work

Something of the progress made by nonoperating companies has been previously mentioned. Of more interest, however, is the development of the ones who have already succeeded, who are now working. A typical statement of the problems encountered in a by-product potash plant and a successful solution of the difficulties is found in the description of the Santa Cruz Portland Cement Company's methods.[4] Given 35,000 cu. ft. of gas per min. at 750° C., containing five lbs. of K_2O and a lot of other material that you do not want,

[1] *Sci. American*, July 16, 1921; This Journal, **13** (1921), 693; *Chem. Met. Eng.*, **25** (1921), 1056.

[2] *Am. Fertilizer*, April 23, 1921.

[3] *Chem. Met. Eng.*, **26** (1922), 1034.

[4] *Ibid.*, **25** (1921), 316.

how would you recover the potash at a profit?[2] If you are interested, read the solution in their article.

The problems of a brine working plant, like that of the American Trona Corporation, were described last year.[5] Progress since that report has been good. Equilibrium study of the system sulfates, chlorides, and carbonates of sodium and potassium between 20° and 100° has been completed for our purpose. Other equilibrium studies have included borax, metaborate, carbonate, bicarbonate, and other combinations. Of some scientific interest is the discovery by Mr. W. E. Burke of still another double salt, $Na_2B_2O_4 \cdot 2NaCl \cdot 4H_2O$, to which he has temporarily given the euphonious name of "teepleite." Some practical applications of these studies have been: (1) An improvement in the grade of potash produced (for the last two months the product made has not in any week dropped below 95 per cent of KCl and several weeks has reached 98 per cent); (2) increase in the percentage of potash recovered; (3) simplified method of making borax; and (4) cheap and simple method of making boric acid.

Work on the other difficulties has been equally successful. Foaming in the evaporators has been entirely under control for a long time. The presence of borax as an impurity in potash has not been a problem for nearly three years, in spite of the fact that our friends, the recent enemy, are still talking about it. Dr. Whitney, Chief of the Bureau of Soils, recently issued another official statement on the high purity of American potash to counteract their propaganda, and agricultural experiment stations all over the country have been doing the same thing. It is amazing how many restatements of truth it takes to kill one lie.

Other improvements in evaporating, cooling, handling, and control have all reduced production costs. Much research work is under way, directed toward recovery of other valuable products from Searles Lake, and this is progressing favorably.

Cost and Market

Potash is one of the very few materials that is cheaper now than it was before the war—64 cents per unit to-day compared with an average of about 80 cents formerly. Converted to marks, this is about 330 marks to-day compared with 3.3 marks in normal times. The German workman used to receive 3.50 to 5 marks ($0.84 to $1.20) for a day's work. Now he receives 150 to 300 marks, say, 30 to 60 cents. In marks his wages have been multiplied by 50, while the price of potash has been multiplied by 100. In dollars he receives less than half what he did before, and works a whole day for what the American workman receives per hour. It takes on the average 12 to 15 days' work in Germany to produce 100 units or one ton of actual K_2O. This sells here at $64 and the labor cost for the 12 to 15 days' work is about $6 or $7. In America we would pay for that same amount of labor about $40. As a matter of fact, the labor spent to produce a ton of K_2O in America is less than four days in a good plant. We can turn out four times as much potash per man-day as they do, but we pay the man eight times the price the German receives. This is bound to continue so long as the value of the mark is falling faster than the price of German labor in marks is rising. There will always be a discrepancy because the American workman demands and we want him to have a higher standard of living than any other workman. This is why the industry needs temporary protection now. It will continue to need it until the production costs can be cut still lower. If we had a standard by which we could measure cost in terms of man-days, power, and steam on an even basis, America could probably sell at a profit to-day at any price that Germany could. But with the American man-day costing 8 to 10 times what the German one does we are calling for temporary help.

Propaganda

In a review of this kind it should not be necessary to discuss propaganda and possibly it ought not to be done, but it is necessary and is going to be done. Last fall we were deluged with a series of interviews from bankers, college professors, and business men. All agreed that there was no American potash industry, never had been, and never would be, and anyway American potash was bad and dangerous and God had given Germany good potash and plenty of it. It was almost sacrilegious to consider any potash but the German. For such a wide diversity of men, none of them directly connected with potash, there was an astonishing unanimity in ideas, and even in words and figures used. One could almost believe the interviews were mimeographed in one office. Then some interviews from fertilizer men complaining of the impurities in American potash, and specifying borax and salt. At that very time the nitrate of soda they were using often contained more borax than any American potash, and the German potash they used frequently contained more salt than it did potash. Again, about June first, we find advertisements in papers like the *Rural New Yorker* and the *Louisiana Planter* still harping on borax in potash, apparently in the hope of influencing some poor ignoramus who had not seen the repeated official government denials that harm could come from American potash more than from any other. These advertisements were signed "United States Soil and Crop Service, Potash Syndicate." This name looks harmless and patriotic but it is the official name of the Propaganda Office for North America of the German Kalisyndikat.

I would not bother you with this recitation except that it is a part of the struggle for existence that American potash has been making for the last two years, and an appreciable amount of time of technical men in the industry has been consumed in combating just that kind of stuff.

Many of us hoped that with the departure of the Kaiser from German affairs God and His Providence would no longer be restricted to Germany, but might be allowed to operate elsewhere. But not so! Within a month, two German business men assured me that Germany had a world monopoly on potash which could never be taken away. God had given it to her and she could starve or feed any part of the world she chose. This is of course hard on America. Who put the potash in the Nebraska and California lakes, the Utah marshes, the cement rock and the molasses, the greensand, alunite, and leucite? Are they not as natural as anything the other side of the Rhine? And are they not more accessible, being on the surface instead of far underground? German propaganda is meant for the unthinking and the unthinking often swallow it, particularly if it is signed with what looks like an American name.

The Future

The foregoing is a picture of the American potash industry during the last two years as I see it. To be a large industry that will protect Americans against future high-priced potash it needs some support and encouragement now. Some part of it will live whether it gets that support or not, but may be not enough to be a real protection. These plants cannot start operation again suddenly if they are allowed to die now. It takes time and money, and money does not lightly reënter an industry that has been allowed to fail from lack of public support at a critical time. We will have a large industry if we support it now, and a small one whether it is supported or not.

[5] This Journal, 13 (1921), 249.

The Fertilizer Industry

By Wm. H. Waggaman

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IN THE PURCHASE of no other commodity offered on the market to-day is the consumer more dependent upon chemistry to protect him against fraud than he is in the buying of fertilizer. Before the advent of state fertilizer control enormous tonnages of relatively valueless materials were sold at a high price on the basis of an attractive name, a rich brown color and a strong disagreeable odor, and even up to the present time certain brand names persist which give the impression that the product offered has peculiar properties or mysterious power rendering it particularly well adapted for giving bumper yields of special crops.

Chemical control was first inaugurated in this country by the Connecticut Experiment Station in 1876, and laws were passed requiring the fertilizer manufacturer to state on his containers the actual quantities of fertilizer ingredients present in his goods. The other experiment stations soon recognized the advantage of such regulations and chemical control is now in effect in almost every state, and the guaranteed composition of fertilizer mixtures are so constantly checked up in laboratories of the state chemists that it is practically impossible for an unprincipled manufacturer to perpetrate a flagrant fraud upon the consumer. Chemical control, therefore, has proved a boon both to the reputable manufacturer and his customer by forcing the dishonest dealer out of business and increasing the efficiency of factory and field practice. It has also educated the farmer so that he is more familiar with the actual value of the various fertilizer ingredients, and brands with alluring titles no longer have the same psychological effect as of old. He wants definite assurance and actual proof that "Excelsior" contains something more than excellent filler, that "Champion" has the substance to deliver a real punch in the field, and that "Black Giant" is backed up by something more substantial than an overpowering odor.

Up until the past few years, however, there was little tendency toward the use of high-analysis fertilizers, owing to two main causes: First, many farmers found it difficult to realize that bulk has little significance and that it was often poor economy to purchase a low-priced fertilizer; second, there were many low-grade materials which for a long time were considered suitable only for fertilizer purposes and though they had unquestionable value as soil amendments it was practically impossible to use them in large quantities for the manufacture of high-grade goods.

The Stimulus of War

Conditions, however, are now changing materially. The farmer has learned the significance of potash, nitrogen, and phosphoric acid, and realizes that more labor and expense are involved when he handles, hauls, and spreads fertilizers containing low percentages of these ingredients than when he uses smaller quantities of higher grade goods. The producer of low-grade organic ammoniates such as tankage, cottonseed meal, and rendered garbage, has also found that these materials are much more valuable and bring a higher price when put into stock food rather than into fertilizer, and so the withdrawal of large amounts of such products from the fertilizer market has caused the manufacturer to turn to other sources of nitrogen to make up this deficit.

It is a curious paradox, but perhaps a fortunate fact, that so many of the materials necessary in the manufacture of explosives and other instruments of destruction are equally important in the production of fertilizers, to which we must now look to help make up the deficit caused by the ravages of war. The world-wide conflict, either by draining our natural sources of fertilizer materials or by cutting off the supplies normally imported from abroad, stimulated chemical research on methods of producing potash, nitrogen compounds, and phosphoric acid as nothing else would or could. Therefore it may be said that while the recent advances in the production of fertilizers are largely due to chemistry, the rapidity of these advances we chiefly owe to war.

Potash Salts

Before the war the supplies of potash salts imported into this country from the enormous deposits in Stassfurt, Germany, were more than ample to meet our fertilizer requirements, and the price of these natural salts was so low that little encouragement was offered to develop methods of obtaining potash from domestic sources. Chemical processes for the production or recovery of potash from silicate rocks and organic materials were little known outside of the laboratory, and while patented processes for extracting this fertilizer ingredient from such sources existed the quantity thus produced was inconsiderable when compared to the enormous tonnage annually imported.

With the advent of war, however, conditions completely changed. Our chief source of potash was suddenly and completely shut off and the spectacular rise in the price of this material rendered it economically impossible to use more than the smallest quantities in mixed fertilizers. Even then the limited supplies on hand were soon exhausted and we were confronted with the possibility of a serious curtailment in our agricultural output.

Chemistry was called upon to help out in this real emergency and nearly every possible source of potash, both organic and inorganic, was given consideration and close study. The feverish energy expended in research was not long in bearing fruit. Substantial quantities of potash were extracted from the mineral alunite, of which we have large deposits in southern Utah. Improved processes for recovering this fertilizer ingredient from such organic sources as kelp and sugar-beet waste were devised. Chemical investigations established the fact that we possessed in our blast furnace and cement industries immense potential sources of soluble or available potash and the latter industry was soon contributing a considerable annual tonnage. Finally the recovery of potash from the brines of certain saline lakes in Nebraska and California was found to be economically feasible and when the armistice was signed a number of plants were turning out potash from this source.

Within four years an American potash industry was built up where none previously existed and in 1918 we turned out 50,000 tons of actual potassium oxide or about one-fifth of that normally consumed for agricultural purposes. While it is generally believed that this industry is not yet sufficiently firmly established to meet foreign competition unless it has a protective tariff, the potash producers claim that such pro-

tection will be needed for a limited time only or until they have perfected or increased the efficiency of their chemical processes.

Whether or not the United States continues to produce a large tonnage of potash is an open question, but we have learned that we have resources of this fertilizer ingredient and in case of emergency we know where and how to get it.

Nitrogen Carriers

The production or recovery of compounds of nitrogen by chemical processes is one of prime importance to the fertilizer industry. Throughout the war difficulty of obtaining adequate quantities of fixed nitrogen caused the allied nations considerable alarm. None of the large nations, with the possible exception of Germany, was producing sufficient amounts to meet its requirements and the imports of Chilean nitrate upon which they were so largely dependent were always threatened by the menace of the submarine. The withdrawal of much of our supply of organic ammoniates for stock feeding purposes had already placed an added strain on our normal output of nitrogen products, and this, coupled with the sudden demands of war, brought us face to face with the danger of a shortage for fertilizer purposes.

In order to enhance our own nitrogen output every effort was made to increase our production of ammonium sulfate by the replacement of the old "beehive" coke ovens with the by-product type, and so vigorous and successful were these efforts that within a period of two years our output of this product was pushed from 197,128 tons to 348,654 tons annually. Thus an almost criminal industrial waste which had been going on for many years was materially reduced. Nothing but the emergency of war could have brought about this rapid increase in the recovery of the by-products of bituminous coal.

But our own supply of nitrogen products was still far short of that required. Moreover, the importance of making ourselves independent of foreign sources gave an added stimulus to researches for the synthetic production of nitrogen compounds from the inexhaustible supply in the air. The cyanamide process was the only one of these methods which had been commercially successful in America and this was not in operation in the United States. The knowledge and advice of the foremost chemists and technologists in the country were sought, and no effort and expense spared to solve this problem so vital to the public safety. While these investigations are still being continued, much progress has been made, particularly on the Haber process, of manufacturing ammonia, and there is little doubt that within the next decade we will be producing synthetic nitrogen compounds at a price sufficiently low to compete with the natural nitrate deposits of South America and the ammonium sulfate obtained from our by-product coke and gas plants.

Phosphoric Acid and Phosphates

While chemical processes were used in the manufacture of phosphatic fertilizers long before they were employed in the production of either of the other two fertilizer ingredients, it was not until about the middle of the last century that we advanced beyond the application of natural sources of phosphoric acid.

In 1840 Liebig and Lawes proposed treating bones and phosphate rock with sulfuric acid in order to render the phosphate water-soluble and more quickly available to crops. So successful has this simple chemical process proved that it is now almost universally employed, and fully 50 per cent of the sulfuric acid produced in this country is used in the manufacture of acid phosphate.

Basic phosphatic slag was first produced in 1875, and while merely a by-product obtained in the manufacture of steel by the basic Bessemer process, it has been a very valuable supplement to acid phosphate. The discovery of basic slag was largely due to an intimate knowledge of the chemistry of iron and a close study of the nature and properties of its impurities.

When war was declared the demand for sulfuric acid so increased that we were hard pressed to produce sufficient quantities for both munitions and fertilizer purposes, and this led to the investigation of other methods of producing soluble and available phosphates. The indications are that at least one of these general processes is going to play an important part in future fertilizer practice. The pyrolytic method of producing phosphoric acid, wherein mixtures of phosphate rock, silica, and coke are heated at high temperatures and the phosphoric acid distilled off and collected, has already proved commercially successful, and though most of the acid thus produced is consumed in the manufacture of baking powder chemicals and other relatively high-priced phosphate products, this process has so many advantages over the sulfuric acid method where cheap power and fuel are available that there is little question it will eventually be widely employed in the production of phosphate fertilizers. By the use of this process many deposits of low-grade rock that are considered unfit for the manufacture of acid phosphate will be made available, and the "run of mine" phosphate can be used directly without the expense and losses entailed in the washing and screening processes now so extensively employed. Moreover, the fact that the pyrolytic process yields a concentrated product which can stand the cost of long shipments may make it possible to develop more quickly our immense reserves of phosphate rock in the far west that have as yet been exploited to only a limited extent because of their distance to the fertilizer market. The success of this method, however, depends on close chemical control, and a careful study of the reactions that take place between phosphate of lime, silica, iron, and aluminium at high temperatures under both reducing and oxidizing conditions.

Concentrated Fertilizers

The trend of the fertilizer industry to-day is toward the manufacture and use of more concentrated products. While increased freight rates and higher labor costs are partially responsible for this movement, a better understanding of the chemistry of fertilizers and the economies effected by the employment of new and improved processes are the main causes for our advance. Along with the direct manufacture of phosphoric acid and the synthetic production of ammonia must come the wider use of definite and relatively pure chemical compounds for fertilizer purposes, for these two fertilizer ingredients must be combined with a base and an acid, respectively, in order to handle, ship, and distribute them successfully. The practice in the past has been to partially neutralize phosphoric acid with lime and to fix ammonia with sulfuric acid in the form of ammonium sulfate, but such procedure appears foolishly extravagant when we consider that neither of these materials adds anything to the value of the product. The logical procedure is to combine the phosphoric acid with ammonia to form ammonium phosphate or with potash as potassium phosphate, and where both ammonia and nitric acid are produced combine them to form ammonium nitrate. In every case a salt is obtained wherein both the acid and the base contribute their share to the market value of the fertilizer.

It is recognized, of course, that great care must be exercised in distributing such concentrated fertilizer compounds in the field, and it may be necessary or advisable to dilute such products before they are actually applied to the soil, but this can be done near the point of consumption and the needless

expense of shipping inert or valueless material thus avoided.

While the manufacture of fertilizers has for many years shown a steady healthy growth, it is now rising from the plane of a big business conducted largely along "rule of thumb" lines to that of a true chemical industry founded upon sound scientific principles, which make for higher efficiency, greater economy, and better service to both the individual and the nation.

Developments in Nitrogen Fixation[1]

By J. M. Braham

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THE PROBLEM of cheaply obtaining nitrogen in forms suitably combined for use in agriculture, the industries, and in munitions is probably the most important one confronting the chemical industry at the present time. The dependence of the food supply of the world on combined nitrogen is well known; nitrogen compounds occupy an important place in the industries; and the very great importance of combined nitrogen from a military standpoint requires no explanation.

The use of the practically inexhaustible supply of free nitrogen in the atmosphere to supplement the inadequate natural sources of combined nitrogen is a development of the last twenty years. This relatively new industry of nitrogen fixation is undergoing rapid developments in many countries. In the present paper an attempt has been made to indicate the general lines of development, the progress and the present status of nitrogen fixation. In such a short article, however, only the most important developments can be considered.

Fixation Processes

Although a large number of processes for the fixation of nitrogen have been suggested and more or less thoroughly tried out, there are at the present time only three in successful commercial operation. These, in the order of their development, are the Arc, Cyanamide, and Direct Synthetic Ammonia (Haber). None of the other processes thus far suggested appear to give promise of commercial development in the very near future.

The Arc Process—The arc process is the oldest and in many respects the simplest, consisting essentially in passing air through a specially constructed electric furnace in which the union of nitrogen and oxygen is effected, and then absorbing the oxides of nitrogen in water. Important experiments in the early development of this process were performed by Bradley and Lovejoy at their plant at Niagara Falls in 1902–1904. The process was being developed at the same time in Norway by Birkeland and Eyde, and in 1903 they succeeded in starting the first successful industrial plant. No improvements of a fundamental nature have been made in this process since the early period of its operation. The changes that have been made from time to time have been largely limited to furnace design and operation, and the various present forms of the process differ only in these two respects.

The principal handicap of the process is the very large power requirement—about 67,000 k. w. h. per ton of nitrogen fixed. Its profitable operation is, therefore, limited to regions in which very cheap electric power, off-peak as well as continuous, is available. Another rather serious handicap is the low concentration of nitric oxide in the furnace gases, which results in high absorption and concentration costs.

Notwithstanding these difficulties, there are at present about twelve arc-process plants located in Norway, Switzerland, Austria, Germany, France, Italy, Canada, and the United States. Their combined maximum production capacity is, however, quite small, being approximately 36,000 metric tons per annum, which is only about 6 per cent of the world's total nitrogen fixation capacity. Norway, with her abundance of cheap water power, produces about 85 per cent of the total output of this process. The arc process plant of the American Nitrogen Products Company of Seattle is the only one in the United States. Its capacity is about 300 tons of fixed nitrogen per annum.

Although somewhat less than 2.5 per cent of the total energy input of the arc process is absorbed in nitric oxide formation, the possibility of drastic reductions in the power requirements by modifications, such as in furnace design, seems quite doubtful. It appears that the process in any of its present forms is essentially a thermal one, the main function of the electric discharge being to produce the very high temperatures that favor nitric oxide formation. From this viewpoint the thermal efficiency is probably much above 50 per cent, and hence the possibility of a large reduction in the power required seems doubtful. The possibility of finding conditions under which the actual energy input more nearly approaches the heat of nitric oxide formation is of course not precluded. Research on the nature of chemical reactions in other types of electric discharge, such as in the corona, may lead to the development of a much more efficient process. Such a process, however, would be of a very different nature from the present arc process.

In view of the exceedingly high-power requirements, the high cost of absorption and concentration of the product, and the fact that the process does not appear to offer possibilities of decided improvements, it seems improbable that the arc process in its present forms will continue to be an important factor in nitrogen fixation.

The Cyanamide Process—That nitrogen combines with calcium carbide, when heated to 1000° to 1100° C., to form calcium cyanamide, was discovered by Frank and Caro in Germany in the course of an investigation on the production of cyanides. Impetus was given to the development of this fixation process by the discovery that the crude product could either be used directly as a fertilizer or converted to ammonia simply by autoclaving.

The first commercial plant was operated in 1906, and following this the new industry grew rapidly. By 1913 there were about 15 plants with an estimated capacity of 300,000 metric tons of crude calcium cyanamide—or lime-nitrogen as it is frequently called—operating in nine countries. It underwent an enormous expansion during the war since it and the arc process were the only ones in operation outside of Germany. At the end of the war there were 35 cyanamide plants located in Germany, Austria, France, Scandinavia, Italy, Switzerland, Japan, Canada, and the United States. Their estimated total maximum production capacity at that time was 1,625,000 metric tons, corresponding to about 325,000 metric tons of nitrogen. Actual production to capacity was not reached, however, since a number of plants were just being completed when the war ended. It is understood that a number of these plants have since been dismantled. There is only one cyanamide plant in the United States. It is located at Muscle Shoals, Ala., and has a capacity of 40,000 tons of fixed nitrogen per annum.

The cyanamide process at the present time is in a comparatively high state of development, and therefore a decided reduction in the cost of fixed nitrogen by this process seems doubtful. In this connection it may be pointed out that since the cost of the raw materials, limestone, coke, and coal, are practically fixed, the possible economies in the process must come principally in the lowering of the energy requirements for carbide production

[1] For a complete discussion of the nitrogen problem, with particular reference to the United States, attention is called to a recently published 350-page report entitled "Report on the Fixation and Utilization of Nitrogen," prepared by the Nitrate Division, Ordnance Office, War Department, assisted by the Fixed Nitrogen Research Laboratory, Department of Agriculture, on which the present brief summary is largely based.

and in increasing the efficiency of nitrification. Approximately 15,000 k. w. h. are required to fix one ton of nitrogen by this process, and the efficiency of nitrification is about 85 per cent. The economies that might theoretically be achieved in carbide manufacture cannot be accurately estimated, owing to the present limited knowledge of the thermodynamics of carbide formation. From a rough calculation, however, it appears that the efficiency of the present-day carbide furnace is quite high, and hence a large reduction in the power cost of this process by improvements in carbide furnace practice seems improbable. No especially promising modifications of the cyanamide process have been suggested. A careful investigation into the thermodynamics and mechanism of carbide formation and nitrification, and the effect of various added materials on these reactions, might, however, lead to very important modifications of the process.

The greatest advantage which the cyanamide process possesses over the other fixation processes lies in the extremely wide variety of products obtainable. Thus, in addition to calcium cyanamide, there may be obtained by transformation processes ammonia, nitric acid (by ammonia oxidation), cyanides, hydrocyanic acid, cyanamide, dicyanodiamide, urea, guanylurea, guanidine, biguanide, etc., and the very numerous derivatives of these latter compounds which are becoming more and more important in the manufacture of munitions, dyes, and drugs. Many of these important compounds, such as nitroguanidine, for example, cannot be furnished in quantity by any other process. Although the use of calcium cyanamide as a fertilizer is limited, it seems, however, that a well-rounded nitrogen industry must of necessity make provision for the production of calcium cyanamide.

THE DIRECT SYNTHETIC AMMONIA PROCESS—The fixation of nitrogen by direct union with hydrogen to form ammonia is the newest commercially successful process, and is the one that offers the greatest possibilities for further development. The equilibrium in the ammonia-synthesis reaction is such that the conversion to ammonia is higher, the higher the pressure and the lower the temperature. The upper pressure limit in this process is conditioned largely by the mechanical problems of equipment strength and the compression of large volumes of the gas mixture. The lower temperature limit is conditioned by the reaction velocity. The use of pressures as high as 1000 atmospheres in this process is now being investigated and the present lower practicable limit of temperature even when using an active catalyst is around 500° C.

The early development of this process was due to Prof. Fritz Haber, in Germany, and it is only in that country that the process has yet been operated on an extensive scale. The first commercial plant commenced operation in 1913 after many years of experimentation. The process experienced an enormous development in that country during the war, the present estimated production capacity being 300,000 metric tons of nitrogen per annum. The low power requirements of the process as operated in Germany, about 4000 k. w. h. per ton of nitrogen fixed, is probably one of the principal reasons for this exceedingly large expansion when compared with that of the other processes.

There are at present four lines of development of the direct synthetic ammonia process, which differ principally in the pressure employed, although the manner of gas production and ammonia removal also varies somewhat. These are: the American (General Chemical Company) process, operating at 100 atmospheres; the original German (Haber) process, at 200 atmospheres; the Italian (Casale) process, at 300 to 600 atmospheres; the French (Claude) process, operating at 600 to 1000 atmospheres.

As to the present development of these four forms, the extensive production of fixed nitrogen in Germany by this process has already been mentioned, the Italian process is now operating on a small scale, and the French process is in a semicommercial stage of development. The American form of the process is the development of the General Chemical Company. In 1917, a synthetic ammonia plant of 8000 tons rated capacity was constructed for the United States Government at Sheffield, Ala., based on the General Chemical Company's designs. The plant, however, did not operate satisfactorily and was closed down in the early part of 1919. In August 1921, the Atmospheric Nitrogen Corporation (General Chemical Company and the Solvay Process Company) began the operation of the first unit of their synthetic ammonia plant at Syracuse, N. Y., with a daily capacity of about 10 tons of anhydrous ammonia. It is understood that it is operating very satisfactorily. The design of this plant is essentially the same as that of the Sheffield plant but embodies the modifications which the trial operation at the latter plant had shown to be necessary.

Aside from the mechanical difficulties presented in handling large volumes of gas at very high pressures and at temperatures of 450° to 600° C., the two principal problems in the synthetic ammonia process are the production and purification of hydrogen and the development of an active and robust catalyst. The importance of the first of these is seen from the fact that in the Bosch method of gas production—which is used in Germany and, in a somewhat modified form, in this country—about 20 per cent of the total manufacturing cost is in hydrogen manufacture and a further 50 per cent in purification before it is suitable for passage through the catalyst. The exceedingly large cost of purification is largely occasioned by the fact that catalysts suitable for operation on impure gas at moderately low temperatures have not thus far been developed. The great opportunities for development along these lines through research are therefore quite evident.

The use of electrolytic hydrogen, whereby the cost of gas purification would be greatly reduced, is now being considered. The advantage gained in this respect, however, would in most countries be largely offset by the cost of additional power required (a total of about 18,000 k. w. h. per ton of nitrogen fixed).

The utilization of the waste hydrogen obtained in the electrolytic manufacture of oxygen, caustic alkali, etc., by installing small synthetic ammonia plants has been suggested. Chances of developments in this direction appear quite promising, particularly along the lines of the Claude process.

It is seen from the foregoing that the direct synthetic ammonia process is being very actively developed at the present time, and therefore a large expansion of the nitrogen industry along this line seems quite certain. Catalyst research will undoubtedly play a very important part in this development.

FUTURE POSSIBILITIES OF NITROGEN FIXATION

The nitrogen fixation industry is to a certain extent now marking time, owing largely to the forced growth of the entire nitrogen-producing industry, including coke-oven ammonia, which was brought on by the war. Many of the war-built fixation plants are now unable to meet the competition by by-product ammonia and Chilean nitrate. Much is yet to be done, and much can be done, toward lowering nitrogen fixation costs. The problem is so large and so difficult, however, that many years may be required for its satisfactory solution.

While nitrogen fixation is undergoing but little expansion at present, there is a decided activity in many countries in nitrogen fixation research and development. The possibilities of fruitful research in nitrogen fixation and utilization are almost unlimited. Thus, research leading to further improvements in existing processes, the investigation of proposed but not fully tried-out processes, the discovery and development of entirely new processes, and studies on the transformation of nitrogen-containing compounds to render them suitable for the various needs in agriculture and the industries, presents most unusual opportunities. In view of the importance of the nitrogen problem and the vigorous manner in which it is now being attacked in many countries, the fixation of atmospheric nitrogen is certain to experience very important developments within the next decade.

Desulfurizing Coke

A study of the desulfurization of coke was begun July 1922, at the Experiment Station of the United States Bureau of Mines, Pittsburgh, Pa. This is a practical follow-up of the theoretical study of the oxidation of iron sulfate in the coke and the subsequent removal of the free sulfur formed by this oxidation. Literature on this subject is being reviewed. Many patents were taken out in the years 1850 to 1870 and few since. Roasting and steaming were favorite methods. In this connection, methods for converting sulfur in coke into the FeS form are being sought. A process based on such method would hold back sulfur that might ordinarily be evolved, then this sulfur could later be removed by oxidation together with much additional sulfur. It seems that Fe_3O_4 mixed with coal being coked decreases the sulfur in solid solution.

Progress in the Canning Industry in the Last Ten Years

By W. D. Bigelow

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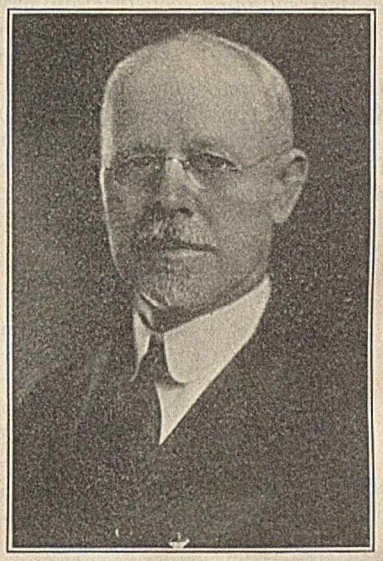
THERE are perhaps two distinguishing features of the canning industry of the present decade: First, coöperation of effort, and second, fundamental and systematic study of the principles on which the industry is based.

During this time the idea of trade secrets in technological operations has disappeared from most branches of the canning industry and technological questions are now discussed freely. This policy has resulted in a greatly improved product, and has made it possible to define within broad limits the information of the industry regarding technological processes and to point out more definitely than was heretofore possible the needs of the industry for improvement in those processes.



Harris and Ewing
W. D. Bigelow

Raw Products

It has become evident that canning is intimately connected with agriculture, and that its future success must depend in large manner on the success of growers in producing canning crops. Increased attention has been given to the development of varieties which yield abundantly and, at the same time, possess the characteristics most desired for the production of canned foods. The importance of planting seed that is true to type and which may yield an abundant harvest under satisfactory growing conditions is now generally appreciated.

Canning Machinery

The last decade has seen the perfection and general use of machines that had been relatively imperfect as well as the development of new machines for operations previously conducted by hand. As a result of the developments in canning machinery, it is now possible to handle many products almost entirely by machine, thus securing greater uniformity, reducing the cost of manufacture, and contributing largely to the sanitation of the canning plants. This improvement in canning machinery is general and applies to nearly all products packed. The following are mentioned merely as illustrations of the progress that has been made in this field:

Corn huskers have come into universal use, and cutters have been so developed that the corn is removed from the cob in a much more satisfactory manner than was formerly possible.

Blanchers have been so developed that they can be used more generally, and many products, such as pumpkins and beets, are now blanched in continuous machines.

Washing machines for preliminary cleansing of all manner of raw products have been brought to a high stage of perfection.

Filling machines for filling the raw product, such as peas and beans, into the cans, have been improved so that the cans may be filled more uniformly and with less mutilation of the product.

Automatic conveyors for the raw product, the empty cans and the filled cans have been highly developed, and greatly facilitate the transportation between different portions of the plant. This improvement in conveyors is advantageous in many ways. It cheapens the cost of production, hastens the operation of canning with a resulting increase in quality, and contributes largely to the general cleanliness of the plant.

Research Laboratory

As a result of the coöperative spirit already mentioned, the canning industry nine years ago established a research laboratory which might serve as a center for studying the fundamental principles of canning technology. In this laboratory it is possible to study the general problems of the industry more adequately than could be done in a laboratory maintained by a single interest. In addition to general problems, the laboratory receives many complaints and inquiries from individual canners, together with their observations regarding the same. Such communications are often accompanied by samples for inspection or analysis and are frequently followed by experimental work at the canning plant. Collaboration is also received from allied industries, and often with governmental agencies.

Tin Plate and Cans

During the last ten years we have really begun to understand the desiderata in tin plate intended for packers' cans. We have learned that increasing the weight of coating does not increase the amount of tin dissolved by certain foods, as was formerly believed by many to be the case. On the other hand, increasing the weight of coating does materially reduce the number of perforations and consequently the amount of loss experienced with certain fruits. A substantial beginning has also been made in the study of steel intended for the manufacture of tin plate.

During this time the sanitary can has been developed to such an extent that its use with vegetables processed at high temperatures has become practicable. As a result, the sanitary can has practically superseded the old hole-and-cap can, thus affording a package which not only reduces the cost of operation but enhances the quality of the product.

Processing of Canned Foods

The characteristic feature of canned foods is that they are placed in hermetically sealed cans and sterilized by heat.

The times and temperatures of processing were entirely a matter of experience, and it was only within the last five years that a systematic study of the fundamentals of processing was inaugurated. This investigation includes: First, the study of the penetration of heat to the center of cans of various kinds of foods; second, the hydrogen-ion concentration of canned foods and the influence of the canning process on the hydrogen-ion concentration of the product; third, the study of the thermal death point of resistant bacteria isolated from spoiled canned foods; and fourth, the correlation of the results of the three separate studies just mentioned and the calculation from the data afforded by those studies of the theoretical time necessary to sterilize various foods at any particular temperature. This theoretical process time is then available for guiding experimental packs of cans of various products inoculated with resistant bacteria. In

this way the processes of the canning industry are being studied and the results already obtained have been found of substantial value in guiding process temperatures and times.

Quality and Appearance of Canned Foods

The improvement in canning machinery previously commented upon has contributed to the improvement in the appearance of the product packed. The proportion of canned foods of high quality is materially higher than it was ten years ago. In many products the highest grade packed also shows a marked improvement, and there is a corresponding improvement in the lower grades. The increase in quality consists both in appearance and in flavor. It is the result of a general movement to bring the raw product to the canning plants in better condition and to handle it by more prompt and more efficient methods. In keeping with the increased quality is a pronounced tendency among canners to so label their product that consumers can have more accurate knowledge of the exact nature of the contents of the can. The improvement in this direction is not yet generally appreciated. Grades are hard to describe, and it is difficult to so word a label as to give the consumer all of the information which he should have. Systematic progress in this matter is being made, however, and various grades are gradually being defined so that a change in labeling will be possible.

Sanitation

In many of our foremost plants careful attention was always given to questions of sanitation. Many difficulties were encountered in such plants, however, because of the inherent sloppiness of many of the operations and the ineffective machinery and system of conveyors formerly available.

Improvements in these directions and in ideas of plant construction have greatly changed the sanitary condition of the best plants. In many plants a striking change of sanitary conditions has been made. The adoption of sanitary machinery and conveyors and the improvement in quality and appearance of the product have contributed to the general movement of improving the surroundings of the canning plant. This is especially evidenced by increased light and cleanliness within the plant itself and more efficient removal of waste products.

A Boom Needed

By H. W. Jordan

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The presidents of three great American universities in addressing their graduating classes struck a common note of warning which university men of the chemical and engineering industries will do well to heed. At Yale, President Angell urged that educated men lead public action against the prevailing swift current of lawlessness and selfishness. At Harvard, President Lowell deprecated the tendency to float with the crowd. He urged growth of the American pioneer spirit that has characterized us as a people creative of great achievements, both material and spiritual. President Hibben of Princeton said, "We are all aware of the fact that there is something wrong with the world. If you think that it is going to the devil, I rejoice in that belief, because I know that there naturally will arise the determination that you, for one, will do everything in your power to prevent it."

The close agreement of these intellectual leaders in their analysis of the idea which they considered most important to impress upon the minds of graduating seniors is no mere accident. Their joint conclusion that there is too much complaisant drifting with the crowd—too little creative thinking by university men as citizens—deserves serious consideration by everyone of scientific training. Clear appreciation of the close relation between the industrial processes of the chemist or engineer and the social economic situation is arising. Edwin Grant Conklin, Arthur Pound, James H. Robinson, Lothrop Stoddard and other far-sighted men of creative mind, who do not drift with the crowd, see that industrial stagnation, high cost of food and housing, coal strikes and the like are ultimate effects, and not primary causes. These thinkers throw the spotlight of science on the waste of energy spent in fighting effects—energy which should be used to discover and correct causes. They show the absurdity of trying to bring the millennium upon earth by means of the revised statutes. The most recent example of this triumph of hope over experience is the appeal to tinker the Constitution of the United States by an amendment permitting its amendment *ad infinitum* "to meet the needs of the people."

This sublime example of trying to balance oneself by the extended left arm with hand gripping the back of a kitchen chair supported by one leg on the top end of a thirty foot pole whose lower end rests on the chin of Congress impels one to rush for the net before gravity gets a start on the wabbly column.

Members of the American Chemical Society need to organize a salvage corps in behalf of engineering industry and of their individual selves for study and action upon the newly discovered relationship between modern, automatic machine industry and the social structure. "You, for one, need do everything in your power" to promote such biological, industrial research. Discussion of the writings of Professor Conklin and his associates—for example, of his article on the "Future of Evolution," in the July *Yale Review*—would be a stout boom thrown across the river of popular thoughtless clamor for national laws designed to regulate us from breakfast to bedtime; a boom behind which many millions of valuable mental, social timber would be impounded for constructive use.

Will you, "for one," help lay that boom?

Help Kazan

Many chemists are deeply interested in the plight of their colleagues abroad and have contributed generously to their relief. Here is a real opportunity to help where help is sorely needed, and through the American Relief Administration we know the utmost economy and efficiency are secured. Read this letter sent to a member of our Society.

Dear Sir:

I take the opportunity to send you my scientific works through the American Relief Administration which is affording now great help to the starving population in the Volga district.

The great war, the revolution, and the civil war in our country did not allow me to send you my works earlier.

Unfortunately the difficult economical situation in our country does not allow us to carry on our work regularly. We are now obliged to spend our physical and mental strength in searching ways of getting foodstuff for ourselves and our families.

We send you and all American chemists our friendly regards, and we beg you all to help the professors and assistants of chemistry of the Kazan University and of the Kazan Technological Institute by sending them food through the A. R. A.

I hope that our scientific works in chemistry, though modest, give us the moral right to send to all our American chemist friends this prayer. The relief received will give us the possibility to regain our physical and mental strength and to continue to work for the science.

Respectfully yours,
Alexander Arbusoff,
Professor of Organic Chemistry

Kazan University
East Russia
May 16, 1922

Recent Chemical and Technological Advances in Our Knowledge of Gelatin and Glue

By Robert Herman Bogue

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THE PAST few years have witnessed advances of a truly startling nature in almost every branch and subdivision of theoretical and applied chemistry, and the chemistry of gelatin has not lagged behind in this forward sweep. The gelatin ionogenic equilibria and their consequences have been studied from many angles[1-31,*] by Loeb, Smith, Sheppard, *et al.*, Kuhn, Miss Lloyd, Procter, *et al.*, Pauli, Davis, *et al.*, Fischer, Bancroft, Bogue, and others. Theories of the structure of gelatin, or of elastic gels in general, have been discussed by Bradford, Hatschek, Barratt, Miss Lloyd, Zsigmondy, Robertson, Fischer, Bancroft, McBain, *et al.*, Holmes, Sherrer, Loeb, and Bogue. Analytical data upon the composition have been accumulated by Dakin, and by Bogue. Still other aspects of the question have been presented by Alexander, Elliott and Sheppard, Thomas, Seymour-Jones, Mees, and others. Lastly, as an index of the awakened interest in gelatin and glue, books are in press or being prepared upon this subject by Sheppard, Alexander, Thiele, and Bogue.

R. H. Bogue

Ionogenic Equilibria

The work which stands above all others in this field is the very important series of investigations by Jacques Loeb.[1] His accomplishments appear to be two in number: First, the protein colloids, as gelatin, casein, egg albumen, etc., are shown to be amphoteric bodies whose general behavior is explainable by an application of the classical laws of electrolytic dissociation and valency; and, second, the special colloid behavior of these bodies and the degree of such action are shown to be determined by an application of the Donnan membrane potential law.

Gelatin is found to exist in three states: as non-ionogenic or isoelectric gelatin; as a metal gelatinate; and as a gelatin salt. At one definite hydrogen-ion concentration, namely, $10^{-4.7}$ N, or pH 4.7, gelatin can combine with neither anion nor cation and is un-ionized. At a pH greater than 4.7 it can combine only with cations forming a metal gelatinate, as sodium gelatinate, and at a pH less than 4.7 it can combine only with anions forming a gelatin salt, as gelatin chloride.

Loeb has more recently shown that the swelling, the viscosity, and the osmotic pressure effects produced by varying the ionogenic equilibrium may be adequately explained and predicted by an application of Donnan's membrane potential law.[32] By calculating from Nernst's formula for concentration cells at 24° C.,

$$\text{p. d.} = 0.059 \log \frac{C_1}{C_2},$$

where p. d. is the potential difference between the two solutions in which C_1 is the H-ion concentration inside the gelatin solution and C_2 the same in the outside solution (separated by a semipermeable membrane). By comparing the observed and the calculated p. d. from the measurements of pH in the two solutions, Loeb obtained very satisfactory concordance. Procter and Wilson[6] had previously made use of the Donnan equilibrium to explain the swelling of gelatin.

The viscosity of two-phase systems has been studied by Hatschek,[33] who calculated formulas to cover the two main conditions of loosely packed and closely packed systems. The viscosity of gelatin sols was studied by Bogue[11] and conformity with Hatschek's formulas could not be obtained. The value K which denoted the volume occupied by unit weight of the dispersed gelatin phase was found to rise to a maximum and thereafter decrease upon increasing the gelatin concentration. The increase was explained as due to increasing hydration, and the decrease to competition of the force of surface tension when the film separating the particles becomes very thin.

Swelling and gelation were investigated by Bogue[11] by the addition of increasing amounts of sodium hydroxide and several silicates of sodium, and by Davis, Oakes and Browne[8] by the addition of acids and alkalies. The pH of maximum viscosity was found to be at 3 to 3.5 on the acid side, and at 8 to 9 on the alkaline side. If the dibasic calcium salts are not washed out, however, the rise on the alkaline side is less marked. Davis, *et al.*, even failed to observe any rise at pH greater than 6.0.

Sheppard, *et al.*,[3] have investigated the effects which temperature, concentration, and H-ion concentration have upon the viscosity, jelly consistency, and melting point of gelatins. In this connection they have devised new apparatus for these measurements, which is more scientific than any before described. The jelly strength is measured by exerting a torque upon a cylinder of the jelly and noting the angle of twist at break, and the breaking load. The results obtained have shown a great disparity of uniformity. It seems that the only conclusion which may be drawn thus far is that the several gelatins used differed from each other in such a way that while each produced a typical curve, these bore no exact or parallel relation to each other, and the variations in elasticity were not a simple function of the concentration or the pH.

Theories of Structure

Differences of some importance continue with respect to the structure assumed to exist in gelatin gels and sols. Procter[6] pictures a compound of gelatin with an acid as a coherent mass from which the gelatin cannot diffuse or separate. The net structure is advocated by Robertson,[16] and a honeycomb or sponge structure by Bancroft.[10]

* Numbers in text refer to reference list at end of article.

Bradford[12] affirms the existence of a definitely crystalline structure in gelatin gels, claiming to have obtained gelatin crystals, but Scherrer[19] has found no trace of interference figures of the characteristic space lattice arrangement upon examining gelatin gels by means of the Röntgen photograph.

Fischer[9] continues to urge his hydration theory, in which he regards gelatin gel as a solution of solid hydrated gelatin in gelatin solution, or, if the solvent is limited, a reversal in type of system is indicated and there is produced solid hydrated gelatin holding within itself gelatin solution.

Miss Lloyd[5] has proposed that gelatin gel consists of a solid and a liquid phase, both of which are continuous. Gelation occurs only on the cooling of a sol which contains in solution isoelectric gelatin and gelatin salts in equilibrium with free electrolytes.

A catenary or filamentous structure for both gels and sols was urged by Bogue[20] in 1920 and again in 1922. According to this theory, gelatin sols appear to consist of slightly hydrated molecules united together into short threads resembling streptococci floating about in a dilute gelatin solution. A lengthening of these threads seems to take place as the temperature falls, and at the same time the water-absorbing powder of the gelatin increases. This accounts for the rapid increase in viscosity with drop in temperature. A solid jelly will result only when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity seems to depend on the relative amount of free solvent in the interstices of these aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is probably dependent upon the length and number of the catenary threads.

Loeb[1] has recently attempted to explain the differences in the behavior of different proteins upon treatment with water and electrolytes by an *occlusion theory*. The idea is advanced that proteins form true solutions in water which in some instances (*e. g.*, in gelatin sols) contain, side by side with isolated ions and molecules, submicroscopic solid particles capable of occluding water, the quantity of which is determined by an application of the Donnan equilibrium. Those substances which change this equilibrium in the direction of an increased number of solid particles at the expense of the molecularly dispersed particles will produce an increase in viscosity and a decrease in osmotic pressure, while the reverse holds equally true.

Chemical Constitution

An accurate determination of the amino-acid constitution of proteins has been unknown until very recently. Fischer, Levine and Anders[34] were able to recover only 42.1 per cent of the total nitrogen of gelatin in the amino acids by Fischer's esterification method, and Skraup and von Biehler[35] only 70.7 per cent. By an important modification of Fischer's method, Dakin[21] in 1920 recovered 91.31 per cent of the total nitrogen of gelatin in the amino acids.

By employing the Van Slyke method[36] for the separation of amino-acid groups, Bogue[22] has shown that the gelatins or glues obtained by long action of the water on the stock differ from the material that is first extracted by containing in the solution the hydrolysis products of proteins other than gelatin, as mucin, keratin, elastin, etc. These solutions, as well as the products obtained by the partial hydrolysis of pure gelatin, were shown to contain also increasing amounts of proteose, peptone, and amino acids. The first extractions are nearly pure solutions of the protein gelatin, but the last extractions contain larger amounts of proteose than protein, and these are derived to an increasing extent from non-collagen (non-gelatin) material.

Technology

The advances in the technology of gelatin and glue have not been so spectacular as in the more theoretical aspects. This is due partly to the disposition of manufacturers to keep secret such improvements as are discovered, and partly to the relatively small number of able colloid chemists who are directly interested in the technological phase of the problem. A number of patents have been taken out upon improved machinery for glue- or gelatin-making. The old method of drying by allowing the liquid to gel in pans, and then cutting the jelly with wires, has been largely replaced by more efficient processes. The Kind-Landesmann machine[37] permits the liquid to run onto a wide endless belt which conveys the liquid through a cool chamber where it gels, and on emerging at the opposite end is transferred to the frames of wire or cloth net for drying. Spray drying has been tried out with some success, and seems to be a highly desirable innovation, as the liquid is rapidly converted into a fine, dry, white powder. Steam-roller drying is used for some products. Improved machinery has also been devised for many other of the manufacturing operations. Continuous extracts for obtaining the gelatin from the stock are of special importance, as much higher grade material may be obtained.

A new system for the evaluation of glues and gelatins has been proposed by Bogue.[38] A method for evaluation that is based upon some fundamental property is needed very sorely, for the methods in common use are both incompetent for accurate differentiation, and the results are purely arbitrary and expressed in terms that mean little or nothing except to the salesman. The proposed system regards the undergraded gelatin content and (for glues) the maximum joint strength obtainable as the most fundamental properties. These are found to be parallel to the viscosity at a temperature near the melting point. The method consists in a measurement of the viscosity at 35° C. of an 18 per cent solution (moisture-free basis) by means of the MacMichael viscosimeter. The results are expressed in centipoises, and the designation of grade referred to this value.

But the forward movement has only begun. We are in an era of chemical progress in industry, and what advance has already been made is but the early glow of that which is later to become the full day.

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Progress on Emulsions

By Leon W. Parsons

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THIS ARTICLE indicates briefly several main channels through which progress is being made in studying emulsions. Several fairly complete summaries of the literature on emulsions are available, to which the reader is referred for details.[1] With emulsions, the "practice of the art," extensive although incompletely understood, is far ahead of the "science," a condition quite universal in applied colloid chemistry. For discussion, a rough division may be made into theoretical aspects and practical applications, subdividing the latter into, first, the formation of stable emulsions, and, second, the breaking of undesirable emulsions.

Theoretical Aspects

Nature of Phases Used—Frequently, the presence of various impurities in the nonaqueous phase has been unintentionally a major factor in determining the behavior of the resulting emulsions. On account of the complexity of these systems, the writer believes that steady progress will be made only by adopting a more "synthetic" program in studying emulsions, namely, using the purest liquids available for the two phases, and, after determining the characteristics in these supposedly simple systems, building up gradually more and more complex phases, determining the effect of the added substances and comparing the effects with the phenomena encountered in complex commercial systems. Bhatnagar has selected pure British Pharmacopeia paraffin oil for important studies on emulsion stability and in this laboratory Nujol, a highly refined mineral oil, has served very satisfactorily as a nonaqueous phase for studying mineral oil emulsions.

Nature and Function of Emulsifying Agent—This factor has influenced greatly various theories of emulsification. Emulsifying agents are either in true or colloidal solutions or are finely divided solids in suspension. Surface tension does not always play a major role. Briggs mentions several very good emulsifying agents which do not lower the surface tension. Holmes' work on gelatin indicates cases where viscosity rather than surface tension determines the stability. Fischer believes that the emulsifier must be a hydrated or solvated colloid combining with the continuous phase. Bancroft, in correlating earlier theories, states that emulsification is due to a solid or plastic film formed between the two phases by adsorption, the type of emulsion being determined by the wetting of the film by the two liquids, whichever wets the film more becoming the external phase. Data obtained by R. E. Wilson indicate that emulsifying agents form a film possessing the properties of a plastic solid rather than a viscous liquid.

Pickering's early work on finely divided solids as emulsifying agents in which is suggested the idea of relative wetting as a determining factor in influencing the type of emulsion has been continued recently by Briggs, who has shown conclusively the similarity between emulsions obtained with finely divided solids and with so-called soluble emulsifying agents, as soaps.

A new theory is proposed by R. T. A. Mees[2] to explain the emulsifying power of soaps by combining the theory of Harkins and Langmuir which deals with the orientation of soap molecules at interfaces and the previously mentioned hydration theory of Fischer.

Several abnormal effects of emulsifying agents have been observed. In this laboratory, it has been found recently that a solution of sodium oleate, after aging, can produce a water-in-oil (Nujol) emulsion, possibly because of the formation of an acid oleate by hydrolysis, a change in degree of hydration, or the formation of a plastic film in the solution. Similar water-in-oil emulsions are obtained with sodium oleate and stearate when ground in oil and shaken with water, but no such effect was noticed on grinding a polyvalent soap in water and subsequently shaking with oil. Ammonium oleate, a monovalent soap, is said to be capable of producing a water-in-oil emulsion.

In brief, there is urgent need for further work on the soaps and the finely divided solids to correlate their physical and chemical characteristics and their behavior when used as emulsifying agents. More definite data are needed on the quantitative determination of relative wetting, on changes which may accompany abnormal effects, and also on the changes in physical structure of soaps. Photomicrographic methods and the ultramicroscope should prove valuable laboratory tools.

Methods of Preparation—These consist fundamentally in breaking up into droplets what is to be the dispersed phase and then causing the emulsifying agent to go into the inter-

[1] Clayton, *J. Soc. Chem. Ind.*, **38** (1919), 113; Liesegang, *Z. deut. Öl- Fett-Ind.*, **40** (1920), 501; A. A. Thomas, This Journal, **12** (1920), 177; Bancroft, *J. Phys. Chem.*, **16** (1912), 177, 345, 475, 739; **17** (1913), 501; **19** (1915), 275, 513; **20** (1916), 1; Bancroft, "Book on Applied Chemistry," **1921**; "The Physics and Chemistry of Colloids," Report of Faraday Society, October 25, 1920, p. 17; Clayton's book on "Emulsions" being published.

[2] *Chem. Weekblad*, **19** (1922), 82.

face. The breaking up is accomplished mechanically and the emulsifying agent may be added either to the internal phase, may be suspended or dissolved in the continuous phase, or may be formed by chemical action at the interface. Briggs has shown that intermittent shaking is considerably more effective than continuous shaking. Clayton believes that shaking is an inferior method of making emulsions, since, as the emulsion becomes more perfect, the smashing action between heavy and light particles decreases, whereas it should increase. He suggests that according to Briggs it would appear that the ideal process of emulsification is one in which the dispersed phase is broken up as much as possible, while the continuous medium is left undisturbed as far as possible; and that continuous shaking might give equally as good results as intermittent, provided the emulsified portions of the mixture are continually removed from the mass so that the energy of shaking is concentrated on the remainder.

Method of Testing Phase Relationships—Both Briggs' drop method and Robertson's color indicator method have been criticized by Bhatnagar; the former, on account of the fact that a single drop may not always represent accurately the emulsion; the latter, on account of possible disturbance to equilibrium by introducing the oil-soluble dye. Bhatnagar has developed an electrical conductivity method for determining the type of emulsion which, it seems, may also be open to criticism because of disturbance of equilibrium. By careful microscopic inspection, aided by a microphotographic attachment, the writer has been able to utilize both the Briggs and the Robertson tests very satisfactorily. Care must be taken, however, to observe closely the internal phase.

Stability—Considerable experimental work is being conducted on the stability of various emulsions. This depends on a number of factors, such as the nature of the emulsifying agent, volume ratio, properties of nonaqueous phase, etc. In emulsions of two pure liquids, the factors affecting stability, such as viscosity, size of particle, difference in specific gravity, and electrical charge, will also influence the stability of emulsions with emulsifying agents, though their effects may not be predominant.

The inversion point evidently marks a region of instability and is of great importance from both a theoretical and a practical standpoint. Clowes and Bhatnagar have both studied this extensively. Similar studies on the effect of different variables on the inversion point have been conducted in this laboratory for Nujol-water systems.

There is a rich field for investigation in studying the action of various electrolytes on the properties of emulsions. Bhatnagar has extended the early work by Donnan, Ellis, Lewis, and Hatschek and has pointed out the resemblance between neutral oil emulsions and suspension colloids. He records a parallelism between the reversal of phases in emulsions and the precipitation of colloid sols in suspensions, and indicates the possibility of clearing up the mysteries of coagulation and of developing a rational theory of colloidal solutions and emulsification.

Practical Applications

Formation of Stable Emulsions—Many liquid emulsions are being developed. The U. S. Bureau of Entomology is studying oil emulsions for contact insecticides and is obtaining interesting results with a nicotine oleate emulsion. The scope of medicinal emulsions is enlarging greatly. The problem of preparing cutting or so-called soluble oils is being investigated by several oil companies, the chief difficulty being in the selection of the most suitable oil-soluble colloids. Attempts are being made to develop an emulsified light fuel for use in tractors.

Many solid or semisolid systems, involving emulsions, are of great commercial importance. Clayton has studied carefully the production of margarine, one of the most complex solid emulsions. By different mechanical treatments with the same material, either type of emulsion may be obtained and the problems in margarine manufacture offer an extremely fertile field for research. The emulsion chemistry of household products, such as mayonnaise, has undergone considerable development. A systematic study of lubricating greases (water-in-oil emulsions) is greatly needed. Various polishes and creams, including toilet preparations, offer great opportunities for development to the colloid chemist. Asphalt emulsions are finding extended use for paving purposes and for application to paper pulp in forming water-resistant stock. Emulsification of mineral oils in the cooking of rags for paper stock has been studied recently.

Some other systems involving emulsions which are being studied are: ready mixed paints; emulsified fats for leather; artificial leather; emulsions of japan in water; soap emulsions of fat solvents; rubber latex; and biological phenomena.

Breaking of the Emulsions—A beginning is just being made to study systematically the breaking of undesirable commercial emulsions, such as those encountered in refining wool fat and particularly in the petroleum industry. At the recent emulsification symposium of the Petroleum Section[3] the general nature of the problems involved was indicated. The systems are extremely complex and illustrate clearly the aforementioned need for more careful synthetic studies. The Bureau of Mines at its Oklahoma Station is starting an investigation of oil field emulsions. This laboratory is also conducting a fundamental investigation of commercial petroleum emulsions. The American Petroleum Institute has outlined a program for studying this problem.

In conclusion, it may be noted that there is great activity along both theoretical and practical lines on emulsion research. Considerable information is necessarily kept secret by various companies, but there is a keen desire to obtain accurate scientific data on emulsions and to apply such data to their particular problems. The need for coöperative research between universities and commercial laboratories is great and, with the rapid advances which have been made in colloidal chemistry during the past ten years, the results of such coöperative research should be extremely valuable.

[3] This Journal, 13 (1921), 1008.

Inventions by British Government Workers

A committee of representatives of British governmental departments and British scientific men has recently recommended a comprehensive scheme of dealing with inventions by government workers or by individuals aided or maintained from public funds. The committee recommends the organization of an interdepartmental patents board. Pending a decision in each case by this board, all rights in inventions made by government employees shall belong to the government. If the inventor can satisfy the board that he derived no assistance from the nature of his employment in making the invention, he shall be entitled to all rights therein. The question of whether the inventor is entitled to any reward in addition to the enjoyment of commercial rights shall be decided by the board. Where the rights in an invention capable of commercial exploitation belong to the government, the invention shall be exploited commercially for the benefit of the government. A system of awards and merits for the inventor is proposed, which should be passed upon by an awards committee, to be organized within the proposed patents board. These are not intended as substitutes for commercial profits, but as a recognition of merit and as an incentive to government workers.

Many people were overcome and $1,000,000 damage was done by a fire in the storage warehouse of the Manufacturers' Transit Co., New York City, July 18. Explosions of magnesium powder used largely in flashlights, were responsible for the blaze.

Vegetable Glue

By C. K. Reiman

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VEGETABLE glue may be defined as a homogeneous mixture of starch, water, and a solvent for amylocellulose such as caustic soda, having the appearance and many of the adhesive properties of animal glue. Cassava (tapioca) starch generally forms the basis of this material. The water content varies from 2 to 4 times the weight of the starch and the caustic is generally about 5 per cent and may vary between 2 and 12 per cent of the weight of the starch. The vegetable glues find their widest use in the veneering industry. They produce a joint as strong as animal glue. They are mixed hot but used cold and they will keep ready for use without deterioration for weeks. They do not have the waterproof qualities of casein, being about the same in this respect as the animal glues. Their chief disadvantage is the tendency of some of these glues to stain certain woods.

Clarence K. Reiman

Patent Controversy

The earliest reference to such a material concerns apparatin, a product patented nearly half a century ago (1874) by Gerard, a Frenchman. This material consisted of what is generally called a solution of starch in caustic and water. It was described as having excellent adhesive properties, and as being useful in the field of textile sizing and as an adhesive for various purposes.

Two others of the many patents dealing with such products deserve attention. In 1897 a patent was granted to Higgins describing an adhesive prepared from a starch that had been partially hydrolyzed by treatment with dilute acids. The various stages through which the starch progressed during this treatment were accurately described. The fact was pointed out that increased strength of joint was obtained by so treating the starch. In 1906 Gerson and Sasche were granted a patent in Germany covering a process for the partial hydrolysis of starch by means of an alkaline oxidizing agent, and the starch base so produced.

Since that time a large patent literature has been produced in various countries on this subject. To-day there are a number of important suits in progress in which the courts are endeavoring to determine to whom should be given the credit for the actual inventions declared in these many patents.

The reason for the court activity at the present time over these old patents is because of the considerable importance which vegetable glues have acquired in the woodworking industry. With the enormous growth in the production of plywood panels and veneered furniture, and with the generally rising price of animal glue the need of a cheaper adhesive for this purpose became more and more urgent.

The first vegetable glues made for this use consisted of raw starch, either potato or cassava, cooked with 8 or 10 per cent of caustic and 3 to 5 parts of water. A 3-ply or a 5-ply panel glued with this type of adhesive contained so much water that drying was difficult, and a large percentage of failures occurred owing to opening up of the glue joints. Animal glue used for this purpose was generally mixed with 2 parts of water. When the raw starch was used with 2 parts of water the resulting glue was altogether too thick to spread, either by hand or by the mechanical spreaders then used with animal glue. It was after this point had been appreciated that the various parties interested in introducing vegetable glue into the veneering field turned for assistance to the almost forgotten patents concerning the partial hydrolysis of starch. When a starch base was used, which had been previously hydrolyzed according to the methods of Higgins or Gerson and Sasche, a glue could be prepared with caustic using the same amount of water that was used with animal glue.

In 1912 the first of a series of patents in the vegetable glue field was granted to Perkins. This patent covered a large number of claims; some of which had to do with the processing of the starch by methods practically identical with those of the earlier patents; some of which dealt with the solution of the starch in caustic with three or less parts of water, the patentability of which has been widely questioned; and other claims which covered the combination of these two steps. In the only case that has come to the Court of Appeals the Perkins patent has been upheld in part, that is, it was declared that neither step alone was patentable but that a combination of the two was.

At the present time there are several large manufacturers of these vegetable glues supplying the plywood and veneering industries. Many of the users of these glues are to-day defendants in suits brought by Perkins. A number of these glue manufacturers and certain organizations composed of the users of these glues have banded together in the defense of these suits. As the outcome is uncertain, both sides are interested in forcing a decision in the near future which will at least serve to clear the air of the large amount of dust at present obscuring activities in these fields.

Current Practice

It is interesting to note that to-day current practice is drifting away from the type of glue described in the Perkins patents. Several of the glue manufacturers have discovered that it is unnecessary to process their starch with dilute acid solutions or alkaline oxidizing agents in order to make a workable glue when mixed with caustic and 2 or $2^1/_2$ parts of water. In practice, if the raw starch is properly cooked with the caustic a workable glue will result. In fact, some of the important developments of recent date have been in the opposite direction from that indicated by Perkins. It has been found possible to so adjust the gel properties of the starch by the addition of certain colloidal materials, that a product as strong as animal glue is obtained when 4 parts or more of water are added to the starch and caustic. It is

obvious that greater economy is obtainable when a glue kettle containing 500 lbs. of mixed glue is prepared with 100 lbs. of starch than when 200 lbs. are required. In fact, the spread obtainable with the glues of the older type containing 2 or $2^1/_2$ parts of water averages between 45 and 55 sq. ft. of glue line per lb. of dry glue. With the 4 : 1 glues to which certain colloidal materials have been added this spread is easily doubled. Thus, it becomes apparent that the amount of water to be dried from a panel glued with a 4 : 1 glue varies but little with that to be dried from one glued with a 2 or $2^1/_4$: 1 glue, since with the former the same amount of starch spreads twice as many panels.

Extent of Industry

The extent of the vegetable glue industry is apparent when it is appreciated that there is an annual market in this field for 20 or 30 million lbs. of starch in this country alone. There are about 1000 concerns using vegetable glues in the manufacture of standard panels, box-shooks, and furniture. There are perhaps a dozen concerns producing these various vegetable glues. The price to the consumer of these vegetable glues is between 6 and 9 cents per lb. A fair price for animal glues for the same purpose to-day is between 13 and 20 cents, and in the past has been even higher. Thus, there is a saving of at least one-half the glue bill when ordinary 2 : 1 vegetable glue is substituted for animal glue and this figure can be reduced further by employing the 4 : 1 glues recently developed.

It should be pointed out there are many varieties and grades of starch, and that not all of them are of equal value in producing a vegetable glue. Moreover, there is a wide variation in most of these grades of raw starch, which makes it a precarious venture for a plywood manufacturer to buy raw starch on the open market and turn this material into a veneer glue. Unless he has a chemist familiar with starches and vegetable glues and capable of maintaining a uniform product, the few cents per pound saved on materials cost will be far overbalanced by the losses from poorly glued stock.

Colloid Chemistry

By Jerome Alexander

Ex-Chairman, Committee on Colloids, National Research Council, New York, N. Y.

THE GROWING realization of the importance of colloid chemistry and its practical applications is evidenced by the fact that whereas the Decennial Index of *Chemical Abstracts* (1907–1916) contains a little over 12 columns of titles indexed directly under colloids, the 1921 index alone contains over 3 columns. In both cases no note has been taken of a large number of titles of papers dealing with colloid-chemical questions, but indexed under a wide variety of other heads.

The *Kolloid Zeitschrift*, which appeared initially in 1906, is now in its 30th volume, and 14 volumes of monographs have been issued in *Kolloidchemische Beihefte*. Since its organization the National Research Council has had its Committee on Colloids, and the British Association for the Advancement of Science has considered the subject of such importance, that since 1917 it has issued three "Reports on Colloid Chemistry and Its General and Industrial Applications." Each report contains a series of separate papers; a fourth report is in press, and a fifth is in preparation. A few years ago the Chemical Society of London and the Faraday Society held a special joint symposium on colloid chemistry which was attended by quite a number of prominent continental chemists, and though the papers read were published in several journals, they were deemed of such importance that they were printed separately, together with some older inaccessible work.

Many universities and colleges here and abroad are giving separate courses in colloid chemistry, and no course in theoretical or technical chemistry is complete without giving it due consideration. Analysts, biologists, and physicians must take note of it. In almost every branch of chemistry and technology, workers of unquestioned reputation and ability are producing striking results. Why is it, then, that there are still some who shrink from recognizing colloid chemistry as a distinct zone in the wide field of chemical and physical science, and cling to the idea that colloid chemical facts must be explained upon the basis of "simple chemical principles?"

Just criticism has been leveled at some who fail to give due weight to purely chemical considerations, or who think that a problem may be dismissed with the mere statement that it is "colloidal." But the main cause of the tendency referred to is an attempt to stretch the original and long-established meaning of the term "chemical" to cover all cases where attractive forces result in combination. Thus S. H. C. Briggs[1] goes so far as to consider as "chemical" the forces which hold atomic kernels and electrons together to form elements. If, with Langmuir, we call all residual electronic forces "chemical," then adsorption compounds are chemical compounds. Atoms or molecules without a residual field of force would form a perfect gas, but even helium does not meet this criterion. Elemental atoms and all molecules are anisotropic or polar, and after the satisfaction of what have been heretofore regarded as the normal chemical valences, there remain powerful residual or stray fields of electronic force which are responsible for what we ordinarily term the physical properties of the substance—its hardness, melting point, boiling point, solubility, viscosity, etc.

Champlain Studios, N. Y.
Jerome Alexander

[1] *Phil. Mag.*, **42** (1921), 448.

POLITECHNIKI ŚLĄSKIEJ

Much difficulty would be avoided if we adopt the classification suggested by P. E. Wells:

1—Electronic forces—those which bind electrons together into atoms.
2—Atomic forces—those which bind atoms together into molecules.
3—Molecular forces—those which bind molecules together into masses.
4—Molar forces—those which affect masses, *i. e.*, gravitation.

There is no sharp demarcation between 2 and 3, and the forces involved in colloid phenomena bridge the gap.[2] So after the novice is taught to distinguish between physical mixtures and chemical compounds, he must gradually learn that no sharp distinction exists.

Without in any way attempting to give a complete or even a critical selection from the wide field, there are here briefly mentioned a few colloid subjects of theoretical interest, followed by a number of instances where recent developments in colloid chemistry have been applied to technical problems:

Theoretical

1—It seems probable that changes in sensitive bio-colloids constitute one important mechanism whereby evolution proceeds.
2—It has been shown that adsorbed ions are necessary to the formation of stable colloidal solutions and jellies.
3—Nephelometers have been developed and applied to many quantitative determinations.
4—With the MacMichael viscosimeter the viscosity of colloids may now be expressed in absolute or c. g. s. units.
5—The size of colloidal particles has been checked with the aid of an oscillating electric field.
6—Much work has been done on fogs, smokes, and adsorbents.
7—Much work has been done on catalysis, its acceleration and inhibition.
8—M. H. Fischer and Wo. Ostwald, among others, have shown the importance of the state of swelling, or solvation in colloids.
9—After showing the importance of H-ion concentration in protein solutions, J. Loeb applied the Donnan theory of membrane equilibria as developed by Procter and Wilson, and worked out a mathematical and quantitative theory of the colloidal behavior of proteins.
10—McBain has developed the idea of colloidal electrolytes, *i. e.*, salts in which one of the ions is replaced by a heavily charged hydrated ionic micelle (a colloidal particle of great conductivity).
11—Many biological reactions have been explained on the basis of colloid chemistry,—*i. e.*, clotting of blood, coagulation of milk, Wassermann reaction, anaphylaxis, etc.
12—Ultrafiltration and ultracentrifugation have been developed.
13—Ultramicroscopy has made rapid strides.
14—Swelling and shrinking of colloids have received wide attention from an experimental and from a theoretical standpoint.
15—The making and breaking of emulsions as well as their reversal of phase have been much studied.
16—Many applications of colloid chemistry to chemical analysis have been noted.

Technical Applications

1. Flotation—Over 60,000,000 tons of ore are treated annually. Adsorption, surface tension, and flocculation are important factors here, and because of the great commercial interests involved, much work has been done on the theoretical and practical sides of flotation problems.

2. Colloidal Adsorbents (silica-gel, specially prepared carbons, fuller's earth)—The importance of proper carbon for gas masks was proved during the war. Patrick's silica-gel is largely used to recover casinghead gasoline, and petroleum distillates are purified by various adsorbents. Zerban reports that impurities in cane-sugar juice are largely colloidal and mainly removable by adsorption,—*i. e.*, with 0.5 per cent Filtercel and 1 per cent Norit.

3. Colloid Mills—These are essentially high-speed disintegrators arranged for wet grinding. A protective colloid is usually added to the water or other fluid used, to prevent re-aggregation of colloidal particles originally formed. The mill is said to find application in the following industries: soap, viscose, cellulose, oil, rubber, sugar, and glue. Products of special properties are without doubt produced, but until definite information is had as to output, cost of power and repairs, judgment as to the commercial status of the mill must be suspended.

4. Ultracentrifuges (and ultrafilters) have been applied to the clarification of many fluids,—*i. e.*, varnishes, wool-scouring liquors (with recovery of wool grease), gelatin.

5. Water-Purification and Sewage Disposal—The *Journal of the American Water Works Association* shows many extensions in this field. New sand filters do not function properly until a bacterial gel or slime forms on their surfaces. The same applies to sewage filters.

6. Tanning—Much valuable work has been done by H. R. Procter and J. A. Wilson, who have applied Donnan's theory of membrane equilibria, which for some time lay buried in the *Zeitschrift für Elektrochem.*

7. Lubrication—W. B. Hardy showed that powerful adsorption at the interfaces involved is an essential in lubrication. Southcombe and Wells patented the addition of a small amount of free fatty acid (about 1 per cent) to petroleum oils. This lowers the interfacial tension between oil and metal. The surface tension between oil and graphite is less than between oil and metal; hence graphitizing aids lubrication.

8. Colloidal Fuel—This consists of finely powdered coal, tar, etc., dispersed in fuel oil with the aid of a protector (usually a lime soap). Most of the dispersed material is far above colloidal dimensions, so the fuel has a "life" limit that may extend to months, after which it may be "revivified" by agitation. It should economize fuel oil and use up culm and other wastes.

9. Metallurgy—Properties of metals and alloys are dependent upon fineness of grain, and this may be partially within the colloidal zone. Scherer showed that even amicroscopic particles of colloidal gold consist of crystals, but that with colloidal silica and stannic acid crystalline and haphazard or amorphous groups of molecules may coexist.

10. Petroleum—The viscosity of oils depends upon their previous history, probably because of variations in the degree of dispersion of waxy bodies present. The breaking of emulsions in refining and their formation in lubrication are colloidal problems.

11. Clay—The use of deflocculators in purifying and casting clays has been largely developed.

12. Agriculture—Colloid problems in soils and fertilizers are being widely investigated. A small amount of "ultra-clay" produces a powerful effect on a soil.

13. Insecticides,—*i. e.*, lead arsenate, are more efficient and stick better when in colloidal state. Minute quantities are sufficient to kill insects, and it is wasteful to supply more than the necessary dose.

14. "Firefoam," used in blanketing fires, is a carbon dioxide froth made by mixing solutions of alum and sodium bicarbonate. A protective colloid, such as glue, dextrin, or saponin, is used to stabilize the finely dispersed foam.

15. Rubber—The importance of the state of subdivision of "fillers" is recognized. Much work has been done on vulcanization, and on the coagulation of latex. Glue is now worked into rubber tires on a large scale, and is said to improve their life.

16. Baking and Bread-Making—The swelling and viscosity of glutens are being investigated, also the prevention of "staling" by milk, fat, etc. The effect of traces of salts on flour is important.

17. Varnishes, Paints and Pigments—Work has been done on thickened oils (linseed and china wood oil), resins and synthetic resins (bakelite), and varnishes. The degree of subdivision of pigments in paints, and their maintenance in dispersion and suspension are important factors in paints.

18. Milk and Milk Products—Ice cream is improved, stabilized, and made more digestible by protective colloids (gelatin, eggs, etc.). Homogenized milk and cream having increased viscosity are largely used, and artificial milks are made. Protective colloids are used in preparing margarines. Little work has been published in regard to cheese.

Besides translations and new editions, increasing numbers of books are appearing originally in English. Laboratory manuals have been issued by E. Hatschek and by H. N. Holmes. In 1921 W. D. Bancroft published in This Journal a list of 200 research problems in colloids, which list was issued separately by the National Research Council.

In looking up indexes for references, it must be borne in mind that many papers and books of interest to the colloid chemist are not indexed under "colloid." Such headings as

[2] In fact many, among them Faraday, have expressed the view that there is only one ultimate kind of force.

gel, sol, hydrosol, jelly, emulsion, coagulation, etc., should be consulted, and many papers, especially those listed in *Chemical Abstracts* under General and Physical Chemistry, and Biological Chemistry, contain colloid chemical work. Thus W. E. S. Turner's book on "Molecular Association" (p. 99) has the following pertinent statement:

The formula of a substance shall be recognized as a function of the physical conditions under which it exists, so that the formula for elements is X_n, for compounds $(XY)_n$, where n is to be specified according to the conditions. Although we are far from realizing how n varies for most substances, the adoption of such formulas would bring home clearly the fact that both the physical and the chemical behavior of the substance may be closely dependent on the value of n.

The Chemistry of Intermediates

By M. L. Crossley

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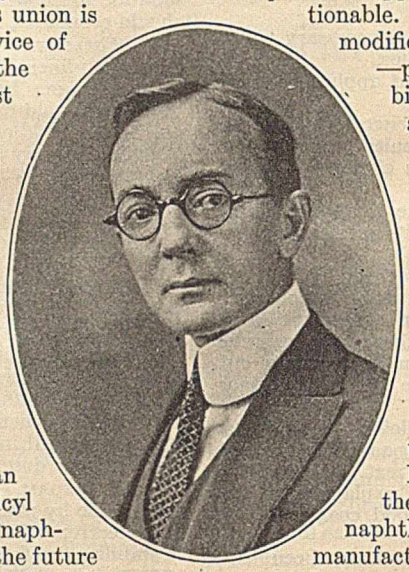
THE PERIOD under review is particularly marked by the successful application of sound physicochemical principles to the solution of the complex problems involved in the manufacture of organic compounds. More than ever before, it has been demonstrated that physics and chemistry are indissolubly linked and that in this union is great potential power for use in the service of humanity. Much of the progress made in the chemistry of intermediates during the past few years has been due to the combined efforts of organic and physical chemists. The catalyst has been the key to unlock many molecules and thus permit reactions not otherwise realizable. Our knowledge of surface phenomena is rapidly leading to a better understanding of the mechanism of chemical reactions.



M. L. Crossley

In one other respect the past few years in the chemistry of intermediates have been noteworthy, that is, in the ever-increasing evidence of the interdependence of dye intermediates and pharmaceutical products. Salicylic acid has given us an excellent nontoxic local anesthetic—salicyl alcohol, and some complex carbamide of the naphthalene series involving H acid is probably the future remedy for sleeping sickness. Although the constitution of "Bayer 205"[1] is not disclosed, it is thought to be one of the several carbamides or closely related substances on which so much research activity centered in Germany during the years 1914–1916.

Progress has been diversified. In a few instances the results have led to the production and utilization of new compounds, while in the majority of cases the achievements have not been epoch-making but rather the necessary improvements to make already existing processes adaptable to modern economic conditions or the development of new processes for old products.

Carboxylic Acids

Both catalytic and electrolytic processes have been developed for the manufacture of carboxylic acids. At the present time the catalytic processes appear to be more economical and practical. Acetic acid[2] is obtained by the catalytic oxidation of acetaldehyde and benzoic acid[3] by both catalytic and electrolytic oxidation of toluene. Many substances have been tried as catalysts in the air oxidation of toluene and naphthalene, and vanadium pentoxide has been chosen, in most cases, as the most suitable for the purpose. It has been shown that a high-grade benzoic acid can be obtained by fusing benzene sodium sulfonate with sodium cyanide.[4] The practical application of this process is, however, questionable. Benzoic acid has also been made by a modification of the Friedel and Crafts reaction[5]—passing phosgene into benzene and carbon bisulfide at a low temperature, then adding aluminium chloride and subsequently hydrolyzing to benzoic acid and recovering the carbon bisulfide. If carbon bisulfide is not used, benzophenone is the main product of the reaction. The benzophenone is converted into benzoic acid by fusing with caustic. This process for benzoic acid is interesting but it does not seem capable of ultimately competing with the catalytic process. It should be of great importance as a process for the manufacture of benzophenone when this product is required as a dye intermediate.

Intensive and well-executed researches on the catalytic air oxidation of benzene and naphthalene have resulted in processes for the manufacture of maleic[6] and fumaric acids from benzene and phthalic acid[7] from naphthalene. It is difficult at this time to correctly evaluate the contribution that these discoveries will make to the economic development of our time, but it is safe to say that they appear to be the most important contribution to the progress of the synthetic organic chemical industry made during this period. With cheap maleic and fumaric acids available new industries will arise. Fumaric acid may yet be the initial raw material for the synthesis of indigo.[8] Cheap phthalic anhydride makes possible synthetic anthraquinone, and this means unhampered progress in the development of the anthraquinone dyes, particularly indanthrene and other vat dyes. Phthalic anhydride will become of increasing importance in the manufacture of intermediates. A new intermediate[9] for azo dyes is prepared by combining phthalic anhydride with 1,7-aminonaphthol.

Sulfonic Acids

Sulfonation has received considerable attention of late. A continuous process,[10] introducing the sulfuric acid and the

[1] "Annual Reports of the Progress of Chemistry for 1921," *Chem. Soc.*, **18** (1921), 187.

[2] Ger. Patent 299,782.

[3] *J. Soc. Chem. Ind.*, **40** (1921), 307R.

[4] *Chem. Met. Eng.*, **24** (1921), 638, 697.

[5] This Journal, **14** (1922), 406.

[6] U. S. Patents 1,318,632, 1,318,633, 1,377,534.

[7] This Journal, **14** (1922), 120; Brit. Patents 164,785, 145,071.

[8] *J. Am. Chem. Soc.*, **44** (1922), 216.

[9] Brit. Patent 145,057.

[10] Brit. Patent 147,967.

hydrocarbon through atomizers into the upper portion of a steam-jacketed tower provided with a condenser, permits the reacting mass to flow down the tower over baffled plates, thus completing the reaction. The product is drawn off at the bottom of the tower and any condensed hydrocarbon returned to the charging apparatus. It has been found that certain catalysts enhance sulfonation and in some cases affect the orientation of the sulfonic group.[11] Benzoic acid, when sulfonated in the presence of a small quantity of iodine, gives the *o*-sulfonic acid.[12] A small quantity of anhydrous sodium sulfate and vanadium pentoxide used as a catalyst in the sulfonation of benzene doubles the amount of benzene sulfonated per minute.[13] By the use of a small quantity of iodine[14] as a catalyst certain sulfonations are made possible with weaker sulfuric acid than would otherwise be required. The time of sulfonation is also shortened. This catalyst is particularly suitable for sulfonations of benzene compounds containing substituents such as OH, NH_2, COOH or halogen, but works with difficulty or not at all with compounds of the benzene series containing SO_3H or NO_2 groups. Other catalysts[15] have been studied and in certain cases found to have marked influence on both the quality and the yield of the sulfonated product.

Certain definite progress has been made in bringing about difficult sulfonations. The problem of finding a satisfactory method for the preparation of chlorobenzene-disulfonic acid has been solved by sulfonating *p*-chlorobenzenesulfonyl chloride[16] with monohydrate at 160° to 180° C. The yield is said to be quantitative. The resulting product is 4-chlorobenzene-1,3-disulfonic acid. Again it has been shown definitely that the product obtained by the sulfonation of metanilic acid is the 3,6-disulfonic acid[17] of aniline. Sulfanilic acid when heated with a mixture of sulfuric acid and phosphoric oxide at 180° C. for eight hours gives aniline-2,4,6-trisulfonic acid. The yield is poor and the process needs further refinement.[18]

Aldehydes

Considerable progress has been made in the preparation of aldehydes on an industrial scale. Acetaldehyde has been made in large quantities from acetylene. Where cheap power is available this should be a practical process for the manufacture of acetaldehyde and its derivatives, particularly acetic acid. Cheap acetic acid is indispensable to the development of the cellulose acetate industry. Benzaldehyde is obtained by catalytic air oxidation[19] of toluene and salicylaldehyde[20] by oxidizing *o*-cresol in the vapor phase with air or a suitable gas containing oxygen in the presence of a metallic oxide which serves as a catalyst. Electrolytic processes have also been developed for benzaldehyde but it is still uncertain whether they are practical. A very interesting catalytic process for hydroxyaldehydes consists in treating phenol or derivatives of phenol with formaldehyde in the presence of nitroso compounds. Vanillin is prepared by treating guaiacol[21] with formaldehyde in the presence of *p*-nitrosodimethylaniline.

Amines

The progress in catalytic reduction of cyclic nitro compounds to the corresponding amines has been slow and uncertain. Many processes have been developed but it appears that they are still in an experimental stage. An almost quantitative yield of aniline[22] is claimed to be obtained by passing a mixture of nitrobenzene vapor and hydrogen or water gas or an alcohol capable of giving hydrogen on dehydrogenation over heated copper oxide. Several catalysts have been studied. Some are effective in the liquid phase and others in the vapor phase. Certain compounds of the type R—CH=NR[23] are reduced to secondary amines by passing hydrogen in the liquid containing a suspension of finely divided nickel. The researches on catalytic reduction continue with unrelenting vigor.

Some progress has also been reported in the reduction of certain substituted nitro compounds with different reducing agents. *p*-Nitrophenol, 2,4-dinitrophenol, and the *o*- and *p*-nitrobenzoic acids have been reduced to the corresponding amines by iron and sulfurous acid.[24] Certain other nitro compounds have been reduced to the corresponding hydroxylamines or amines in an aqueous emulsion with alkali sulfides. Nitrobenzene gives by this method a yield of 72 to 74 per cent of practically pure crystalline β-phenylhydroxylamine. Mononitroaniline and *p*-nitroaniline are reduced to the corresponding diamines.[25]

The catalytic alkylation of amines has received some attention. A mixture of monomethylaniline and dimethylaniline has been obtained by passing a mixture of aniline and methanol over aluminium oxide or silica gel. Methylxylidines and naphthylamines have also been prepared by similar processes, that is, by passing a mixture of alcohol and amine vapors over alumina at 360° to 380° C.[26] The butylanilines have been prepared and are now available as intermediates. Likewise, N-methylvinylaniline[27] has been prepared and studied. The unsaturated group is hydrolyzed later to acetaldehyde. A catalytic process for diethylaniline[28] has been described, which consists of heating aniline hydrochloride, ethyl alcohol and a mixture of sodium bromide, cupric chloride, and calcium chloride for several hours in an autoclave. Alkyl-*m*-phenylenediamines[29] are prepared by heating primary or secondary alkylamines or their salts with resorcinol. The reaction appears to be accelerated by sulfurous acid.

Improved processes have appeared for the preparation of neutral alkyl esters of sulfuric acid to be used as alkylating agents. Diethyl sulfate[30] is made by passing an excess of ethylene or mixtures of ethylene and an inert gas into monohydrate or into a sulfuric acid solution of ethyl hydrogen sulfate at about 75° C., and subsequently either extracting the diethyl sulfate with ligroin or benzene or using the reaction product directly for alkylation. A process has also been patented to make dialkyl sulfates by treating acyclic alcohols with SO_3 in the presence of dehydrating agents such as phosphorus pentoxide, anhydrous sodium sulfate or anhydrous copper sulfate.[31]

Certain new amino compounds have been proposed as intermediates. *m*-4-Xylidine-5-sulfonic acid[32] and 6-nitro-*m*-4-xylidine[33] give, when diazotized and coupled with certain phenols, naphthols, and their derivatives, azo dyes and lakes superior in fastness and brilliancy in hue to similar

[11] *J. Chem. Soc.*, **117** (1920), 1405.
[12] *Ibid.*, **117** (1920), 1405.
[13] This Journal, **12** (1920), 968.
[14] *J. Soc. Chem. Ind.*, **40** (1921), 40A, 715A
[15] Private communication.
[16] Ger. Patent 260,563.
[17] *Rec. trav. chim.*, **39** (1920), 499.
[18] *Ibid.*, **39** (1920), 194.
[19] Brit. Patent 165,076.
[20] U. S. Patent 1,380,277.
[21] Brit. Patent 164,715.
[22] *Bull. soc. chim.*, **29** (1921), 217; Brit. Patent 166,283.
[23] *Compt. rend.*, **172** (1921), 280; *Bull soc. chim.*, **29** (1921), 106.
[24] Brit. Patent 165,838.
[25] *J. Chem. Soc.*, **119** (1921), 765.
[26] *Compt. rend.*, **171** (1920), 1154.
[27] *Ber.*, **52** (1919), 2261.
[28] This Journal, **12** (1920), 636.
[29] Brit. Patent, 168,689.
[30] Brit. Patent 157,578; *J. Soc. Chem. Ind.*, **40** (1921), 195A.
[31] Brit. Patent 143,260.
[32] Brit. Patent 164,053.
[33] *J. Chem. Soc.*, **119** (1921), 717.

dyes made from xylidine. Cyclic nitroamines[34] are obtained by boiling chloronitrocylic compounds with ammonium acetate. 2,4-Dinitroaniline is obtained by saturating acetic acid of 80 to 90 per cent strength with dry ammonia gas and then adding slowly 1,2,4-chlorodinitrobenzene, maintaining the temperature of the reaction between 124° and 130° C. Ammonia is passed into the reacting mixture during the reaction to replenish the ammonium acetate as fast as it is used up. Methyl-β-naphthylamine-6-sulfonic acid[35] is produced by heating a mixture of Schaeffer salt, methylamine hydrochloride, and caustic soda solution in a rotating autoclave at 180° to 200° C. for six to seven hours. A yield of 72 to 74 per cent of the sodium salt of the acid is obtained. This promises to be an important initial product for the preparation of the N-substituted derivatives of β-naphthylamine. Acyldiaminodiarylsulfones[36] appear to be useful intermediates. They are prepared by the acetylation of diaminodiarylsulfones synthesized from the corresponding chlorodinitro compounds and alkylsulfinic acids. Methyl-β-naphthylamine has been condensed with *p*-toluenesulfonyl chloride to give the corresponding toluene-*p*-sulfonylmethyl-β-naphthylamine,[37] which serves as the initial product for the preparation of a new group of intermediates. N-Arylthiomorpholines[38] are obtained by condensing primary cyclic amines having a free ortho position to the NH_2 group with β, β′-dichlorodiethylsulfide. They are proposed as dye intermediates. When β-naphthylamine is sulfonated with 94 per cent sulfuric acid a mixture of 35 per cent of the 8-sulfonic acid and 65 per cent of the 5-sulfonic acid, together with small quantities of the six and seven isomers, is obtained.[39] The mixture of isomeric sulfonic acids is converted into the corresponding sodium salts and these are separated by crystallizing them from sulfuric acid solution.

Anthraquinone and Its Derivatives

Particular activity has centered on anthraquinone and its derivatives. Anthracene is now satisfactorily oxidized to anthraquinone by catalytic[40] and electrolytic[41] methods. Synthetic anthraquinone is a reality and the future of the anthraquinone dyes is assured.

Many new derivatives of anthraquinone have been prepared. β-aminoanthraquinone is chlorinated to 3-chloro-2-aminoanthraquinone[42] in an inert organic solvent and 1-hydroxyanthraquinone dissolved in nitrobenzene is chlorinated in the presence of a small quantity of iodine and a sufficient amount of solid sodium carbonate to neutralize liberated hydrochloric acid to 1-chloro-4-hydroxyanthraquinone.[43] It has been shown that the dibromoanthraquinone used by Graeber and Libermann in the synthesis of alizarin was not the 1,2-dibromo product as they thought, but the 2,3-isomer.[44] β-Halogen derivatives of anthraquinone[45] result when α-halogen anthraquinones are heated with sulfuric acid to 200° C. This is an interesting case of intramolecular isomerization and necessitates research to establish the mechanism by which it and similar reactions come about. Alkylaminoanthraquinones[46] are produced by the action of alkyl sulfates on aminoanthraquinone in the presence of a mild alkali and in an inert high-boiling solvent like nitrobenzene. Arylaminoanthraquinones[47] are formed by treating an aminoanthraquinone containing one or more NH_2 groups with metal amides and in the presence of primary cyclic amines such as aniline or its homologs.

Benzophenone

In view of the fact that benzophenone has been prepared from benzene[48] and that such a process should give a relatively cheap product it is important to know that very vivid scarlet dyes, fast to light, fulling and washing are produced from 4,4′-diaminobenzophenone[49] by tetrazotizing and coupling the resulting tetrazotized product with β-naphthols and β-naphtholsulfonic acids.

Para-Cymene

A determined effort is being made to utilize *p*-cymene—a waste product from the sulfite-cellulose industry. It is nitrated and reduced in alkaline medium to hydrazocymene,[50] which is then rearranged to the corresponding 3,3′-dimethyl-6,6′-diisopropylbenzidine. 5-Nitro-2-amino-1-methyl-4-isopropylbenzene, 5-amino-2-acetylamino-1-methyl-4-isopropylbenzene, and 2,6-diamino-1-methyl-4-isopropylbenzene have been prepared from cymene and proposed for intermediates for azo dyes.[51] Aminocymene has been proposed as an intermediate for azo, sulfur, and indigoid dyes.[52]

Hydrazines

Certain cyclic hydrazines have been prepared and converted into the corresponding pyrazolones. The process for *p*-nitrophenylhydrazine[53] has been improved by the substitution of ammonium sulfite for sodium sulfite in the reduction. By condensing phenylhydrazine-*m*-sulfonic acid[54] with dioxytartaric acid a pyrazolone is obtained which dyes wool and silk a yellower hue than ordinary tartrazine. The 1,4- and 1,5-naphthylhydrazinesulfonic acids[55] give pyrazolones which dye wool and silk red and brownish red colors.

Hydronaphthalenes

Marked progress has been made recently in the production and utilization of hydrogenated naphthalene.[56] It is found to be an excellent solvent particularly useful in the purification of naphthalene[57] when a very pure product is required. Several derivatives of di- and tetrahydronaphthalenes have been prepared and used as intermediates for azo dyes.

It is not possible at the present time to say just what advantages the hydrogenated derivatives of naphthalene possess as intermediates. The difficulties in nitrating the hydrogenated naphthalenes appear to have been overcome and both nitro[58] and amino[59] compounds are now made. Tetrahydro-β-naphthol,[60] difficult to obtain by hydrogenation of β-naphthol, is now obtained by sulfonating tetrahydronaphthalene and subsequently fusing the sodium or potassium salt of the resulting sulfonic acid.

[34] Brit. Patent 169,688.
[35] *J. Soc. Chem. Ind.*, **41** (1922), 1T.
[36] *Ibid.*, **41** (1922), 3T.
[37] *J. Soc. Chem. Ind.*, **41** (1922), 3T.
[38] Brit. Patent 133,108.
[39] *Giorn. chim. ind. appl.*, **3** (1921), 97.
[40] U. S. Patent 1,355,098.
[41] U. S. Patent 1,397,562.
[42] Brit. Patent 172,682.
[43] Brit. Patent 172,682.
[44] Annual Reports, *J. Soc. Chem. Ind.*, **6** (1921), 95.
[45] Brit. Patent 169,732.
[46] Brit. Patent 147,964.
[47] U. S. Patent 1,394,851.
[48] This Journal, **14** (1922), 406.
[49] Ger. Patents 338,683, 333,077, 330,824.
[50] U. S. Patents 1,314,924, 1,314,923; *Ber.*, **53** (1920), 78.
[51] U. S. Patents 1,314,925, 1,314,926, 1,314,924, 1,314,921, 1,314,922.
[52] U. S. Patents 1,314,928, 1,314,929.
[53] *J. Chem. Soc.*, **121** (1922), 715.
[54] *J. Soc. Chem. Ind.*, **40** (1921), 176T.
[55] *Ibid.*, **40** (1921), 176T.
[56] *J. Chem. Soc.*, **117** (1920), 241, 1574; Ger. Patents 299,603, 324,861, 305,104, 298,541, 298,553, 301,275, 336,615, 299,014, 326,486, 337,157, 316,218, 335,477, 335,602.
[57] Ger. Patent 317,634.
[58] British Patent 148,923.
[59] Brit. Patent 170,867.
[60] Brit. Patent 148,408.

Isatin and Derivatives

By condensing aniline with chloraloxine in acid medium and ultimately warming the condensation product with sulfuric acid, isatin[61] results. In a similar way 4-chloromethoxyisatin[61] is produced from the hydrochloride of *p*-chloroanisidine. The 5-sulfonic acid of isatin, condensed with indoxyl, gives an indirubine[62] which dyes wool and silk a violet color. 6-Methylisatin, obtained from methyltoluidine and esters of mesoxalic acid, gives a substituted indigotin,[63] which dyes wool and silk but has only slight affinity for cotton. Many other such derivatives have been prepared and used to introduce desired groups in the indigotin molecule, but it does not appear that any of them have practical application.

Naphthols

Activity in this group has been largely confined to the improvement of existing processes for the manufacture of staple intermediates. It has been shown that losses in the manufacture of H acid[64] are caused by the formation of naphthalene-1,3,5,7-tetrasulfonic acid, to destructive oxidation and to the formation of 1,6- and 2,7-disulfonic acids which only sulfonate to the 1,3,6-trisulfonic acid with great difficulty. Some improvement is seen in the process for the naphtholsulfonic acids and anilides of β-oxynaphthoic acid. Anilides of cyclic acids are produced by heating acids of the cyclic series with anilides of acyclic acids, the acyclic acid being liberated. The 1,5,7-aminonaphtholsulfonic acid, M acid,[65] has been prepared and used as an intermediate in the manufacture of blue cotton dyes. Also, the 2-amino-5-naphthol-1-sulfonic acid, A acid,[66] has been used in certain combinations to give azo dyes.

Nitro Compounds

Attention is again directed to continuous nitration of benzene to mononitrobenzene by a process which uses mercury compounds as catalysts.[67] It is not clear from the available information what advantage the process has over other methods of nitration. Continuous operation of a process is not always advantageous.

Much progress has been made in the preparation of certain nitro compounds. The factors governing the nitration of phenolsulfonic acids to picric acid have been carefully considered and it has been shown that the best yield of picric acid is obtained when the sulfonation product of phenol contains over 80 per cent phenoltrisulfonic acid.[68] The yield varies with the proportions of mono- and disulfonic acids. The accumulation of SO_3H groups appears to stabilize the molecule or to inhibit oxidation during the nitration. Low yields are also often due to the presence of dinitrophenolsulfonic acids from incomplete nitration. Another process[69] sulfonates phenol to the disulfonic stage and then nitrates at about 30° to 40° C., while another process[70] proposes to nitrate the sulfonated phenol below 70° C. to the mononitrate product and then complete the nitration above 70° C. Trinitroresorcinol[71] has been obtained in a similar way by nitrating resorcinoldisulfonic acid suspended in concentrated sulfuric acid with 90 to 100 per cent nitric acid. *o*-Nitroanisol[72] is produced by boiling a mixture of o-chloronitrobenzene, methyl alcohol, potassium carbonate and an aqueous suspension of slaked lime. An interesting process for β-nitronaphthalene[73] consists in nitrating tetrahydronaphthalene, freezing out the β-nitro product from the first fraction distilled, dibrominating this and then vacuum distilling the resulting product to obtain β-nitronaphthalene. It is questionable whether β-naphthylamine can ever be made commercially from β-nitronaphthalene made in this way.

[61] *Compt. rend.*, **172** (1921), 1234.
[62] *Ibid.*, **172** (1921), 330.
[63] *Ibid.*, **172** (1921), 220.
[64] *Helvetica Chim. Acta*, **4** (1921), 381.
[65] Fr. Patent 516,853.
[66] *J. prakt. Chem.*, **103** (1921), 129.
[67] U. S. Patent 1,380,185.
[68] *Bull. soc. chim.*, **27** (1920), 140, 199, 195, 370.
[69] *J. Am. Chem. Soc.*, **42** (1920), 2665.
[70] U. S. Patent 1,380,186.
[71] Brit. Patent 162,578.
[72] Brit. Patent 167,582.

Phenanthraquinone and Retene

The utilization of phenanthraquinone and its derivatives has received some attention for several years but not until recently have the results appeared encouraging. Watson[74] and his co-workers have obtained dye intermediates from phenanthraquinone, the oxidation product of phenanthrene, by introducing substituents into the nucleus which serves to develop the condition essential for the manifestation of color and which makes possible dyeing properties. Phenanthraphenazine dyes[74] are obtained by condensing aminophenanthraquinone with *o*-phenylenediamine. Both wool and other dyes have been obtained—the 2,7 substituted phenanthraquinones give cotton dyes and the 4,5 derivatives, wool dyes.

Retene, methylisopropylphenanthrene,[75] is now available in large quantities as a pure product having been recently isolated from the high-boiling oils from pine tar. Diazonium compounds of retene have been prepared and converted into azo dyes[76] by coupling with naphtholsulfonic acids. Further work is necessary before any prediction can be made of the future of retene as a raw material for dye intermediates.

[73] Ger. Patents 299,014, 332,593.
[74] *J. Chem. Soc.*, **119** (1921), 1211.
[75] Private communication.
[76] U. S. Patent 1,395,238.

Industrial Films

A six-reel motion picture film, "The Story of Steel," has been produced under the auspices of the Bureau of Mines and the Department of Commerce in coöperation with the United States Steel Corporation. It will be used extensively in the United States and abroad for the purpose of acquainting the peoples of the world with the many interesting operations employed in the American steel industry. The film depicts the various processes from the mining of the iron ore to the finished steel product. The manufacture of rails, plates, shapes, axles, rods, wire products, pipe, tin plate, and other products of steel is told in a graphic way, and before the picture is brought to a close the audience is shown the many welfare and social activities which are carried on by the United States Steel Corporation for the benefit of its employees. The film will be loaned without cost to all dependable persons desiring to use it for educational purposes. Application for its use should be made to the Department of Commerce, Washington, D. C.

"The Story of Natural Gas" has been produced by the Bureau of Mines in coöperation with the Natural Gas Association of America, and shows in an interesting and informative way the various steps in the development and utilization of natural gas supply, from the drilling of a gas well to the delivery of the gas to the consumer. The same Bureau has released "The Story of Oxygen," which was produced in coöperation with the Air Reduction Company. This picture shows, by the aid of animated cartoons, how pure oxygen is produced from air by liquefaction and expansion. This is followed by an exposition of the manifold uses to which oxygen is put in industry. Requests for the loan of these films should be addressed to the United States Bureau of Mines, 4800 Forbes St., Pittsburgh, Pa.

Under terms of a coöperative agreement with the Department of Commerce, the Pittsburgh Station of the Bureau of Mines also has available for distribution copies of the following films: "The Story of an Automobile;" "The Story of an Electric Meter;" "The Story of a Watch;" and "The Story of Compressed Air."

The motion-picture film, "The Story of Petroleum," prepared by the Bureau of Mines and the Sinclair Consolidated Oil Corporation, is to be exhibited in Jugoslavia and Czechoslovakia.

Science in the Textile Industry

By E. D. Walen

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IT IS ONLY within the last few years that we have heard very much regarding the application of research or science to that branch of textile industry devoted to the actual manufacturing of yarn and fabric. The chemist has already made tremendous strides in the application of basic principles to the finishing and dyeing part of the textile industry, and since it is so well started there has been perhaps less discussion of its advantages.

E. D. Walen

The textile industry is one of the oldest and although it is not quite clear that cotton manufacturing is the oldest industry, it is, nevertheless, an ancient art which has grown to be of tremendous economical importance. An examination of the ancient textiles, such as those of Peru by M. D. C. Crawford, indicates strongly that there is very little new in the design of cloth and the construction of fabrics and yarns. A comparison of the quality of these yarns with the present-day yarns indicates that the greatest strides in the cotton industry have been along the lines of increased production and ease of manufacture, and we sometimes wonder if the basic principles of manufacturing have not been lost sight of to some degree.

The progress of science in the manufacture of textiles has been rather slow, and it is rather difficult, owing to the fact that the people engaged in the industry are hampered by the many generations of inertia; and in addition, the industry depends so much upon the existing machinery that it is difficult to conceive of valuable results until these machines have been substituted by those designed on new principles. Progress in other industries, however, has led many manufacturers to believe that there are possibilities in the application of the laws of natural science to the textile industry.

The governments of the several textile countries have maintained laboratories and scientific men for the investigation of cotton growing and to some extent cotton manufacturing, and much good has resulted from these studies. Perhaps the biggest research project that has gained any headway has been the British Cotton Industry Research Association, which dedicated its laboratories in the early part of this year. This association, we understand, is of a coöperative nature in that all British manufacturers are eligible to membership and the results are for their benefit.

In this country the formation of a large research body has been somewhat along different lines. Apparently, each association interested in cotton has a research section which varies considerably in its conception of research and in its activities. The National Association of Cotton Manufacturers, which probably represents the majority of cotton manufacturers in the country, has for some time maintained a research committee which has branched out into a research department. This department is still in its infancy and it is attempting to justify its growth by actual accomplishments.

The largest single project of individual research in this country was started in 1918 by the Lockwood, Greene & Company and the Pacific Mills interests. The first organization consisted of a committee which served as a clearing house of ideas for the several mills. This committee developed the fact that it was necessary to have a laboratory study the various problems, and in July 1919 the Cotton Research Company was incorporated. The stock ownership of this company was shared by the Pacific Mills and Lockwood, Greene & Company. It was planned to allow the company to operate for a probationary period, in order to give the project a fair chance to prove its value. This period has passed and the project is believed to be worth while continuing.

The company is essentially an industrial laboratory and it was not thought at first that it would be necessary to engage along the lines of pure research, but it has been interesting to note that as the work has progressed the demand for the solution of problems along basic lines has steadily increased and the practical mill man has been found to be more interested in knowing the underlying cause than in knowing the immediate effect.

The original equipment consisted of much textile machinery for conducting tests and very little laboratory equipment for the study of the samples prepared. Since that time about 50 per cent of the machinery has been disposed of and the laboratory equipment enlarged. The laboratory equipment available for the study of manufacturing is extremely limited, and it has been found necessary to design and construct all of it.

The organization of the company has been built up around four groups:

1—The directors, who represent the financial interests and determine the policies along broad lines.

2—An advisory council, composed of mill agents and superintendents of the various mills interested, who convene at intervals to discuss the policies and to determine the scope of the immediate problems.

3—A group trained along the scientific lines of physics, chemistry, and microscopy.

4—A group of practical men trained in the laboratory to conduct tests who are familiar with the application of laboratory developments as applied to the study of manufacture.

The activities have been built up around the study and maintenance of quality and the economy of manufacture, and all the developments are necessarily focused on the mills as soon as they become of value. The adaptation to the mill is carried on by the group of practical men and the advisory council.

It has been necessary in a program of this sort to develop methods for accurately and quickly measuring the physical properties of the raw materials. The immediate application

of such measurements is interesting from the viewpoint of the selection of proper types of cotton, the probable value of new crop cotton for yarn made at a particular plant, study of the efficiency of a manufacturing operation from the viewpoint of the raw product, tracing the cause of poor yarn, and the application of correct measurements based upon accurate knowledge of cause.

Contrasted to this study and application there is another important study based on the assumption that an industry as old as the cotton industry must have in each mill a number of good features. This involves the careful noting of all details of the factors of production and quality, a proper analysis, and adaptation of the good points to the mills concerned.

The photomicrographic analysis of materials has been of the greatest help in recording arrangement of fibers, uniformity, effects of settings, degree of dye and size penetration, balance of structure, and many other things which are important but not discernible to the naked eye.

Our activities along the chemical lines have been rather limited and have been confined largely to the study of warp sizing. This problem has been considered as a problem in physics, using chemistry as a means of designating the materials.

We believe that much progress has been made and that the results warrant the existence of a research organization, but the surface has hardly been scratched and developments in the future years are bound to be nothing short of phenomenal.

Heat Treatment Progress during 1921

By A. E. White

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THE PROGRESS of ferrous metallurgy, especially that closely allied with the heat treatment of steel, has shown no outstanding milestones this past year, progress having been one of refinement and lacking in spectacular accomplishments in matters of materials, equipment, and in the character of the personnel employed.

With regard to materials, there has been a growing interest in the developments of heat-resisting and nonoxidizing alloys. There is daily a greater appreciation that we must have alloys which will withstand oxidation and deformation at temperatures higher than the normal atmospheric temperatures; also that we must encourage the use of alloys that at high temperatures retain to the greatest degree a proper combination of strength and ductility. The use of carburizing boxes that will withstand warpage and oxidation under the conditions of service to which such boxes are subjected has received considerable attention. One of the recent alloys brought out for this general purpose is known as *Calite*, composed essentially of nickel, aluminium, and iron.

The structural material that has received the greatest consideration this past year, though not of this year's development, is molybdenum steel. It is an alloy steel comparable to our nickel steels, chrome-nickel steels, and chrome-vanadium steels. Practice seems to indicate that the chrome-molybdenum type is an acceptable forging steel, and that the nickel-molybdenum type is a satisfactory case-hardening steel.

In the matter of equipment used for the heat treatment of steel, there have been no outstanding developments, though many plants throughout the country have made changes in furnaces and furnace appliances which go a long way toward placing the heat treatment of steel on a scientific basis. Pyrometric control is now available so that temperature in the furnace is no longer subject to the variations of manual control. This pyrometric control, at one time only possible in electrically heated furnaces, is now possible in both gas-fired and oil-fired furnaces. There also is a growing tendency toward the use of conveyor type furnaces, and this in turn tends to eliminate the human factor. Combined with all these facts is an increased use of fixtures for quenching, better designs of furnaces to secure more uniform temperature in the same furnace, and better refractories, resulting thereby in a decided reduction in maintenance costs.

Combined with all of these factors the personnel in the heat treatment departments of the various plants throughout the country has improved. This has been due in some measure to the depression, since only the better men were retained and they realized that in order to hold their positions they must operate as intelligently as possible. In the heat treatment rooms there are many college-trained men, and large numbers of the others have had at least a high school education. These men are keen to absorb new ideas and new methods, and they appreciate also that to procure them they must exchange ideas. This broadmindedness on the part of those engaged in the steel heat treating field has no doubt been one of the reasons why it has developed so rapidly. There are but few shops in the country that prevent their men from freely exchanging ideas with their fellows.

An appreciation on the part of our technical societies that their function is in large measure the bringing together of the technically trained men and the operatives whose advantages in their given field have not been as great, has been of no little moment in the advance of the art of heat treatment.

Numerous investigations in this general field are under way. On some, preliminary reports have already been made, whereas on others the work has not progressed to a degree warranting publication. Some of the most outstanding investigations are: The work of Professor Moore and his colleagues on "The Fatigue of Metals," the work in progress on "Drill Steel" under the combined auspices of the United States Bureau of Mines, the American Institute of Mining and Metallurgical Engineers and others; and the work of the U. S. Bureau of Standards on:

1—Gage steels.

2—High temperature tests of commercial steels.

3—Proper mixtures for use in selective carburization.

4—A suitable method for the measurement of hardness in hardened steels.

5—The use of magnetic testing for the determination of uniformity in steel.

Heat Transmission and Evaporation

By W. L. Badger

Chemical Engineering Department, University of Michigan, Ann Arbor, Mich.

THERE is scarcely a process with which the chemical engineer is concerned that does not involve the transfer of heat in some form. In a great variety of circumstances he must pass heat through a separating wall with sometimes liquids, sometimes vapors, and sometimes permanent gases on either side. But if he wishes to design such apparatus intelligently and accurately he finds the literature practically devoid of information that might help him.

W. L. Badger

This has come about for several reasons. The fundamental principles of heat transfer (such as the fact that it is proportional to temperature drop) have long been familiar; but though more than a generation ago the variables which affect heat transfer were thoroughly discussed, only a couple years ago an engineer stated in the proceedings of an important society that since copper had seven times the thermal conductivity of iron, an evaporator with copper tubes should do seven times the work of one with iron tubes. Actually, while a plate of copper 0.1 in. thick and 1 ft. sq., with a difference of 1° F. between the two sides, will transmit about 25,000 B. t. u. per hr., a layer of water 0.01 in. thick on each side will reduce this to about 200 B. t. u. The resistance of the copper will then be only about 1/150 of the total, and the substitution of iron for copper would have practically no effect. This film concept as applied to heat transfer has been more or less recognized for about 30 yrs., and other factors, such as the effect of viscosity, circulation, elevation of boiling point, hydrostatic head, etc., were recognized even further back; but the number of engineers who fully appreciate the significance of these factors is disappointingly small.

A series of heaters were designed by a man well known in his field of engineering and installed in a plant operated by graduate mechanical engineers. The heaters were not doing what they should and the writer was called on to revise the equipment. It was found that each heater had three hundred and sixty $2^1/_2$-in. tubes, all in one pass. The amount of material being circulated was such that its average velocity was about 0.1 ft. per sec. Inquiry developed that neither the designer nor the operating engineers had ever thought of figuring liquid velocity.

While we may expect to see in the near future a certain amount of information in fairly satisfactory shape on heat transfer when heating liquids or gases, we will have to wait a long time for information on evaporation. When a liquid is actually boiling, conditions are so complex that as yet they have defied mathematical analysis. The evaporator, whether single or multiple effect, is one of the chemical engineer's most important tools, yet we really know very little about it. Hausbrand's classic analysis leaves us just short of being able to really design an evaporator, and constants are almost wholly lacking. Even the standard types still need much study.

If one attempts to list the particular points in which progress is being made in this field, he must first admit that so far as general engineering practice is concerned, the last few years have seen little change. Rising coal prices have thrown the weight of opinion toward triple or quadruple effect evaporators, where before the war the double effect was most common. Mechanical engineers have made progress in the design of surface condensers and their auxiliaries. A few new ideas have been advanced, notably that of recompression of vapors, but this is not yet commercially feasible in this country. At the University of Michigan we are trying to make some headway on a study of evaporator theory. The Massachusetts Institute of Technology has published some beginnings of a study of real film coefficients. Some of the larger corporations are making tests and developing new ideas, but this work is rarely made available by publication. Perhaps the most promising feature is the increasing number of engineers who are really thinking accurately about heat transmission problems, and who are coming to realize the need for work in this field.

Our work at the University of Michigan is only beginning and is as yet largely empirical. The writer has literally dozens of problems in connection with standard evaporator design which have not yet been touched; and if one also considers the possibility in the way of new types, the field is correspondingly broadened. For instance, the average evaporator operates with a heat transfer coefficient of somewhere from 100 to 400 B. t. u. per sq. ft. per hr. per ° F. Feedwater heaters may, under special conditions, reach 1000 to 1100 B. t. u. The writer has seen a special evaporator in operation for which 1500 to 2000 B. t. u. are claimed. This was accomplished by accepting the film concept and attempting to scrape off the film.

The problems now facing us are varied. How can we predict accurately the temperature distribution in a multiple effect evaporator? What are the exact effects of such factors as viscosity, circulation, hydrostatic head, etc., on the film coefficient between boiling liquids and metal surfaces? What is the effect of superheat in steam on heat transmission? Why do salt crystals grow on the heating surfaces instead of in the solution? If we turn to artificial circulation, where shall we find increased heat transmission offset by cost of stirring? What is the field for re-use of vapors by recompression? Where are we to get the physicochemical data (such as elevation of boiling point, solubility, specific gravity, specific heat, latent heat of evaporation, etc.) for the strong solutions which we use in practice and which the physical chemist has not considered because they fail to follow his laws for dilute solutions? Several of these problems we have already attacked, and on one or two we have made considerable progress. There is plenty of room, however, for more workers.

Besides the vast amount of experimental work yet to be done, there is much ahead of us in educating engineers to think in terms of the heat balances of a plant as a whole.

Few engineers outside of the sugar industry appreciate what can be done by a proper interlocking of power units, evaporating units, and heating units. Such economies are possible, when this group of operations is considered as a whole as no power specialist and few heating or evaporating specialists realize. For instance, in beet-sugar manufacture, 12 to 15 per cent coal is burned (calculated on the weight of the beets) in the best practice in this country. It is said that 9 per cent is reached in Germany, but German mills do not produce a finished sugar. There is a mill in this country which was well built by a good sugar engineer. It has been operated for some years by wholly untrained superintendents. Owing mainly to a lack of knowledge of how to coördinate the power, heating, and evaporating units, the fuel consumption has risen year by year (as the original design in the mill has been altered) until last season it used 25 to 30 per cent coal on the weight of the beets.

There are many other similar fields in chemical engineering which need extensive work. Practically all of the unit operations are in the same state as heat transfer. Distillation and drying are receiving considerable attention at present. Mixing and stirring have not been touched; filtration has been worked on only enough to outline the problems; in fact, chemical engineering, as such, is still in almost every phase a new and undeveloped field.

The Vegetable Oil Industry

By David Wesson

Technical Director, The Southern Cotton Oil Co., New York, N. Y

THE PAST two years have brought to light few, if any, great changes in products or manufacturing methods, though a great deal has been done toward improving existing methods with a view of securing greater economy of operation and improvement of product.

In the matter of solvent extraction there has been considerable progress in Europe. In England there is a large plant operating on palm kernels and copra, producing upward of 80 to 100 tons of edible oil per week. In this country one or two large plants, which were highly successful during the war, have closed down on account of peace conditions.

The manufacture of by-product coke has made available large quantities of benzine at a reasonable price. This is an ideal solvent for peanuts, copra, palm kernels, and other seeds that are free from coloring matter. The petroleum people are giving attention to the production of a fraction with low boiling point distilling within close limits, also suitable for this purpose.

The literature discloses twenty or more patents mostly relating to apparatus. A novelty is the proposal by McKee to use sulfur dioxide as the extraction medium.[1]

In refining the oil various innovations have been presented for removing the free fatty acids in such a manner as not to saponify neutral oil or carry out the same with the soap formed in the usual method of saponification.

E. R. Balton and E. J. Lush[2] convert free fatty acids into glycerides by heating to 200° to 250° C., and treating with glycerol vapor. They claim that the resultant neutral fat can be refined.

H. Schlinck and Company[3] neutralize the fatty acids by boiling the fat containing same with glycol under a reflux condenser using 11 per cent glycol by weight of the fatty acids present, and removing the water formed by operating in vacuum or passing an inert gas. They also add a suitable catalyst and pass hydrogen to hydrogenate at the same time.

C. and G. Muller Speissefett fbr. A. G.[4] dissolve the fat in a solvent miscible in water, such as acetone, then add sufficient water to precipitate the neutral, leaving the fatty acids in solution. The solution of fatty acids is drawn off and more water added to precipitate them.

L. Schmidt[5] dissolves the oil in a suitable solvent, then agitates with alkali and removes the resultant soap by filtration. The process is said to be operated in Switzerland, Italy, and Germany.

The bleaching of oils for edible purposes continues to be done mostly with fuller's earth, with or without the addition of bleaching carbons in some of the various forms. A large variety of fuller's earths are now on the market. Most of them are natural products prepared by drying and grinding, while others are made by action of sulfuric acid on suitable clays. Some of these artificial earths have marked bleaching properties.

David Wesson

The past two years have witnessed a large number of new bleaching carbons mostly of vegetable origin, made by the treatment of waste materials. Some of them pound for pound are far more active than boneblack, but their increased activity is largely offset by advanced price.

This operation of hydrogenation seems to be pretty well standardized, though numerous patents have been taken out on apparatus and catalysts. Electrolytic hydrogen seems to have been pretty generally adopted. The low prices of hard animal fats have largely curtailed the output of hydrogenated oils.

Vitamins have been very much in the limelight the past two years. Many new facts have been discovered and many of the previous exaggerated ideas exploded.

Dr. H. C. Sherman in his recent work, "The Vitamins," published by the Chemical Catalog Co., gives a fair summing up and classification of most of our knowledge to date on this matter, so voluminous in the literature and so meager in exact chemical facts.

Dr. Casimir Funk in an address before the Institute of Mar-

[1] U. S. Patent 1,376,211.
[2] Brit. Patents 159,587, 163,352 (1919).
[3] Ger. Patents 334,659, 315,222 (1916).
[4] Ger. Patent 339,027 (1918).
[5] U. S. Patent 1,395,998 (1921).

garin Manufacturers, published in *The American Food Journal* for June 1922, points out the deficiencies of the fat-soluble vitamin in butter fat in the case of rickets and shows that cod-liver oil contains fat-soluble vitamins in much higher concentration than they occur in butter fat. He also indicates recent researches in analytical methods which extend the hope that we may soon be able to identify the different bodies.

The Department of Agriculture has started a comprehensive research on cottonseed and the products therefrom, in coöperation with the Interstate Cottonseed Crushers' Association. Drs. Jamieson and Baughman of the Bureau of Chemistry have already published a method for the analysis of crude vegetable oils, giving the amount of absolute oil obtainable from any sample of crude by alkali refining. The published results show that in refining crude oils by alkali, only 95 to 96 per cent of the available refined oil is obtainable in factory operations with existing methods. Work is now being done to separate and identify the various impurities present in the crude oil and to determine their effect on losses and quality of the refined oil. The same writers have also published analyses of cottonseed and peanut oils prepared from authenticated seeds from many localities and pressed under known conditions in the laboratory. These results give us the variations in the chemical constants of these oils and are far more reliable than those commonly published in the literature. For a full statement of the work done by the Bureau of Chemistry, the reader is referred to a very able article by Dr. W. W. Skinner in the *Chemical Age* for June 1922.

Considerable work has been done toward more accurately describing the colors of vegetable oils. A progress report of the Committee on Color of Oil and Seed was presented before the June meeting of the American Oil Chemists' Society. The report showed a highly improved colorimeter recently brought out by the Eastman Kodak Co., which makes it easily possible to report on the color of oils in the terms of yellow, red, and neutral tint or darkness. It is also possible to obtain color matches impossible with previous methods.

The same report gave a description of the color analyzer just perfected by Keuffel & Esser, whereby it is possible to obtain a spectrophotometric curve of any sample of oil, and from the curve to determine whether it has been put through various refining processes. It also shows the difference in color between different oils. The instrument, needless to say, adds greatly to the facilities for research.

The constant requirements in manufacture call for more exact chemical information and methods, and call for travel on a little explored field. In the analyses of the oils themselves, we can separate the various fatty acids of the mixed glycerides; but what do we know of the mixed glycerides themselves, and their structure? It is highly desirable that methods should be devised for separating the different glycerides, both for analytical information and the proper control of manufactured products. This is particularly true in the industries dependent on hydrogenation. We may know the proportion of different fatty acids present, but have little more information regarding the structure of the fat and its resultant properties, than we could obtain regarding the design of a building by studying the bricks and stones constituting its ruins.

In the operating of bleaching oil by fuller's earth, we know little regarding the properties of the color removed, or just what action the earth has on the oil. We do know that the earth apparently oxidizes and polymerizes a portion of the oil and removes the same in addition to the color, but why and how we know not.

In deodorizing the oil by steam, certain malodorous principles are distilled off. It is not improbable that these might be developed into desirable perfumes.

In the extraction of crude oil by pressure, about 15 per cent of the total remains behind in the press cake. We know that it can be removed by solvent extraction. It is simply a question of mechanical and chemical research to substitute solvent extraction processes for the clumsy hydraulic presses. Solvent extraction produces choice oils in the laboratory, and with suitable apparatus can do the same in the factory.

The factors involved in the rancidity of fats and best means for preservation are important subjects for research of great practical value.

Each of the separate problems mentioned above resolves itself into many minor ones, so it may safely be said that the field of research in the edible fat industry is still a large one and well worthy of cultivation.

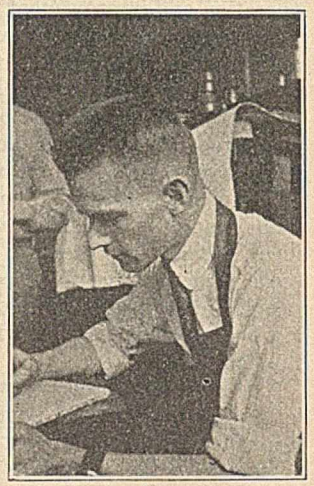
Solvent Extraction of Vegetable Oils

By C. F. Eddy

Research Associate, Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

THE STRESS of war conditions gave the solvent extraction industry a big impetus, especially in Europe.[1,*] The success obtained has helped to break down prejudice and has stimulated investigation and discussion.

The higher yields obtainable by solvent extraction are clearly shown in a table given by Shrader,[2] and Pickard's report[3] that in five normal years before the war a solvent extraction plant for flaxseed gave a net return of $1.50 per ton of raw material more than for a similar pressing plant, shows that the advantage is not merely theoretical.



C. F. Eddy

Thiele[4] has recently pointed out another advantage of this higher extraction of oil. When the oil has developed an appreciable amount of free fatty acids, a very low oil meal will be free from objectionable rancidity. In this connection, some have claimed that the steaming necessary to free the meal from solvent also increases its value for feed purposes.

Another advantage of the solvent extraction method that is being developed is in connection with the removal of free fatty acids from the extracted oil. In refining by the same method samples of pressed and solvent-extracted cottonseed oil, Shrader reports[5] refining losses for the extracted oil much less than for the pressed oil. In a previous article[6] he refers to having tried Dr. Wesson's suggestion of refining the oil in solution instead of refining after the solvent had been removed. The only observation made was a comparison of the color of the oils refined by the two methods. If he was aware of the much greater simplicity of apparatus and method possible with refining in solution he did not mention it, and others have secured patents on the method.[7,8]

The developments of processes and new types of apparatus[17-23] have been very numerous, but some of them, especially some unpublished ones, have been great improvements.

* Numbers in text refer to Bibliography at end of article.

With the proper apparatus, fire hazards,[4] dangers of poisoning to workmen,[9,10] and solvent losses are being greatly reduced, if not eliminated.

Unfortunately the apparatus or process that is the best for one oil is not necessarily the best for another, and poor judgment in selecting apparatus or process has resulted in many failures. Then, even if research has shown the proper apparatus and method to be used and a prime product is produced, there is no question but that many a hesitant buyer will swear that he tastes solvent in the product. Sievers reports[11] troubles with samples of benzol-extracted corn oil that recall similar experiences. The author and others with whom he has compared notes have slipped in samples of pressed oil with solvent-extracted samples and had men swear they tasted solvent in all of them. Masahiro Aida[12] has given a test for minute quantities of petroleum spirit in vegetable oils and there should be a test for small quantities of the more commonly used benzol to settle the argument when there is any doubt.

It sometimes happens that the steam distillation necessary to remove the last traces of solvent will also remove some of the characteristic odor or flavor of the oil, leaving a more neutral or flat taste. Once again the buyer may hesitate because it is not what he is accustomed to.

Further research along certain lines is absolutely essential if solvent extraction is to fulfil the expectations of its advocates. Such moot questions as the proper solvent to use for certain oils, the effect on the color and taste of the oil if hulls or shells are present during extraction, the effect of the metal of the extractor on the finished product, etc., must be answered sooner or later if the industry is to progress.

With the improvements constantly being made in processes and in apparatus, and with the light that is being thrown on the subject by careful study and discussion, added weight is given to Pickard's conclusion[3] "that the future of the vegetable oil industry lies in the adoption of the extraction process."

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The Trend of Prices

In the June number of the *Chemical Bulletin* S. L. Redman makes a comparison of 1913–1922 foreign and domestic prices of typical chemical apparatus. He summarizes the situation as follows:

To sum up briefly, there has been a continued downward trend in the price of laboratory supplies during the past eighteen months, except in those staple lines of glassware and porcelain whose prices remained stationary during the war and post-war period of rising costs. Prices will probably continue to recede gradually throughout a period of years until the pre-war level is reached. Special instruments, whose cost of development was very high, were introduced at rather high prices and, as the process of manufacture has been perfected, generous price reductions have been made. No immediate relief is to be expected from the importation of German goods, since the difficulties experienced by German manufacturers with raw materials purchased with a depreciated currency, with restricted fuel supplies and labor troubles combine to make prices higher than those of the corresponding grade of American-made materials. Chemical prices reached bottom last year and if any change occurs in the near future, it will probably be in an upward direction.

These conclusions are based upon the following tables:

Retail Prices

	1913	1919	May 1922	Aug. 1922
Evaporating dish, No. 0	$0.19	$0.24	$0.24	$0.23
Griffin beaker, 250 cc	0.22	0.25	0.25	0.25
Florence flask, 400 cc	0.24	0.27	0.27	0.24
Cylindrical graduate, 100 cc	0.50	0.63	0.60	0.57
Thermometer, 110° C	0.80	1.20	1.10	1.05
Bunsen funnel, 3 in	0.18	0.43	0.35	0.35
Soxhlet extraction apparatus, 100 cc.	2.70	3.85	3.80	3.50
Bunsen burner	0.22	0.45	0.35	0.35

Comparative Prices (May 1, 1922)

	American-Made (Coors, Pyrex, Taylor, etc.)	German-Made (Royal Berlin, Jena, Siebert & Kuhn, etc.)
Evaporating dish, No. 0	$0.24	$0.35
Griffin beaker, 250 cc	0.25	0.25
Florence flask, 400 cc	0.27	0.32
Cylindrical graduate, 100 cc	0.60	0.80
Thermometer, 110° C	1.10	1.10
Bunsen funnel, 4 in	0.44	0.38
Soxhlet extraction apparatus, 100 cc.	3.80	4.00
Globe-shape separatory funnel, 250 cc.	1.65	2.15

Instruments differ so widely in characteristics that it is difficult to draw any comparisons as to makes. The tendency toward lower prices, however, may be illustrated by taking the Abbé refractometer. A well-known American manufacturer developed one of these two years ago which sold at a retail price of $425. About a year ago, the price was reduced to $320, and just recently to $275. Another American maker has placed an Abbé refractometer on the market at a price of $250. The first American-made saccharimeter retailed two years ago at $710. This was later reduced to $525.

Platinum Theft

The chemical laboratory of the Westinghouse Electric & Manufacturing Co., East Pittsburgh, Pa., has recently lost the following pieces of platinum:

	Weight
One dish	32.2450 g.
One dish	40.2720 g.
One crucible	36.8328 g.
One crucible marks No. 8 and (B)	18.0254 g.

Local Anesthetics

By Henry Gilman

Department of Chemistry, Iowa State College, Ames, Iowa

THERE are two main classes of anesthetics: general, where the patient suffers temporary loss of consciousness; and local, when the patient retains consciousness during the operation. General anesthetics may be inorganic or organic compounds, such as nitrous oxide, ether, chloroform, ethyl chloride, etc. Local anesthetics may be inorganic or organic compounds, but organic compounds are used almost exclusively.

The history of local anesthetics is intimately and for a time was altogether associated with cocaine, which substance was introduced in local anesthesia about forty years ago. Without entering into a discussion of the relative merits of general and local anesthesia, it is sufficient to remark that statistics indicate a steady growth in the use of local anesthetics for both minor and major operations.

Henry Gilman

Need of Substitute for Cocaine

In surgery, particularly in dental work, cocaine, has been rather largely superseded by synthetic local anesthetics. The reasons for this are several and concern themselves with inherent comparative disadvantages of this naturally occurring alkaloid. First, cocaine is relatively more toxic or poisonous than some commonly employed synthetic compounds. Second, cocaine is a habit-forming drug and carries with it the added disadvantage of such drugs—the need of conforming with the proper legal exactions of the Harrison narcotic law. Other disadvantages are often cited, but these two may be considered as of prime import.

Substitutes for cocaine (and we here refer to synthetic organic compounds) should satisfy the following requirements:

(1) They must be less toxic than cocaine in proportion to their local anesthetic action.

(2) They must not cause irritation or tissue injury, and largely for these reasons compounds that react strongly acid or alkaline are not used.

(3) They must be water-soluble, and give solutions sufficiently stable to be sterilizable by boiling.

(4) They must be compatible (possible of mixing without serious alteration) with adrenalin. Adrenalin is an organic compound obtainable from the suprarenal glands and is also prepared synthetically. It has the extremely valuable property of constricting blood vessels. This not only renders the tissues of an area comparatively bloodless during operation, but also increases local anesthesia and decreases the general toxic action by reducing the rate of absorption by the system.

(5) For particular operations involving mucous membranes they must be able to penetrate rapidly.

For such mucous membrane work as eye, nose, and throat the anesthetic is applied topically, being absorbed directly from a wad moistened with the compound. For most other work the solution is injected. The cost factor, on the whole, is not always of major consequence: someone has made the trite remark that although ether is more expensive than chloroform in general anesthesia it is less costly than a funeral.

The success which has attended the efforts of organic chemists in this field has naturally developed from the methods of attack, which have been followed in the solution of related problems.

Essentially this is the problem. Cocaine is a naturally occurring organic compound with certain physiological properties, particularly that of producing local anesthesia. It has some inherent defects which must be remedied or circumvented. Inasmuch as cocaine is a pure organic compound this involves either an alteration of the cocaine molecule or the synthesis of new compounds having at least the desirable properties of cocaine with few or none of its disadvantages.

Method of Attack

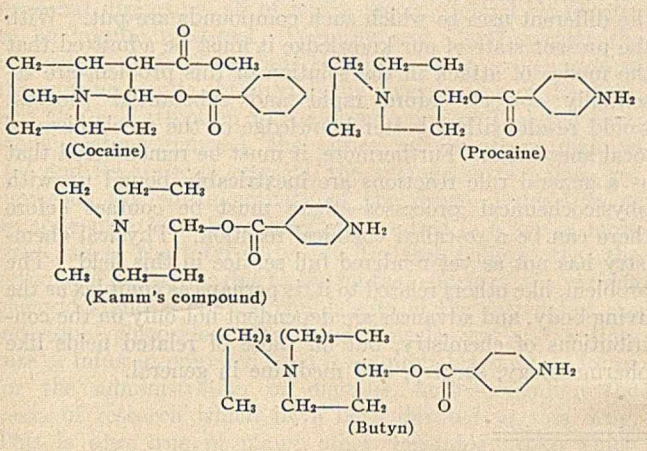
With such problems the first procedure is one of analysis. This involves in order: separation and purification, qualitative analysis, quantitative analysis, and molecular weight determination. From these the molecular formula can be obtained. The work has only begun, for the molecular formula alone is essentially worthless with complex organic compounds, such as cocaine, $C_{17}H_{21}O_4N$. The structural or constitutional formula, which shows the manner of arrangement of atoms and groups in the molecule, must next be determined. This is arrived at by a process of analysis or fragmentation, the breaking down of the molecule by standard reactions into reasonably large parts which are isolated and then identified by reference to previously known compounds. Generally, this structure is confirmed by a synthesis using known compounds and standard or reliable reactions.

That which follows is essentially empirical at first. Alterations are made in the disposition or arrangement of groups in the molecule, in the kind, and number of groups. After each new compound has been made it is pharmacologically tested, at first on lower animals, to determine the effect of such changes on the physiological properties. In this way we arrive at certain rules or generalizations which serve to correlate physiological action with chemical constitution. With new drugs this involves the synthesis of many new compounds, first, in order to determine the effect of variations in structure, and second, if we would synthesize a substance with optimum physiological properties. A large proportion of these compounds may appear to be of doubtful value. The method is orderly, rational, scientific, and, for the present, inevitable. Arsphenamine, or "606," the organic compound so widely used in syphilis and allied diseases, is one of the most important drugs the world now has and only came into being after Ehrlich had previously prepared 605 solutions.

Procaine

Following the methods of procedure just indicated, chemists have synthesized a number of organic compounds whose physiological properties have warranted their rather wide

adoption in medicine. Foremost among these compounds is procaine, formerly known in this country as novocaine. It is the hydrochloride of the *p*-aminobenzoate of β-diethylaminoethyl alcohol. The hydrochlorides of these basic compounds are generally used, but for convenience the free bases are graphically presented for comparison.



It will be observed that procaine bears some structural resemblance to cocaine. There are a few essential differences. Procaine is simpler in the sense that it has not the "bridges" or cyclic structures so characteristic of cocaine. There is also a para-amino group in the benzene nucleus of procaine. A third difference is in the number of carbon atoms between the nitrogen and oxygen atoms. In cocaine there is a chain of 3 carbon atoms between the nitrogen and oxygen atoms, whereas in procaine there is a chain of only 2 carbon atoms between the corresponding nitrogen and oxygen atoms.

Kamm[1] forecasted that the introduction of another carbon atom between nitrogen and oxygen would give a compound whose physiological action would be intermediate between that of cocaine and procaine. This prediction of the action of a new compound by analogy to structures of known compounds was admirably substantiated. The compound, recently synthesized by Kamm, was found to be slightly more toxic than procaine but less toxic than cocaine; it was more effective for surface anesthesia than procaine but less effective than cocaine.

Butyn

Here, then, was a valuable clue for the synthesis of a compound that was to have the excellent property of cocaine for surface anesthesia. This property of surface penetration has limited the application of procaine in mucous membrane work. The need of such a compound in eye, nose, and throat work was urgent. As a result of the elegant synthetic work of Adams, Kamm and Volwiler,[2] butyn was prepared; it was selected as the best drug from some 40 compounds made by them. After a thorough and eminently satisfactory series of clinical tests, the compound is now used for mucous membrane work. Butyn is the sulfate of the *p*-aminobenzoate of γ-di-*n*-butylaminopropyl alcohol. This compound is probably the most important local anesthetic recently prepared. It is distinctly an American product, and was made possible by the excellent collaboration between the university, the drug house, and the physician. In passing, it might be mentioned that unpublished results indicate butyn to be less toxic than cocaine even when injected in man.

Other work has been done recently with compounds related to procaine. In a study of the effect of unsaturated groupings on local anesthetic action, Braun and Braunsdorf[3] have replaced one of the ethyl groups in procaine by an allyl group, and by a cinnamyl group. Both compounds were found to have a stronger anesthetic action than procaine. V. Braun has made many important contributions to our knowledge of local anesthetics and this is his most recent work. Prior to this Kamm and Volwiler[4] prepared the diallyl analogs of procaine and butyn. Osterberg and Kendall[5] have prepared the *o*-diethylamino-cyclohexanol ester of *p*-aminobenzoic acid, a homolog of procaine with larger molecular weight. No report has yet been made on the physiological action of this compound. Mention should be included here of apothesine, the cinnamate of γ-diethylaminopropyl alcohol, a product of American origin introduced during the war and used quite extensively.

Anesthesin

Another class of local anesthetics insoluble in water but used in powder form includes anesthesin, the ethyl ester of *p*-aminobenzoic acid. Brill[6] has prepared a series of related esters one of which, the *n*-butyl ester of *p*-aminobenzoic acid, is the subject of a patent by two drug manufacturers, one American and one French. Thoms and Ritsert[7] have studied the effect of replacing one of the amino hydrogen atoms of anesthesin by various positive and negative groups. Only in the case of ethyl *p*-hydrazinobenzoate, where a second amino group was substituted for a hydrogen atom, was the anesthetic action comparable with that of anesthesin. Altwegg and Landrivon[8] have patented the β-haloethylaminobenzoic esters and the corresponding compound obtainable by replacing the halogen by the diethylamino group. Adams and Volwiler[9] have prepared the allyl-*p*-aminobenzoate.

Benzyl Alcohol

Another class of local anesthetics owes its origin to the researches of Macht,[10] who, in connection with a study of the physiological action of various alkaloids, examined the anesthetic properties of benzyl alcohol and some of its simple derivatives. This field has been worked almost exclusively by Americans. Benzyl alcohol is used to a slight extent as a local anesthetic. A number of local anesthetics have additional valuable properties, such as antiseptic action and narcotic action. In this connection it should be said that various esters of benzyl alcohol are very useful as anti-spasmodics. Recent work has indicated a close, but not complete, correlation between the anti-spasmodic action and the rate of hydrolysis of these benzyl esters.[11]

Other Local Anesthetics

The success of Macht and co-workers with benzyl alcohol has served to extend our knowledge of the local anesthetic properties of related compounds. Hjort and collaborators, in a study of various aromatic alcohols, have found benzoyl carbinol to be quite effective as a local anesthetic.[12] A series of related studies by Hirschfelder[13] and co-workers has shown the practicability of saligenin as a surgical anesthetic. Very favorable clinical reports have recently been made of this compound.

[1] *J. Am. Chem. Soc.*, **42** (1920), 1030.

[2] U. S. Patent 1,358,751; *C. A.*, **15** (1921), 412. Clinical report by Bulson in *J. Am. Med. Assoc.*, **1922**, 78, 343.

[3] *Ber.*, **54B** (1921), 2081; *C. A.*, **16** (1922), 1084.

[4] U. S. Patent 1,388,573; *C. A.*, **16** (1922), 990.

[5] *J. Am. Chem. Soc.*, **43** (1921), 1370.

[6] *Ibid.*, **43** (1921), 1320.

[7] *Ber. pharm. Ges.*, **31** (1921), 65; *C. A.*, **15** (1921), 2851.

[8] *C. A.*, **14** (1920), 1595.

[9] U. S. Patent 1,360,994; *C. A.* **15** (1921), 575.

[10] *J. Pharmacol.*, **12** (1918), 263; *C. A.*, **13** (1919), 41.

[11] Nielsen and Higgins, *J. Lab. Clin. Med.*, **7** (1922), 1; Volwiler and Vliet, *J. Am. Chem. Soc.*, **43** (1921), 1672; Schonle and Row, *Ibid.*, **43** (1921), 361.

[12] *Science*, **51** (1920), 497; *C. A.*, **14** (1920), 3476.

[13] *J. Pharmacol.*, **15** (1920), 261; *C. A.*, **15** (1921), 274.

Two products of French origin, stovaine and alypin, have found use in other countries. They may be considered as typical of still another class of local anesthetics. Recent papers on such compounds have been published by Fourneau[14] and by Launoy and Fujimori.[15] Pharmacological tests indicate that the compounds described are of doubtful value.

Two new local anesthetics, the hydrochlorides of nevralteine and its methyl derivative, have been studied by Valenti.[16] They are described as having marked anesthetic properties.

Mention should be made of recent work by Japanese authors. A pharmacological examination by Kubota[17] of allocaine-S, a new local anesthetic, has shown this amino ester to be of limited use. Ogata,[18] in a study of a large number of amines, has shown that both aromatic and aliphatic amines have anesthetic power provided that at least one of seven or more carbon atoms is attached to nitrogen.

[14] *Bull. soc. chim.*, **29**, 413; *C. A.*, **15** (1921), 3876.
[15] *Compt. rend. soc. biol.*, **82** (1919), 732; *C. A.*, **14** (1920), 3462.
[16] *Arch. farm. sper.*, **25** (1918); *C. A.*, **14** (1920), 775.
[17] *J. Pharmacol.*, **12** (1919), 361; *C. A.*, **13** (1919), 2246.
[18] *J. Pharm. Soc. Jap.*, **456** (1920), 81; *C. A.*, **14** (1919), 3476.

With our present knowledge of the relationships between physiological action and chemical constitution, it would be extraordinarily disappointing to some to omit the stereotyped remark that the ideal local anesthetic has not been found. It is quite possible that there is not one ideal local anesthetic; it is more probable that there are several when one considers the different uses to which such compounds are put. With the present state of our knowledge it must be admitted that the modes of attack in the solution of this problem are essentially correct. More rapid and substantial progress would result with a better knowledge of the mechanism of local anesthesia. Furthermore, it must be remembered that as a general rule reactions are inextricably bound up with physicochemical processes—there must be contact before there can be a so-called chemical reaction. Physical chemistry has not as yet rendered full service in this field. The problem, like others related to it, is perhaps as complex as the living body, and advances are dependent not only on the contributions of chemistry, but on those of related fields like pharmacology, surgery, and medicine in general.

Pharmaceutical Chemistry

By Frank R. Eldred

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THE COMPLEXITY of the problems of life in health and disease is a serious limiting factor in the progress toward more efficient remedial agents. The important advances in this field have usually resulted from the work of many individuals trained not only in chemistry but also in the various branches of biology and medicine. Chemical studies undertaken with no thought of their bearing upon the treatment of disease often supply the foundations for the development of most valuable medicinal products.

Frank R. Eldred

In an attempt to inventory our progress in medicinal chemistry we are confronted by a vast number of individual researches which contribute directly or indirectly to our knowledge of disease and its treatment by chemical agencies. Progress is probably more rapid than at any previous time, owing to the widespread interest in the subject and to the application of newly discovered chemical principles; nevertheless if we had some adequate means for coördinating the work of the army of clinicians, pharmacologists, biologists, and chemists upon whose researches the health and happiness of the human race are so largely dependent, the rate of progress would be increased many fold. Any lack of coördination and coöperation in the attack upon disease constitutes a tragedy many times reënacted.

An example of the time that may elapse between the synthesis of a new compound and the discovery of its physiological properties is afforded by the anti-oxime of perillaldehyde, which was prepared in the laboratory of a German chemical plant in 1910 and nine years later was made the subject of a Japanese patent on account of its sweetening power, which is said to be from four to eight times as great as that of saccharin.

It is consequently difficult to evaluate the progress in this field during any definite period or to give credit to those whose work may lead to most important discoveries. In the limits of this brief review no attempt has been made to give complete references or credit for progress to which many workers have contributed.

During the last two years there has been the usual flood of new remedies, but comparatively few of these represent real progress while many of them are distinctly inferior to products already available.

In many instances there is a marked tendency to return to older forms of medication, which have in the meantime been largely replaced by newer remedies or "pure principles." Some of the so-called pure principles fail to represent the activity of the crude product from which they are derived, thus disclosing the need for further knowledge of the chemistry of the parent product as well as of the substances that can be prepared from it. This is especially true of the crude vegetable drugs, since in the preparation of "pure" plant principles physical and chemical changes take place, with the resulting destruction of the original colloidal complexes and accompanying changes in the solubilities of active constituents and their absorption when administered to animals. John Uri Lloyd was a pioneer in pointing out these facts and has made many valuable observations upon the colloidal nature of plant constituents. His original studies, published in the *Proceedings of the American Pharmaceutical Association*, 1876–1889, are very interesting in the light of recent developments.

Digitalis offers an excellent example of the failure to isolate substances which fully represent the physiological activity of

the plant. Probably no drug has a more voluminous literature than digitalis, which has been the subject of extensive researches by Schmiedeberg, Kiliani, Cloetta, Kraft, and many others. Cloetta[1] now reports the isolation of pure crystalline digitoxin which differs from any of the previously prepared digitoxins, all of which are considered by Cloetta to be impure mixtures. Pomeroy and Heyl[2] suggest the ready hydrolysis of digitalis principles as an explanation of the varying results obtained in the investigation of the drug, and also call attention to the observation of Tschirch that, while acetone removes the entire activity from digitalis leaf and its aqueous extracts, the acetone extract does not represent the entire activity of the drug. Extraction of an aqueous extract by chloroform resulted in a loss of more than half of the total activity. Tschirch believes that the activity of digitalis is due to the mutual effects of the various glucosides and is not the simple sum of the activity of the individual glucosides. Powdered digitalis leaf and a tincture or infusion prepared from it are probably the best forms for the administration of digitalis, notwithstanding the years of research which have been devoted to this drug. This is also true of many other vegetable drugs which are imperfectly represented by the constituents that have been isolated or from which no active principle has been separated.

Although there is a vast accumulation of data upon the composition of plants, we know very little about the exact physical condition and chemical composition of the substances as they exist in the plant cell before any changes have taken place. The methods which Osborne and his co-workers[3] applied in the investigation of fresh spinach and alfalfa would undoubtedly yield valuable results if employed in the analysis of vegetable drugs.

Cod-liver oil, always popular with the laity, had for a long time been neglected by the medical profession until it was found to be very rich in vitamin-A. Since this discovery was made its use has been constantly increasing and its properties have been generally ascribed to its vitamin content. It has been shown to have a marked effect upon the calcium metabolism, but this property is probably not due to vitamin-A, since cod-liver oil is much more effective than butter fat in preventing rachitic conditions, even when the latter is added to the diet in sufficient quantities to supply much more than the normal requirement of vitamin-A.[4] It has also been reported that cod-liver oil retains its antirachitic properties after the destruction of vitamin-A by exposure to heat and air. It is probable that the physiological effects of cod-liver oil are due in part to its unsaturated fatty acids and its iodine content. It is interesting to note that the American Relief Administration in Russia is supplying cod-liver oil to many day nurseries and children's homes.

Chaulmoogra oil which has been used for many years in the treatment of leprosy with indifferent success has acquired new interest since the preparation of the ethyl esters and sodium salts of the unsaturated acids has made it possible to administer the remedy intramuscularly. Brilliant results are being obtained and the treatment seems to be specific in leprosy.

The administration of substances by inhalation for their systemic effects was suggested by the studies of war gases and in some cases this may prove to be a valuable means of treatment. A rather crude attempt is the proposed treatment of tuberculosis by the inhalation of finely divided calcium carbonate. James Todd[5] has made interesting experiments on the treatment of infected animals by inhalation of ozonized air, and has followed this, with the coöperation of physicians, by the treatment of human cases of tuberculosis and other germ diseases with ozonized oils.

The physiological effects of benzyl alcohol and its esters were studied by Macht who found that they had a relaxing effect on smooth muscle. Together with the known benzyl esters, a number of new benzyl compounds having the typical benzyl effect have been utilized with success in the treatment of many conditions where a sedative action on smooth muscle tissue is desired.

The relative toxicity of a number of alcohols has been determined by Macht,[6] who found an increasing toxicity in the series methyl, ethyl, propyl, butyl, and amyl. The secondary alcohols were less toxic than the corresponding primary alcohols. Kamm[7] tested the normal alcohols on *Paramecia* and reduced his results as well as those of Macht to the numerical expression $1 : 3 : 3^2 : 3^3 : 3^4$--, the molar toxicity of any member of the series being three times that of the preceding member.

Pure isopropyl alcohol is now available in such quantities that it can be used, where applicable, as a substitute for ethyl alcohol. Although more poisonous than ethyl alcohol, it is also more active as an antiseptic and it might therefore replace ethyl alcohol where used for its preservative action.

Denatured alcohol is finding wider use in the manufacture of medicinal products and in the interest of economy its use will no doubt be further extended.

The autoxidation of ethyl ether, with the formation of ether peroxide, hydrogen peroxide, aldehyde, and acetic acid, which is described by Clover,[8] may have an important bearing on its use as an anesthetic. The oxidation is greatly accelerated by light.

A number of dyes, particularly the acridine dyes, find a continually increasing use as antiseptics. Further studies in the acridine series have led to the preparation of 2-ethoxy-6,9-diaminoacridine, which is said to be superior to the acridine compounds now in use. A number of other dyes have been found to be active germicides. Mercurochrome, dibromo-oxymercury-fluorescein, seems to be a very useful urinary antiseptic and Hirschfelder[9] has found the mercury compounds of saligenin and of *p*-hydroxy-*m*-nitrophenyl carbinol to be effective as antiseptics. Johnson and Lane[10] have prepared several new derivatives of resorcinol, and have found that the phenol coefficients of the series, *viz.*, resorcinol, ethyl resorcinol, *n*-propyl resorcinol, *n*-butyl resorcinol, increase in the following order 0.3, 1.5, 4.3, 8.0. This observation will be of value in future work on antiseptics. The comparative toxicity of germicides to bacteria of different species, or even different strains, is not constant. The application of this "specificity of disinfectants" to the practical testing and use of germicides was first emphasized by Walters.[11] It has been found that even the various chlorine disinfectants differ greatly in their relative toxicity to various organisms. Attention is called to the efficiency of steam-distilled pine oil in killing *B. typhosus* and the high resistance of *M. aureus* and *B. anthracis* to this agent.[12]

Cymene and piperitone, a constituent of certain eucalyptus oils, may serve as sources for the commercial production of thymol, one of the valuable remedies in hookworm infections. Carvacrol has been found to be fully as effective as

[1] *J. Chem. Soc.*, **120**, 1 (1921), 39.
[2] *Am. J. Pharm.*, **92** (1920), 394.
[3] *J. Biol. Chem.*, **42** (1920), 1; **49** (1921), 63.
[4] *Ibid.*, **50** (1922), 5.
[5] "Experiments with Oxygen in Disease," Pittsburgh, Pa., **1921**.
[6] *C. A.*, **15** (1921), 122.
[7] *Science*, **54** (1921), 55.
[8] *J. Am. Chem. Soc.*, **44** (1922), 1107.
[9] *Ibid.*, **42** (1920), 2678.
[10] *Ibid.*, **43** (1921), 348.
[11] *Am. J. Pub. Health*, **7** (1917), 1030.
[12] *U. S. Dept. Agr., Bur. Chem., Bull.* **989** (1921), 11.

thymol, and since it can be readily prepared from cymene, it should find extensive use. Chloroform and carbon tetrachloride have also been successfully used in hookworm infection.

Cinchophen continues to increase in popularity and a number of closely related compounds have been placed on the market. Bogert and Abrahamson[13] suggest that a new thiazole derivative which they have prepared, 2-phenylbenzothiazole-6-carboxylic acid, may, from its analogy to cinchophen, have similar physiological properties.

A number of new barbituric acid derivatives have been prepared and some of them have been placed on the market, but barbital seems to be fully as efficient as any of the newer derivatives. Luminal has been found particularly valuable in epilepsy.

The organic arsenic derivatives are the subject of much important research. Arsphenamine and neoarsphenamine remain as the most valuable remedies in syphilis, although promising results have been attained with some of the newer compounds. Much progress has been made in the methods of manufacturing and testing arsphenamine and neoarsphenamine, and products less toxic than the original imported products are now available. Stieglitz and co-workers[14] have prepared 5,5′-mercuri-bis-3-nitro-4-hydroxyphenylarsonic acid and are continuing the investigation with the object of producing a compound for therapeutic use containing both arsenic and mercury.

Bismuth, administered intramuscularly, in the form of potassium and sodium tartrobismuthate suspended in oil or bismuth and ammonium citrate in aqueous solution, is reported to act as a specific in syphilis.

Extensive researches have been devoted to the cinchona alkaloids. Jacobs and Heidelberger have prepared many new derivatives in the cinchona series with the object of finding compounds that will have a specific action in pneumonia. Through the studies of Bass, the quinine treatment of malaria has become much more effective, but it is not improbable that some new derivative of the cinchona alkaloids will be found which will be even more efficient than quinine. An alkaloidal product from *Lobelia inflata* prepared by a patented process is now on the market. Wieland,[15] who studied the alkaloids of lobelia, isolated two crystalline alkaloids, lobeline and lobelidine. These alkaloids will probably be useful therapeutic agents. Cushny has made the interesting observation that *l*-hyoscine is 15 to 18 times as active as *d*-hyoscine as a mydriatic, but that the two forms are identical in their action on the central nervous system and therefore in their production of "twilight sleep."

Karrer[16] and co-workers have prepared a number of new amino alcohols and cholines, some of which have an action on the uterus similar to that of ergot. Shepherd's-purse (*Capsella bursa-pastoris*), which was used during the war as a substitute for ergot, has been found to contain choline and acetylcholine; the presence of tyramine is regarded as probable and that of histamine doubtful.

The manufacture of digestive enzymes from animal sources has been carried on chiefly for medicinal preparations but they are now being used in increasing quantities in the food, leather, and textile industries.

The use of gland extracts in medicine is rapidly increasing and valuable contributions are being made to our knowledge of the composition of these extracts. Notable among such studies is the work of Kendall on thyroxin, the active substance of the thyroid gland. A concentrated preparation of the internal secretion of the pancreas is said to have been used with remarkable success in cases of diabetes. The active principles of the pituitary have not yet been determined, although much progress has been made by Abel, Dale, Dudley, and others. Drummond and Cannan[17] state that tethelin is an impure mixture of lipoids, and that the anterior lobe of the pituitary does not seem to influence growth. Ovarian and placental extracts have been found very useful in disturbances of menstruation and pregnancy.

Vitamins are to be considered from the standpoint of foods, as cod-liver oil and certain yeast preparations are the only useful vitamin-containing products that can be classed as medicines. It is possible that with further knowledge of the functions of vitamins and their separation from plant and animal products, vitamin preparations will become valuable as medicines.

McClendon[18] has suggested that our use of refined table salt is a mistake, and that it might be well to substitute a sterilized sea salt which would supply not only iodine, but also numerous other elements which may be deficient in the diet.

The relation of calcium metabolism to rickets has been the subject of much study. Sunlight has been found to have an effect similar to that of cod-liver oil on rachitic animals. Mason states that calcium chloride is better absorbed than calcium lactate and it is interesting to note that a single dose of cod-liver oil administered with the lactate seemed to increase the absorption of calcium.

Colloidal metals have been used, in many cases with apparent success, in combating various infections. Colloidal antimony is reported as being very efficacious in the treatment of leprosy.

Corresponding to the toxic relations between arsenic and arsenious acids, the ions of selenious and tellurious acids have been found to be much more effective in killing bacteria than the ions of selenic and telluric acids. Germanium dioxide has been found to stimulate the formation of red blood-cells.

Viewing the manufacture of medicinal products from an industrial standpoint, small-scale operations are the rule and engineering and factory practice is frequently not up to the standard required for larger operations. Much can be gained by a careful study of the methods employed in other branches of chemical industry where success is dependent upon progress in engineering and upon economical management.

[13] *J. Am. Chem. Soc.*, **44** (1922), 826.
[14] *Ibid.*, **43** (1921), 1185.
[15] *Ber.*, **54** (1921), 1784.
[16] *J. Chem. Soc.*, **120**, 1 (1921), 228.
[17] *C. A.*, **16** (1922), 1974.
[18] *Science*, **55** (1922), 358.

Final arrangements have now been completed for the sulfur investigations to be administered by the Crop Protection Institute, utilizing funds supplied by the Union Sulphur Co., the Freeport Sulphur Co., and the Texas Gulf Sulphur Company. The phytopathological phase of the work will be carried out by Mr. H. C. Young at the Missouri Botanical Garden, St. Louis, under the direction of Dr. B. M. Duggar. Approach to this phase of the project will be along the line of the fundamental effects of temperature, moisture, and other conditions on the fungicidal action of sulfur. The entomological phase of the investigation will be conducted at the Geneva, N. Y., Experiment Station and in part at Ohio State University, by Mr. F. H. Lathrop, under the direction of Prof. P. J. Parrott and Dr. Herbert Osborn. Each phase of the project will run for two years, during which time it is expected that substantial progress will be made and real contributions to the knowledge and use of sulfur will be achieved.

After constituting for almost four years a division of the Czechoslovak Federation of the Chemical Industry, the dyestuffs-producing interests of Czechoslovakia have become associated in an independent federation, to be allied with the Federation of Czechoslovak Industrialists. This separate organization was considered necessary for closer unity with respect to customs needs and the operation of the commercial agreement with Germany. The federation comprises seven sections divided according to nature and use of products.

Chemistry as an Aid to the Tobacco Industry

By A. L. Chesley

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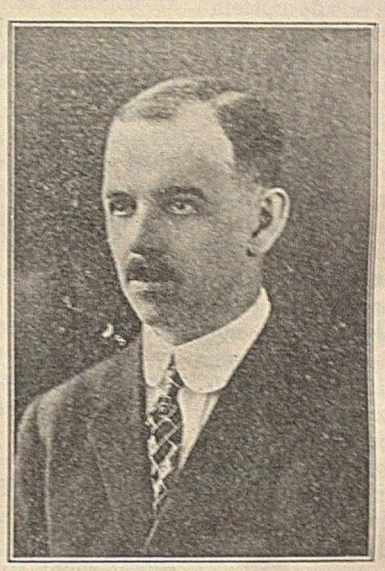
IT IS OFTEN asked, "What need has the tobacco industry for a chemist?" Every process, every treatment that tobacco undergoes, from the time the seed is planted until the cured and aged tobacco is ready for the consumer, is based on chemical reactions and changes. A few of these are understood, but in most cases neither the cause nor effect is known. For instance, what causes Turkish tobacco grown in Turkey to have an entirely different aroma from tobacco grown in the same way and from the same seed in California? Why will not plants grown in Cuba, and transplanted into Florida with Cuban soil around the roots, mature into the same quality of leaf as if they had matured in Cuba? Why are Sumatra wrappers grown in Florida thicker and heavier bodied than those grown in Sumatra? Could these questions be answered it would be a great boon to the tobacco industry; but because tobacco is such a complex product of nature, and so many things, such as color, aroma, burning properties, body, toughness, and pliability, have a direct bearing on the quality of the leaf and the sale of the manufactured article, chemists have not been able to make the great strides in aiding, controlling, and improving the various primary processes that they have in other industries. The main reason for this is because the intricate chemical reactions carried on by the plant are but little understood, and there are many variables to contend with.



A. L. Chesley

Tobacco Growers' Problems

But let us see what the chemist has accomplished. If we take up the primary processes, we find many instances where he has been of great aid to progress in this industry. His knowledge was needed in solving the fertilizer problem. The ratio of ammonia, phosphoric acid, and potash in the fertilizer is of great importance and must be controlled to suit the type of tobacco raised far more closely than in growing most crops. Too much plant food is as injurious as too little. Lack of ammonia causes the growth to be backward, and to obtain a good quality the growth must be rapid and uninterrupted. Too much ammonia makes it very strong, dark in color, and increases the nicotine content. A fertilizer deficient in potash or containing chlorides will cause the tobacco to be of poor burning quality. While an excess of sulfates is harmful, they are not as injurious as chlorides. A large cigar company has just issued instructions to its representatives in Porto Rico to reduce the amount of ammonia in the fertilizer in order to obtain leaf of lighter color. The custom was to use lime with the fertilizer to improve the burning quality. It was found, however, that alkaline materials create conditions favorable to certain fungus diseases, especially root rot. To-day this class of materials is not used except when it is impossible to obtain the desired quality in any other way. The source of the fertilizer has a great deal to do with the various qualities of the leaf. Stable manure, for instance, should not be used where a very light color is desired; it also increases the chlorine content of the leaf.

After the "topping" process, which means the cutting off of the flower bud, the leaves become thicker, heavier, brittle, and begin to droop. This is also a sign of maturity. The reason for it has been shown to be that the plant food which ordinarily would be carried into the flower and seeds is forced into the leaf. Thus chemistry has explained why "topping" produces a larger and better bodied leaf than by allowing the plant to pursue its natural course.

In the curing of most plants, the only object is to bring about such a condition that the material can be stored until the next crop without deteriorating. In the curing of tobacco, besides the storage qualities, there are more important objects to be attained, production of a good aroma and light color, fixing the color, and securing a tough and supple leaf. Curing was formerly accomplished by building a fire underneath the leaves and allowing the smoke to escape through them. To-day only export tobacco is cured in this manner. Tobacco for home consumption is cured by evaporating the moisture in the plant juices in such a manner that the life processes of the plant will continue to function until certain food materials have been consumed and other compounds produced in their place. In some methods of curing the sugars remain and in others they disappear; citric, malic, and oxalic acids are produced from the sugars; later these are changed to a large extent into carbon dioxide and water; citric acid is not as readily oxidized during this change as the other two. In another method the acetic acid increases six times and the nitric acid decreases one-half. In another there is a transmigration of the salts through the veins to the midrib and into the stalk.

You have often seen a cigarette sputter while held in the hand, and have probably thought it due to added potassium nitrate. This is not so, but is due to a crystal of potassium nitrate which occurs naturally in the tobacco. As much as 2 per cent of potassium nitrate is found along the midrib. Years ago it was the custom to add potassium nitrate to improve leaf of poor burning quality. To-day this is made unnecessary by the use of proper fertilizers and control of the growth and curing of the leaf.

While many of the changes that take place are known, it has not been possible to induce them by artificial means or even to shorten the time necessary for them to take place. Several processes have been patented, for which startling claims have been made, but they have proved to be of no value. As a rule they only injured the tobacco so it was not suitable for use.

It has been possible to aid by controlling the temperature and humidity so that those conditions which best suit the production of these changes may be obtained under adverse climatic conditions. To-day all large growers have modern curing barns so they can keep the temperature in the barn slightly higher than the outside temperature, thus increasing

the moisture absorptive power of the air. On the other hand, as the changes during curing are chemical, the air must not have too great a drying power or the changes will not take place.

Protection of Brands

The chemist in the tobacco industry is concerned with everything entering into the manufacture of the various brands and the placing of them upon the market, but the tobacco itself. The main assets of a tobacco concern are its brands; therefore, one of his chief duties is to keep up the standard of those brands. There is probably nothing in which slight changes are so noticeable as in tobacco smoke. The manufacturer has learned by experience, and often to the detriment of his profits, that he must keep his brands uniform in every way from day to day, and it is along this line that the chemist is of the greatest value. It is here where the greatest progress has been made.

Many supplies are peculiar to the industry itself. For some of them no standards had been set. Even the suppliers, in some instances, had no knowledge of the quality of their products. To-day, in our company, every supply must first pass the test of quality before it can be purchased. Even the suppliers themselves have to a certain extent been investigated. Preference is often given to the one who has proved that his quality can always be depended upon, even when his price is slightly higher and another's sample analyzes equally as good. Thus, after the first few years, supplies below standard decreased; so that one year but 30 samples were received that were below requirements, and most of these were rejected before purchase. Suppliers learned that the quality of their goods was being watched and took care to see that their goods met our specifications. Since the war there has been quite an increase due principally to competition and to stocks bought for speculation.

Fading of Lithographs

Probably the largest single piece of research undertaken during the last two years was on the fading of lithographs. At the time the matter was agitated it caused quite a furor among ink manufacturers. They claimed there was no need of it, that their inks were permanent and they would guarantee them. They would not, however, back their guarantee with cold cash, using the argument that they did not have control of the paste, or that the posters might be exposed where fumes would cause fading. A concern had suffered because of the fading quality of the ink used on its lithographs. It received reimbursement for the posters but not for the posting. A national posting is for 30 days and costs about $275,000, the posters costing about $25,000. Obtaining reimbursement for the cost of the posters is not much satisfaction when the entire outlay is considered. As no concern would guarantee us against this loss, it became necessary to find some way to protect ourselves. We made over 1000 tests on a billboard, through the months of June, July, and August, with inks of known composition, and compared the results with tests made on the Fade-O-Meter. As the humidity and temperature around New York City is the most trying on lithograph inks, it was only necessary to find the equivalent for this section in order to protect ourselves all over the United States. It was found that 50 hrs. on the Fade-O-Meter were equivalent to 30 days on a billboard having a southern exposure for these months in this vicinity, and would protect us in practically every instance. It was also found in these tests that a color would have different fading qualities according to the other ingredients used with it, and that some supposedly fast inks would fade. The Fade-O-Meter Company has since published results showing that 40 hrs. are equivalent to 30 days' posting in Chicago.

Cigarette Paper

Outside of tobacco, the most important article used in cigarette manufacture is the paper. It must be odorless, tasteless, of sufficient opaqueness, and burn evenly with the tobacco. This paper, except a small quantity used for special purposes, is made of pure linen stock and an inert filler, calcium carbonate. The latter is necessary to give the necessary whiteness to the paper, prevent air being drawn through it, and make it burn readily. During the war there was a great deal of trouble with poor burning paper. Very often cigarettes which would not stay lighted would be found on the market. The trouble was found to be in the purity of the filler. It really should not be called an impurity as it had always been allowed, and some manufacturers claimed it to be beneficial. It was found, however, that in the amounts in which it was occurring it had a fireproofing action which varied according to the type of tobacco in the cigarette. Tests were immediately made in all factories on every reel of paper. One factory alone rejected 1000 reels, which would have made 40,000,000 cigarettes. The effect on the brands of this large amount of bad burning cigarettes can be imagined.

At about the same time cigarettes having a foreign odor appeared on the market. This odor was also located in the paper, and tests were installed in the factories to prevent any such paper being used. The cause was not determined until some time later when it was traced to the bleach used in the cleaning of the linen stock. Almost all cigarette paper comes from France, and the manufacturer, because of war conditions, had to find a new supply of bleach. This he obtained from Switzerland where spring water was used in its manufacture. This water contained a trace of iodine compounds which caused the trouble. It was not possible to get an iodine reaction in the paper itself, the quantity present was so slight, yet the odor was noticeable in the smoke.

In times past, manufacturers of cigarette paper, it is said, have used potassium nitrate to aid the burning quality. This is absolutely unnecessary when the paper is properly manufactured, and the right quality of stock is used. A cigarette paper containing potassium nitrate indicates that the manufacturer does not know how to control his process or he is trying to cover up a case of poor manufacture. It is useless to test paper which has been taken from cigarettes for nitrates, as nitrates occur naturally in tobacco and the paper often absorbs a sufficient quantity to give the reaction. Because of these war troubles a great deal of work was done, and is still being done, on cigarette paper. As a result there are but one or two manufacturers who make a paper considered satisfactory for our use. Some time ago, a manufacturer wrote that he was glad he had at last got the quality of his paper so that it satisfied the chemical department.

Adhesives

The matter of adhesives is a very important one with a tobacco concern, as they have to be of many qualities and kinds. Each purpose and each type of machine require an adhesive of special properties. Two of the most important properties are that they shall be odorless and transparent. A short time ago the concern furnishing paste used in cork-tipping cigarettes went out of business. No other concern was making this paste as this concern had developed it for this special purpose. This paste had already been analyzed and by modifying a paste used for another purpose our needs were immediately met. In another instance the revenue stamps were not adhering properly to the cigarette shells. It was found that because of the printing ink used, the paste did not contain enough water to penetrate the surface of the shell before it had dried. For sealing shipping containers, research

was carried out on various grades of sodium silicate on the market. It was found we could get a better bond, increase the speed of the men, and use less silicate by getting the right kind. In some instances there was a difference of 50 per cent in the number of containers sealed by two different silicates. When the last railroad strike occurred, a supply of paste for use in attaching labels at one of our southern factories was delayed. The lack of this paste meant shutting down the entire factory. A formula had previously been worked out for a similar paste, but it was not being used. This factory was able to run the entire time by getting in its raw materials by parcel post and making its own paste. While the actual value of this cannot be figured in dollars and cents, the loss a shutdown would have entailed will probably cover the cost of the department for some time. This factory is now making its own paste at a saving of about $7500 a year. The savings on adhesives alone since the chemical department has been in existence, figured on an accumulative basis, are approximately $75,000.

In order to better protect cigarettes from drying out, a layer of paraffin was used for pasting the paper to the tinfoil. During the summer months complaints were received about cigarettes being stained. It was found that although the melting point of the paraffin was 130° F., if kept at 119° F., it would become fluid enough to soak through the paper. Furthermore, a container placed in the sun would absorb sufficient heat, so that, with a temperature of 89° F. in the open air, the temperature in the container reached 122° F. It was further found that in a mixture of two paraffins of different melting points, the staining point was about six degrees below the lower melting point.

Control of Moisture Content

Up to two years ago we were receiving a material which varied very greatly in the amount of moisture it contained, mechanical impurities, and condition in which it was received. As a result there was a loss of 15 to 20 per cent on all that was bought. The handling of the material was costly. It was very hard to tell whether we were using the same quantity each time or not, and getting the material out of the containers was difficult. Often it would be fermented and have to be thrown away or would have a scorched taste because the evaporation had not been properly controlled. It was claimed that we could not obtain this material in any other way, inasmuch as it would be impossible to educate the producers, who are mostly small farmers. This material is maple sugar, many pounds of which are used each year by the tobacco industry. Our present specifications call for it to be put up in boxes of 60 lbs. each, lined with paraffined paper, to contain not over 7 per cent of moisture and not more than 6 per cent of invert sugar. The amount of invert sugar is a guide as to what temperature the evaporation has been carried, and as to whether the sap used was fresh or fermented. To be sure, we have to pay a higher price but the quality is worth the increased cost.

Few materials are so affected by changes of humidity as tobacco. It will take up or give off moisture very readily. The writer has found that if conditions are favorable, tobacco will take on moisture until it contains as much as 30 per cent. Being high in nitrogenous matters, when the moisture content becomes too high it is apt to mold. It is therefore necessary for tobacco concerns to manufacture their goods under absolutely sanitary conditions to prevent a very large loss in returned goods. It has been found necessary in one or two instances, especially in cigar factories, to close the factory and fumigate with formaldehyde to get rid of the mold spores. To-day probably 99 per cent of the tobacco which becomes moldy is through no fault of manufacture, but because of the conditions in small retail stores. Yet, the manufacturer, in order to protect his brands, must keep moldy goods off the market and suffer the loss for which he is not to blame. He has, however, made wonderful progress in this respect, when it is considered that the state of Texas probably accounts for 25 per cent of the moldy tobacco of the whole United States and the states bordering the Gulf of Mexico account for 75 per cent. Last fall the writer saw a box of tobacco manufactured in 1908, and although this had been in a retail dealer's store for twelve years the tobacco was in excellent condition. During the first three months of this year, cigarettes manufactured during 1921 showed but one moldy out of every 140,000 manufactured. When it is considered that some of these had been on the market for fourteen months, the extreme care used in manufacture and packing is evident. The manufacturer who does not understand thoroughly the necessity of the utmost cleanliness in his plants will find himself in all kinds of trouble.

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During the war we were shut off from the source of supply of a very important material. A similar product was native to America but had never been gathered. On testing out the American variety it was found to be perfectly suitable, and, if anything, better suited to our needs. Up to the present time we have been able to obtain all we need from American sources, and unless something unforeseen happens shall not return to the use of the foreign variety.

Thus the chemist has his place in the tobacco industry, and has assisted in its forward progress the same as he has elsewhere. Although he is not yet able to be of the assistance he would like to be in the maturing, curing, aging, and preparation of tobacco for the machines, because of his limited understanding of plant processes, there are problems arising every day where his services are of value. He cannot introduce the characteristics of one tobacco into another, make good burning tobacco out of poor, or light colored out of dark, for the reason that it is impossible to dissolve out one substance without removing others which are necessary, and he cannot add something to tobacco in the same way that nature does. The chemist has been of great assistance to the farmer in the control of his soil, fertilizer, and insect pests, and rotation of his crops to obtain the greatest yield. But if a manufacturer wants more Turkish he must import more; Virginia tobacco cannot be changed into Burley, or Burley into Perique. If a mellow tobacco is wanted it must age for from two to three years. Perhaps in the future the chemists will solve these problems.

Royalties received from the production of minerals on leased public lands are becoming quite an important item of Federal revenue. The Bureau of Mines reports receipts totaling $5,766,507 to June 30, 1922, from the production of oil, gas, and gasoline in the states of Wyoming, Montana, and California. Oil and gas royalties are now being reported in excess of half a million dollars per month, receipts for June 1922 amounting to $565,199. Royalties from the production of oil, amounting to $550,708, constitute the bulk of the June 1922 receipts. Royalties on gas amounted to $11,719, and on a natural-gas gasoline were $2771.

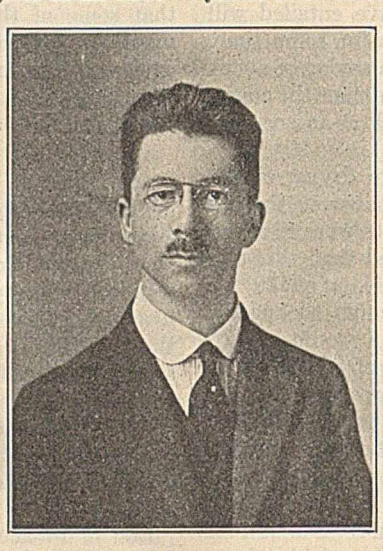
Reports made to the United States Bureau of Mines by all manufacturers of permissible explosives covering the year 1921 show that 93.5 per cent of such explosives sold during that year belong to the ammonium nitrate class. The total quantity of commercial ammonium nitrate used in permissible explosives during 1921 aggregated 25,381,500 lbs. The total quantity of nitroglycerin and "modified" nitroglycerin used in permissible explosives aggregated 3,974,000 lbs., for the manufacture of which approximately 1,766,000 lbs. of glycerol were used. By "modified" nitroglycerin is meant the products obtained by the nitration of a mixture of glycerol and certain compounds.

Recent Contributions of Chemistry to Photography

By S. E. Sheppard

Eastman Kodak Co., Rochester, N. Y.

ADVANCE in photography in the last two years has not been marked by radical innovations such as new processes, but rather by a deepening of knowledge of fundamental processes and the opening up of new points of view. At the same time the sum of progress in all directions, theoretical and applied, has been considerable. The reviewer has had to condense this article from a preliminary survey of some four times its present magnitude, and even then scant justice was done to the more important subjects. The present review is, therefore, selective; many interesting items must pass unnoticed, and others be only imperfectly documented.



S. E. Sheppard

Support or Base for Sensitive Coatings

Many new compositions of cellulose, and of its nitrates and acetates, have been patented, as well as new methods of manufacture of the acetates. The number of commercially available solvents appears to be increasing, and in this connection the hydrogenation derivatives of benzene and naphthalene show promise.

Gelatin and Emulsifying Media

During the past two years contributions of physical chemistry to the technology of gelatin and glue have continued. The writer has dealt recently with the role of gelatin in the photographic process,[1,*] and a brief account must suffice. The function of gelatin in photography has two main aspects: first, in emulsion making; second, as a colloid vehicle of the developable, developing, and developed image. Of the former, the statement of B. V. Storr[2] on the insufficiency of the physical properties as guides to the suitability of gelatins for emulsions and the relative unimportance of the more obvious chemical properties holds true. In this connection a paper by F. L. Seymour-Jones[3] on the "Chemical Constituents of Skin" deserves note as a compact and up-to-date account of the proteins and albuminoids of hide substance.

On the second count, progress has been steady. H. R. Procter's theory of swelling[4] as a function of chemical combination has been mathematically and experimentally confirmed by J. A. Wilson[5] and by J. Loeb.[6] The last named has cogently demonstrated the unique importance of the hydrogen-ion concentration for all primary physical and chemical reactions of the ampholyte, gelatin. Donnan's membrane equilibrium and the determination of pH are likely to assume almost as fundamental importance for photographic processes as for tanning. The depressing action of neutral salts on swelling in presence of alkaline developers is in agreement with this result.[7]

It is likely, however, that some part remains for the suspensoid colloid theory, particularly after treatment of gelatin with dehydrating and tanning agents. The important contributions of R. H. Bogue,[8] C. R. Smith,[9] and H. Oakes[10] to the structure theory of gelatin solutions and jellies demand notice in this same connection, as also the development of more precise methods of measurement of such properties as "jelly strength" (elasticity), "setting point," viscosity, etc.[11] Moreover, from the photographic standpoint, the nonisotropic character of the swelling and drying of gelatin jellies is of considerable importance, and the writer and F. A. Elliott[12] have suggested that this and certain hysteresis factors can be explained without internal structure theories.

While nothing has yet displaced gelatin as general carrier for sensitive salts, mention may be made of J. Rheinberger's[13] work on modifications of collodion, and on the Cellophane Company's[14] processes for utilizing viscose cellulose as carrier of silver halides, generally formed by impregnation.

Negative Emulsions, and the Latent Image

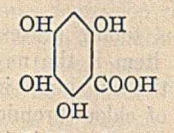
With respect to fundamental negative material of photography, the gelatino-silver bromide emulsion, no small progress is to be recorded. It was known that in coarser grained emulsions the grains were crystalline, and investigations in the Research Laboratory of the Eastman Kodak Company[15] have shown that the crystals are entirely of the regular system, and the diakisdo-decahedral class. This remains true for solid (homogeneous) solutions of bromide and iodide. Wilsey[16] has shown that the effect of the iodide is to change the lattice spacing somewhat, also that the grains of the finest colloid emulsions are crystalline, of the same system. The suggestion of Trivelli and Sheppard[17] that "silver iodide acts as a crystallization buffer substance* * * * restricting increase in size of grain" was confirmed by C. A. Schleussner and H. Beck[18] in a study of primary gelatino-iodo-bromide emulsions. Precipitation of iodide with bromide lessens the crystallization of the grains. They also note that the optimum iodide content depends upon the emulsification process, and lies between 1 and 5 per cent. An interesting optical sensitizing effect for red light by iodide (and cyanide), discovered by F. F. Renwick,[19] has been shown by Sheppard[20] to be specific to certain emulsions. While Renwick attributes it to a direct coagulating effect on silver amicrons already present, Sheppard suggests that it is due to an orienting effect of iodide on colloid silver formed by exposure itself. The panchromatic sensitizing by bathing plates in bisulfite followed by alkaline washing, observed by Capstaff and Bullock,[21] is also attributed to optical sensitizing by colloid silver, in line with Lüppo-Cramer's original discovery.

The distribution of sizes of grain in an emulsion as affecting its photographic properties, attention to which was first directed by Mees, has become the subject of important work. R. Slade and G. I. Higson[22] broke ground in this direction, correlating the steep gradation of "photomechanical process" plates with uniformity of grain size. This has been questioned by Renwick,[23] but seems to have a limited validity, provided the sensitivity distribution follows the size. The general question of the relation of sensitivity of grains to

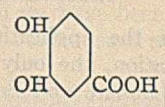
their size has been brought to the fore by The. Svedberg[24] and collaborators. This well-known colloid chemist introduced a very valuable method of grain analysis; preparing a one-grain layer, in a manner similar to that of other workers, after definite exposure steps and development he removed the developed silver grain with a silver solvent. He was thus able to determine by difference counts and size measurements the grains made developable by light (and other agencies, as X-rays, α-rays, hydrogen peroxide) and found not only that grains of the same size might have different sensitivity, but also that within the same emulsion the sensitivity increased with size of grain. The size-classification methods used by Svedberg were comparatively rough. More precise and closer methods have been developed and used by E. P. Wightman and S. E. Sheppard,[25] and by Wightman, Trivelli, and Sheppard,[26] by which the size-frequency curves of a large number of emulsions of widely differing "speeds," etc., have been measured. These results show again a very general correlation of "speed" with grain size. In their work Svedberg and Anderson found in the case of α-rays that the projective area of a grain determined its chance of being hit, and referred to the possibility that exposure to light might follow a similar law, if light had a discrete nature, as suggested by Einstein and J. J. Thomson. A "normal" law of exposure, based on such a hypothesis, had already been suggested by Ross;[27] the hypothesis was mathematically developed by L. Silberstein[28] on the assumptions (*a*) that a grain becomes developable when fully hit by one quantum, and (*b*) that the chance of being hit is proportional to the projective area of a grain or contiguous clump of grains. Silberstein's formula found close experimental confirmation by A. P. H. Trivelli and F. L. Righter[29] using Svedberg's procedure. This result raises the issue, whether the variable "sensitivity" of grains of the same emulsion is purely a question of projective area and quantum encounter, or whether inherent sensitivity differences exist; such differences are feasible on the hypothesis that the grains contain reduction nuclei, *e. g.*, the "Reifungs-Keime" suggested by J. M. Edér, and by the existence of which Lüppo-Cramer[30] has interpreted many interesting observations. In fact, in the second Hurter and Driffield Memorial Lecture, F. F. Renwick,[31] after ably marshaling the strong evidence that the latent image consists of colloid silver dispersed in silver halide, suggested that its formation, at any rate in "high speed" plates, is due, not to photochemical decomposition of silver halide, but solely to a photoelectric coagulation of silver amicrons to neutral particles capable of acting as nuclei in development. This view has been criticized,[32] but there exists considerable evidence for a primary role of sensitizing nuclei.[33] The issue has been more sharply defined by very recent work of Svedberg.[34] He has refined his method of grain analysis by utilizing M. B. Hodgson's[35] observation that on early interruption of development of a single grain layer, development is found to have commenced at one or more centers in the grain. Svedberg assumes that these centers are distributed according to the laws of chance, and a grain becomes developable if possessing one or more of a certain size. The probability expression derived for relation to size of grain and chance of developability agreed with observations for two size-classes of grains exposed to light and X-rays. The outcome of work in this direction is of capital importance, not only for the theory of photographic emulsions, but for radiation theory.

Developers and Development

The gamut of photographic possibilities is fairly well covered by existing developing agents. Hence the introduction of new ones, if photographically adequate, is likely to depend mainly on production cost. *p*-Amino-carvacrol, derived from *p*-cymene,[36] a by-product of the pulp industry, has not come into use. "Neol" (*p*-amino-salicylic acid) introduced by Hauff & Company with the usual claims of abnormal capabilities,[37] has been found[38] to belong to the "slow" group, like hydroquinone. A useful review of organic developers has been made by A. and L. Lumière and A. Seyewetz.[39] These authors also[40] find that the reported developing properties of the leuco-bases of rosaniline dyes[41] were probably due to impurities. The question of constitution has been further discussed by B. Homolka,[42] who concludes that the failure of gallic acid and protocatechuic



Gallic acid



Protocatechuic acid

acid to develop is due to anhydride condensation between the COOH and a para-OH group; if prevented, such substances develop. The possibility of more accurately relating constitution to developing power (as reduction potential) is increased by A. Nietz'[43] work on the physical chemistry of development, particularly by his improvement of Sheppard's method of determining reduction potentials by bromide depression of density. The formation of an initial adsorption compound of developer and silver halide is suggested and experimentally supported by Sheppard and Meyer.[44] Such adsorption effects, including both displacement of one adsorbent by another, and incipient peptization, probably play a large part in the effects observed by Lüppo-Cramer[45] of dyes in development. These included accelerating, restraining, and fogging effects. A. Steigman[46] has brought out interesting results, bearing on the difference between physical and chemical development, in his studies in the reduction of silver solutions by sodium hyposulfite.

In relation to manufacture, a process assigned to The Barrett Company[47] for the catalytic oxidation of benzene to quinone is of interest, and one of F. F. Kitchin[48] for the electrolytic oxidation of benzene in 10 per cent sulfuric acid to quinone, while the electrolytic manufacture of *p*-amino-phenol[49] has been described by A. S. MacDaniel and collaborators.

Desensitizing and Desensitizers

Logically this should be discussed in connection with emulsions and the latent image. Practically, Lüppo-Cramer's noteworthy discoveries have joined it up with development. Following up his observations on the desensitizing action of organic developers, notably amidol, he found this due to their oxidation products.[50] This led him to search for dyes that might, in small quantities, act as desensitizers in development. In phenosafranine[51] he found a desensitizer, such that pre-treatment for 1 min. in a 1:2000 solution allowed an exposed plate to be developed in strong yellow light; by addition to the developer white light could be used.[52] In many cases, however, the alkalinity of the developer precipitates the free dye base. Besides dyes of the safranine class, Methylene Blue, Auramine O, and Brilliant Green were found effective, but liable to fog. This fogging appears to be general for basic dyes, but may be neutralized by acid dyes, such as Erythrosine, without destroying the desensitizing effect. In a later paper, Lüppo-Cramer[53] concludes that this type of desensitizing is an oxidation process, affecting the nascent latent image. The apparent improbability of an oxidation process occurring in the presence of developers of high reduction potential is met by A. Steigman[54] with the suggestion that the desensitizer is adsorbed strongly compared with the developer.

Fixing and Hardening

The physical chemistry of the acid-fixing bath in relation to gelatin has been investigated by Sheppard and collaborators.[55] The reinforcement of the action of formalin by salts such as sodium sulfate, for hardening prior to development has been patented in England.[56] In the recovery of silver from waste "hypo" the zinc dust method has been considerably used,[57] and A. Steigman[58] has proposed the use of sodium hyposulfite.

Intensification and Reduction

Besides the application of various toning processes to intensification, the only noteworthy item is the modification of Lumière and Seyewetz[59] of the chromium intensification process by the use of salts of chlorochromic acid. These authors also discuss the use of *p*-quinone[60] in intensification, bleaching, and reduction. The chemistry of persulfate reduction has received considerable attention. The importance of acidity was brought out by Lumière and Seyewetz[61] while S. E. Sheppard (with A. Ballard)[62] and G. I. Higson[63] have shown that silver ions catalyze the decomposition of persulfate in the reaction $S_2O_4'' + H_2O \longrightarrow 2HSO_4' + 0$.

Positive Processes

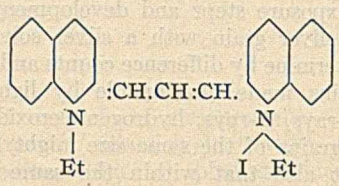
F. Weigert's work on print-out processes has been noted. The photochemistry of thallous chloride is discussed by C. Renz.[64] J. M. Eder[65] has used the light sensitiveness of leuco-bases of dyes in collodion for actinometry. Donisthorpe's dye-impression process, for making color prints on paper or other gelatin coated base by imbibition from a differentially dyed negative, has been further developed.[66] A dye printing process of the Badische Company is discussed by Eder.[67] F. Formstecher[68] has given a good account of the theory of the print-out process in relation of tone to subdivision, while R. Schwarz and H. Stock[69] found that the release of bromine from exposed silver bromide approximately paralleled the photographic blackening.

Toning

The most important advance in toning processes is dye mordanting. In this, the silver image is converted either into an insoluble silver compound mordanting dye, as in Traube's diachrome process with silver iodide, or eventually into other insoluble inorganic compounds capable of mordanting. J. M. Blaney[70] has patented conversion of the image to stannic ferrocyanide; F. E. Ives[71] bleaches the image with potassium ferrocyanide and chromic acid to mordant basic dyes; a copper salt is proposed by J. H. Christensen,[72] and in a British patent A. Traube[73] describes general methods for production of double salts of copper, uranium, iron, etc., to be dyed with basic dyes. The use of iron toned images for mordanting dyes was patented by J. I. Crabtree.[74]

Color Sensitizing

Apart from dye toning, the chief contribution of chemistry to color photography is in dyes for optical sensitizing and selective screening. The impulse given by the war to investigation and production of such dyes in America, Britain, and France has been continued. The isocyanines, resulting from the condensation of quinoline alkiodides or quinaldine alkiodides by alkaline hydroxides, have been investigated very fully by W. J. Pope and W. H. Mills,[75] although the relations advanced between actual sensitizing power and constitution can only be regarded as provisional. The term carbocyanines has been assigned by these authors[76] to the important group (of which Pinacyanol = Sensitol Red is the chief) of dyes produced by the condensation of two molecules of quinaldine alkiodide with one of formaldehyde in presence of alkalies. W. H. Mills and F. M. Hammer[77] assign to pinacyanol the constitution



This is derived from its mode of formation, its content of two nitrogen atoms but only one acid equivalent, its molecular weight, and products of oxidation. The 3-carbon linkage :CH.CH:CH is the feature distinguishing carbocyanines from isocyanines. E. O. Adams and H. L. Haller[78] have described a series of dyes, termed kryptocyanines, obtained from lepidine alkyliodides, formaldehyde, and alkali; absorption maximum near 700$\mu\mu$, sensitizing at 740$\mu\mu$. A general article on the cyanine dyes is due to O. Fischer and Z. Scheibe[79] while A. and L. Lumière and H. Barbier[80] have described a new series of sensitizing cyanine dyes. Pantochrome from the condensation of dimethylamino-quinaldine with dimethylaminobenzaldehyde showed a nearly uniform action up to 700—, with a slight minimum in the blue-green. Pinaflavol, a new sensitizer for green, is described by E. Konig[81] and J. M. Eder[82] as superior to pinaoverdol.

The effects of isomerism and substitution in the isocyanines, on absorption and sensitizing, are dealt with by F. M. Hammer.[83] The reviewer, from a comparison of his own former work with later experience, cannot regard the values of sensitizing powers given as definitive, since so much depends on purification and methods of sensitizing. On the latter, the article by F. M. Walters and R. Davis[84] and the development of so-called "hypersensitizing" by the use of ammonia, alcohol, and water[85] may be studied. A recent paper by Mills[86] describes a new cyanine type of the benzothiazole series, resembling isocyanines in having a :CH linkage; also analogs of the carbocyanines.

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A course in chemistry is now required in all the schools of the Pennsylvania State College. In the Schools of Agriculture, Engineering, Mines, Natural Science, and Home Economics, various specialized courses are given, while in the School of Liberal Arts only a course in general chemistry is required, though others may be elected. In order that all departments and schools of the college may be expanded in preparation for the development of the institution into the Pennsylvania State University, a campaign for $2,000,000 is now being carried on.

Glass Technology

By George W. Morey

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

THE WAR period preceding that under review was marked by extraordinary activities in the field of glass technology, and it is to be expected that the period of business depression through which we have been passing should show a diminution in activity. While such a diminution has taken place and while no such developments as that of pyrex glass or the remarkable upbuilding of the optical glass industry during the war are to be chronicled, still the development of the industry has been steady and the technologic advances important.

George W. Morey

In the line of fundamental research probably the most outstanding contribution has been the comprehensive paper by Adams and Williamson on the annealing of glass, for which the authors were awarded the Longstreth Medal by the Franklin Institute of Philadelphia. Glass annealing is an ever-present problem in all branches of the industry, the solution of which has been in the past groped for in the dark. It had not been realized that "slow cooling" was not sufficient to ensure good annealing; to be sure, slow cooling is essential at a certain stage in the process, but most commercial installations succeed in cooling ware too rapidly in its critical stage, and draw out the cooling to unnecessary lengths when the necessity for control has passed. Adams and Williamson have given a striking illustration of the possibilities in carefully controlled annealing. As is well known, optical glass must satisfy particularly rigid specifications in the matter of strain, and the type of glass known as borosilicate crown is particularly difficult to anneal. Yet by precise furnace control, guided by the very definite rules which they have given, they were able to anneal a slab of borosilicate crown 2 cm. (0.8 in.) thick in 4 hrs. and 50 min. from the time the cold glass was placed in the cold furnace. Annealing problems as difficult as this are not common in practice; yet it is not unusual for days to be given to poorly anneal the more tractable plate glass of the same thickness. By the application of scientific methods superior annealing could be obtained in less time, thereby releasing equipment, increasing production, and decreasing cost. Adams and Williamson's paper is noteworthy in that it not only discusses the annealing of glass from the scientific viewpoint, but also gives explicit detailed instructions for the annealing of various types of glass in various thicknesses. A noteworthy instance of the successful application of these results is the 40-in. reflector disk manufactured in this country during the past year, an achievement described in the June issue of This Journal.

The relation of the physical properties of glass to chemical constitution is of fundamental importance in glass technology, and several investigators have been active in this field. In this country the activity is chiefly shown in the number of composition patents that have been issued, including patents on a glass which, while opaque to visible radiation, transmits the infra-red, and also on a glass which, while opaque to the visible, transmits the ultraviolet. An industrial development of technical importance, especially in the application of automatic machines, is the conversion of the electric light bulb from a lead glass to a lime-magnesia glass which can be melted successfully in tanks. Attention should also be called to the work of Peddle, published in the *Journal of the Society of Glass Technology*, which is the most complete and extensive study of the relation between chemical composition and physical properties that has yet appeared. The work to date includes the soda-potash-lime, the soda-potash-lead, and the soda-potash-barium glasses. The physical properties determined are primarily those of interest to the optical glass manufacturer: refractive index, dispersion, comparative "fusibility," and resistance to weathering and to the action of reagents, these latter properties being of importance in all branches of the industry. The important factor of viscosity has not been determined in these extensive experiments, but that is a problem in itself, a problem the study of which is still awaiting the development of a satisfactory technic. Attention is being given this problem, however, both by the manufacturers themselves and by such institutions as the Department of Ceramics of the University of Illinois and the Bureau of Standards, and it is to be hoped that we will soon have not only methods but also data at our disposal. Much additional work is necessary in order to satisfactorily correlate physical properties with chemical constitution, and the subject appears the more difficult as, with the more accurate determination of physical properties, the futility of attempting to represent any property of a glass on a purely colligative basis becomes apparent.

Purely technical developments have followed the lines laid out in previous years. Unfortunately, there is still litigation over some of the important new processes, but final decision has been reached in the "cold bait" patents, of importance in several branches of the glass industry. A development of prime importance, which has been foreshadowed by years of experiment on the part of many firms, is the commercial success of the sheet glass drawing process, which has reached such a stage that 84-in. sheets can now be drawn, and two drawing machines operated from one tank. A striking development has been the rapid extension in the field of application of glass feeders, and the development of several new types, though the Hartford-Fairmount machine still appears to be in the lead. A 15-arm machine of the Owens type for bottle work has been developed. The field of application of automatic machinery has been further extended to bulbs, the manufacture of the latter by machine being now on a commercial basis. The semi-automatic machine has been successfully applied to tumblers and thermos-bottle liners. It appears probable that the next few years will see a still more widespread application of glass feeders and automatic machines, with resulting transformation of the glass industry "from a small scale, many unit skilled craftsman's constant personal triumph over miserably poor and inefficient equipment into an engineering enterprise of first magnitude."[1]

This review has so far confined itself to technical progress, but progress has been made along another line which may in the last analysis prove of more value to the industry as a whole than the more purely material achievements. During the period since the war, there has been developing a spirit of recognition not only of the value of scientific research and control, but also of the value of coöperation and an *esprit de corps*, which bids fair to sweep away the mists of trade secrecy that have in the past oppressed the glass industry. Two new trade journals have appeared, *Glass Industry* and *The Glass Container*. The latter of these is the organ of the Glass Containers Association of America, itself an example of the new spirit in the glass industry. This association is not only supporting a journal, but has taken an active part, with the coöperation of the Bureau of Standards, in the standardization of glass containers, and in encouraging and supporting research. The phenomenal growth of the Glass Section of the American Ceramic Society, the only common meeting ground of glass chemists and technologists in this country, also shows that the men in the glass industry are awakening to a realization that the path to progress is one of respect and coöperation, not one of secrecy and distrust.

[1] Dowse and Meigh, *J. Soc. Glass Tech.*, **5** (1921), 152.

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Review of Analytical Work Applicable to Leather and Tanning, 1920-1921[1]

By F. P. Veitch and R. W. Frey

Chemist in Charge and Associate Chemist, Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C

PROBABLY few, if any, of our important industries offer to chemists as fertile a field for research and scientific work as does that of tanning. Certainly in no other industry is so little known of the composition of the principal raw materials and of the mechanism and control of the fundamental processes. In the past few years, however, there has been an increasing interest and activity in leather and tanning chemistry which is indeed gratifying, and it is hoped this will continue until the art of tanning has been put on a sound scientific basis.

Many problems of analytical nature are still unsolved and probably will remain so until there is a better knowledge of the fundamentals involved. Progress in this branch, however, can certainly be claimed, as will be readily realized from the following review of work done in the short space of two years.

R. W. Frey

Tannin Analysis

In this country the work of Wilson and Kern on the hide powder method of tannin analysis has redirected attention to fully recognized sources of error in this method and has also revived considerable interest in the subject by the rather startling results obtained. In their first paper[1,*] they describe a method which consists essentially of shaking the tannin solution with purified hide powder until all tannin, as determined by the gelatin-salt test, has been removed from solution. The tanned hide powder is then washed free from soluble matter, dried, and analyzed for tannin as in the regular procedure for vegetable tanned leathers, and from this figure the percentage of tannin in the original material is calculated. Figures from comparative analyses of 8 common tanning materials by this new method and by the official hide powder method of the American Leather Chemists Association are from 43 per cent to 220 per cent higher for tannin by the latter method, due chiefly to the removal by this method of nontannins, such as gallic acid, pyrocatechol, and so on, which do not make leather and are readily washed out. The presentation of Wilson and Kern's paper brought forth considerable discussion[2] in opposition to it and also quite a controversy between the authors and Schultz and Blackadder.

The two last-named authors[3] in a detailed study of the new method take exception to several assumptions involved in it and give data to indicate that two are in error: namely, "that there is a definite chemical compound formed between the tannin in the tannin solution and the collagen in the hide powder during a 6-hr. shaking, which chemical compound is stable with regard to water and also insoluble in water;" and "that one definite chemical compound is formed throughout the whole of the hide powder used in the analysis." They show particularly that from the washings of the tanned hide powder a certain amount of tannin can be recovered as determined by the new method and that the tanned hide powder is very heterogeneous physically, being made up roughly of a distinctly fibrous portion and a relatively fine powdery portion. The last is more heavily tanned than are the coarser particles and being so very fine is apt to be lost during washing. The loss of this relatively tannin-rich powder leaves the residue proportionally poorer in tannin and causes a loss of tannin as determined by the new method.

In further defense of their new method Wilson and Kern[4] give data to show that tannin once combined with hide cannot be washed out by any amount of washing that would be practical, and that concentration of the nontannins and washings from the tanned hide powder converted certain nontannins into substances capable of tanning.

In continuation of the controversy Schultz[5] presented a very elaborate study showing that the detannized solution and washings according to Wilson and Kern's method contain materials which, without concentration, will combine with hide powder and be resistant to washing. An experiment is also described which indicates that concentration does not bring about a chemical change with conversion of nontannins into tanning materials, and according to Schultz such phenomena are probably explained by the dispersed state of the tannin under various conditions. Results from a rather extensive series of experiments, involving a strict comparison of the basic principles of the official hide-powder method and of the new one, show that the effects of the three factors influencing the absorption of tannin by hide powder, namely, the amount of hide powder, concentration of tannin, and volume of solution, are as pronounced after washing the tanned hide powder as they are without washing. Schultz concludes that the Wilson and Kern method of tannin analysis is based on a series of false assumptions and gives neither the true value of tanning materials nor the true tannin content.

Since considerable objection was raised to the Wilson and Kern method on the ground that it was too cumbersome and time-consuming, these two authors presented a modification[6] which greatly simplified their procedure and also removed several possible sources of manipulative errors which previously had been pointed out. Comparative analysis, by the original and revised procedures, however, of 6 typical extracts gives practically identical results Replying to the work of Schultz, Wilson and Kern[7] refute many of his objections and particularly show that the new method will give the same tannin figure for varying quantities of hide powder. Answering this paper Schultz[8] gives further argument against the work of Wilson and Kern and in support of his findings.

Baldracco and Camilla[9] have proposed a modification of the official method of tannin analysis of the Society of Leather

[1] Published by permission of the Department of Agriculture.

* Numbers in the text refer to Bibliography at end of paper.

Trades' Chemists using a prepared, lightly chromed hide powder. It is contended that the usual washing of hide powder removes acid which is necessary for complete combination of the tannin and hide powder, and that ready chromed hide powder as prepared by them[10] always contains sufficient acid for complete detannizing and is much more convenient to use. Schell[11] in criticism of the work of Baldracco and Camilla states that their tannin figure includes more nontannin than in the case of the official method and that their method is not as exact nor is the hide powder they propose as well defined as the official one. Lauffmann[12] claims that the reagents used by Baldracco and Camilla are not suitable as they give similar reactions for tannins, and also that proof has still to be produced that hide powder with the filter method absorbs materials which should really be estimated as nontannins. In reply Baldracco and Camilla[13] point to their previous work showing that tanning by the filter method is too high as some nontannins are absorbed, while by the official shake method of the International Association of Leather Trades' Chemists the tannic acid is not all removed from certain extracts.

Moeller[14,15] has done considerable work on the error in nontannin determinations due to the presence of hydrolyzed hide substance. Determination of the dissolved hide substance in the nontannin residues from about 50 tanning materials showed that it usually amounted to several per cent of the nontannin residue. Parker and Terrell[16] in some notes on the filtration of tanning solutions show the superiority of the filter candle to filter paper, as the latter continues to absorb soluble matter even after considerable quantity of solution has passed through. Thompson, Seshachalam, and Hassan[17] have shown that in tannin analysis the time of filtration, color, tannin content, insolubles and so on are all liable to considerable variation with different degrees of acidity. Sollmann[18] in studies on the precipitation of proteins by tannin has determined that in concentration (0.1 to 0.5 per cent) necessary to produce astringent action, precipitation is greatest at a pH of 2 to 5. There is no precipitation when the alkalinity is pH 8 to 8.3.

Frey and Clarke[19] have proposed a practical simplification and shortening of the washing of chromed hide powder for tannin analysis and give data to show that results are in agreement with those from official practice. The report of the British tannin analysis committee[20] shows that in washing the chromed hide powder only distilled water should be used. Baldracco and Camilla[10] have described the preparation of a ready chromed hide powder.

Leather Analysis

Vegetable Tanned Leathers—A committee of the American Leather Chemists' Association under the chairmanship of Small[21] has gone very thoroughly into the subject of the sampling of leather and its preparation for analysis. This excellent report gives complete analysis of the leather from all parts of hides and sides of various tannages, thus emphasizing the variations in composition and showing what sections to combine for the most representative sample. From these data a chart has been prepared showing the locations for sampling of all commercial trims. A French committee on leather analysis, with Chambard[22] as chairman, has also done some work which shows a large zone between the shoulder and butt of nearly constant composition and recommends sampling in this section.

Veitch and Jarrell[23] in a detailed study of the determination of moisture in leather show particularly the influence of atmospheric humidity. With ungreased leathers a difference of 35 per cent relative humidity gives on the average a difference of 0.5 per cent in drying losses. It is also shown that repeated drying of leather at constant humidity gives a progressive loss in weight; that the electric oven at 100° C. gives results slightly higher than the combined evaporator and drier; and that the vacuum oven at 70° C. gives results lower than the drier or electric oven at 100° C., but at 97° to 98° C. gives higher results.

The determination of hide substance in leather has been studied by several workers. Chambard[24] considers incomplete oxidation and too small a charge of leather as the most likely sources of error. He obtains good results with a modification of the Kjeldahl method as for silk analysis using a relatively large sample (2.8 g.) of leather and digesting with sulfuric acid, potassium bisulfite, and anhydrous copper sulfate. F. G. A. Enna[25] proposes a rapid method using a drop of mercury which is afterwards precipitated out. Cochrane,[26] from work on feeds and feces, shows that the addition of permanganate does not cause a loss of nitrogen and that using the same method without the addition of permanganate results are less concordant and uniformly lower. Kahn[27] considers as important sources of error in the Kjeldahl method the following: lack of uniformity of the powdered leather; insufficient decomposition; the possibility of alkali, acid or particles of zinc being carried over in the distillation; and of some ammonia escaping with the air bubbles. Parker and Terrell[28] have investigated the use of perchloric acid in Kjeldahl digestions of leather and have found that it gives satisfactory results and considerably shortens the time of digestion.

Active work both here and abroad has been continued on the much-mooted question of a suitable solvent for the extraction of oils and greases from leather. Two English committees[29] have compared numerous solvents from which they conclude that either chloroform or benzene should be officially adopted with preference for the latter if the color of the extract is of importance. Veitch and Clarke[30] have summarized previous work on the subject and give data on the extraction, particularly of soaps, in leather. It is shown that the presence of moisture increases the quantity of soap fats extracted by chloroform and petroleum ether; that the presence of tannic acid increases the solubility of soap fats very greatly, especially in chloroform; that magnesium salts added to leather will lead to the extraction of the soap as a whole if opportunity is given for the formation of magnesium soaps, since these are very soluble in both chloroform and petroleum ether; and that calcium soaps are extracted by chloroform in a colloidal state but are practically insoluble in petroleum ether.

A committee report of the American Leather Chemists' Association by Terrassee and Anthes[31] on water-solubles in leather gives the results of a study of the official method from which it is concluded that the sample should be finely ground and freed from grease and that the extraction should be carried out in a specified apparatus on 30 g. of leather at 50° C. Two liters of extract should be collected in three hrs. without any previous period of soaking. A later committee under the chairmanship of Wilson[32] undertook to study primarily the influence of temperature and whether or not a definite end-point could be reached in the water extraction of leather. The committee results showed very little agreement on these two points. Apropos of the subject, Veitch and Frey[33] have published some notes showing that there is no absolute end-point even for a 148-hr. extraction but that the extraction appears to settle down to a practically constant value.

A subject for considerable work has been the determination of glucose in leather. Rogers[34] as chairman of an American Leather Chemists' Association committee made quite an elaborate report showing that five drops of toluene per liter will preserve leather extracts for at least three days without loss of sugar; that when sodium carbonate is used for neutralization

after hydrolysis in the presence of Epsom salts high results are obtained because of the precipitation of magnesium; that caustic soda if used in excess will precipitate the magnesium; that there does not appear to be any advantage in using stronger solutions for analysis; and finally, a point of considerable importance, that low results when using sodium hydroxide for neutralization are possibly not due to any action of the sodium hydroxide on the dextrose but to sodium plumbite which has a reducing action on the sugar. Continuing his committee work, Rogers[35] sought the best reagent for complete removal of lead and as a result recommended that a strong solution of disodium acid phosphate be made the object of further study. To shorten the time for sugar determination van der Hoeven[36] has proposed a volumetric procedure which is a modification of Schoorl's method. Quisumbing and Thomas[37] have made a very thorough, careful study of conditions affecting the determination of reducing sugars and have proposed a procedure which eliminates most sources of error.

In the determination of magnesium in leather Frey[38] has shown that Epsom salts determined from the ash of the leather ranges from 0.05 per cent to 0.25 per cent higher than when determined from the water extract and also that Epsom salts either alone or in solution in the water extract loses practically 40 per cent of its weight upon 16 hrs.' drying in the evaporator and dryer. The work of an American Leather Chemists Association committee with Frey[39] as chairman has shown that the volumetric procedure for magnesium as outlined by Handy gives results in agreement with those by the gravimetric method.

For the determination of sulfuric acid in leather Thomas[40] has proposed quite a departure from the usual suggestions. The principle of his method is based on the displacement of the sulfuric acid by ions of a higher valence and is effected by digestion of the leather with potassium dihydrogen phosphate solution. A modification of this same method is also given by Thomas and Frieden[41] for the determination of hydrochloric acid and neutral chlorides in leather.

Mineral Tanned Leathers—Hou[42] in some experiments on the volumetric determination of chromium in leather by the sodium peroxide fusion method has emphasized the need of taking the fusion solution down to a small volume to insure decomposition of all peroxide and also of controlling the acidity of the solution for titration. An English committee, of which Innes[43] was chairman, has reported on methods which they have so far found best for the analysis of chrome leather. Brgeniner[44] has made a detailed study of the methods and factors influencing the determination of chromium.

Grasser,[45] one of the pioneer workers in iron tanning, has published a quite complete article on the subject and given methods for control analysis.

Vegetable Tan Liquors—Claflin[46] has proposed a very practical method for determining the plumping power of tanning solutions, which consists essentially of measuring the volume of solution absorbed by hide powder under properly controlled conditions. The simplicity of his method, together with the practical value of results by it, has proved very attractive. Working along the same line McLaughlin and Porter,[47] using pieces of limed and hydrated steer hide instead of hide powder, have made a study of the swelling of white hide in tan liquors, dealing particularly with the usual organic acids and calcium acetate and lactate. Their results emphasize the significance of direct results obtained in this manner. Atkin and Thompson[48] have published a very informing paper on the determination and control of the acidity of tan liquors by a colorimetric method using indicators.

Blackadder,[49] in a report on the color measurement in tanning solutions, describes some experiments with a tint photometer, from which he is inclined to conclude that any use of blue in a combination of color to match a tanning solution is unnecessary and may lead to error; and that while an apparatus based on matching a built-up color standard against an unknown color will not prove satisfactory, a machine based on spectrum analysis ought to be capable of adaptation. Wilson and Kern[50] have shown an interesting relation between the hydrogen-ion concentration of a tan liquor and its color value. Tan liquors change in color with change in pH value over a range from 3 to 12 and this change in color is completely reversible if the liquors are not long exposed to air. Liquors exposed to air continue to darken, with accompanying rise in the pH value, but this change is not reversed by lowering the pH value. Exposed to air at pH values of about 9, liquors give bulky precipitates when their pH values are brought to 3.

Chrome Liquors

The analysis of chrome liquors has apparently been a subject of considerable interest. Thomas and Foster[51] have described a conductance-barium hydroxide titration method for chrome liquors which "is to be preferred to the American Leather Chemists Association titration method not only on account of theoretically truer results but also convenience." Adsorbed chromic sulfate in the precipitated hydrous chromic oxide is the chief cause of low results by the American Leather Chemists Association titration method. Dhavale and Das,[52] from detailed experiments incidental to an investigation of the effect of neutral salts on the basicity of chrome liquors, have shown that the addition of sodium chloride causes a marked increase in the acidity of chrome liquors as found by the Procter and McCandlish method and also that the values obtained by this method are influenced by the temperature of titration and speed of adding the alkali but not by the dilution of the liquor under titration. Thomas and Foster[53] also deal with the effect of salt on the titration of chrome liquors and give some data which indicate that the alkalimetric titration method for acidity of chrome liquors could be made to yield more correct results by the addition of about 50 g. of sodium chloride before titrating. Burton and Hey,[54] in the course of investigations on chrome tanning, have pointed out the influence of carbon dioxide, sulfur dioxide, and volatile acids on the American Leather Chemists Association method of titrating acidity of chrome liquors, showing that it is inadequate since it fails to take these into account, and they have recommended that the titration be made by adding the caustic soda to the diluted liquor in the cold and by continuing the addition of alkali during the period of heating up to the boiling point. Pickering[55] has pointed out several precautions to be taken in determining basicity figures for chrome liquors, describing also a means of illumination for a clear end-point in titrating. Schorlemmer[56] and Grasser[57] have both discussed and suggested systems for expressing the basicity of chrome liquors. Thomas and Kelly[58] have proposed a rapid estimation of chromium in chrome liquors by means of the immersion refractometer.

Lime and Lime Liquors—English committees on lime-yard control under Burton,[59] Atkin and Palmer,[60] Pickles,[61] and Atkin and Atkin[62] have been very active in reviewing, criticizing, and proposing methods best suited for lime liquor analysis. F. G. A. Enna[63] has described a method for determining the available sulfide in a lime liquor based on the fact that a quantitative separation of hydrogen sulfide from its alkaline salts is effected by carbonic acid, while thiosulfates and amino acids are unaffected. Singer[64] has made a comparative study of various methods for analysis of lime liquors.

Grasser[65] has pointed out the advantages of determining lime in unhaired skins from solution by wet oxidation rather than from solution of the ash. Veitch and Jarrell[66] have reviewed the various methods for determining available calcium oxide in lime and after considerable study have proposed and outlined in detail modifications of the tannery method and Scaife method so as to insure accurate and concordant results.

Identification of Tanning Materials

Grasser[67] has published some very interesting observations on the behavior of various tanning materials during electrodialysis which may be developed for the identification of tannins. Lauffmann[68] has discussed in detail the tests for the identification and examination of tanning materials and extracts. Lauffmann[69] has also described a modification of the indophenol reaction so that it can be used for identification of that class of synthetic tannins formed by the condensation of formaldehyde with the sulfonic acids of phenol, cresol, naphthalene or anthracene.

De Hesselle[70] has published a modification of Appelius and Schmidt's cinchonine test for sulfite-cellulose. With this test certain synthetic tannins react partially like vegetable tannins; others like sulfite-cellulose; and some do not give the reaction at all. Hough[71] has described a method for determining bisulfites in extracts.

For differentiation between old fustic and quercitron extracts Justin-Mueller[72] has found that the ether extracts upon solution in sulfuric acid and dilution with water remain bright orange-yellow for old fustic but are decolorized for quercitron. Atkin and Marriott[73] have shown that the application of polarized light in the microscopical analysis of sumac gives more definite and quicker results than does the ordinary microscopical procedure. Groll[74] has published considerable data on gambier and its adulteration, and Jablonski and Einbeck[75] have done likewise for quebracho, emphasizing particularly the value of a fluorescein reaction for its detection. Mimosa extract, however, gives a similar reaction.

Sulfonated Oils

A committee of the American Leather Chemists Association, with Schultz[76] as chairman, has made quite a study of the determination of combined SO_3, total fatty matter and neutral fat in sulfonated oils. Hart[77] has published a method and formula for the determination of inorganic impurities in sulfated oils, which formula he improved in a later paper.[78] Bunicke[79] has also offered an improvement of the Hart method. Pickering[80] has done considerable work on methods for the commercial examination of sulfonated oils. Kern[81] has proposed the determination of sulfate in sulfonated oils by means of a solution of monosodium phosphate which will give a practically complete separation of oil from solution with sulfonated oil without the addition of a solvent and will extract all of the free and none of the combined sulfate.

Miscellaneous

Thomas[82] has described some experiments on estimating the tryptic activity of bating materials, using two methods developed from the work of Sherman and Neun. Matos[83] has discussed the testing of dyes in the leather industry. Welwart[84] has given a method for determining ammonia in oil and fat preparations. Hoffman[85] has proposed a means of detecting and separating lactic acid as a complex sodium ferric lactate. Froboese[86] has dealt in considerable detail with the examination of leather substitutes. Bogue[87] has published a very comprehensive article on glues and gelatins, giving a most complete and excellent bibliography on the subject.

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Vegetable Tanning

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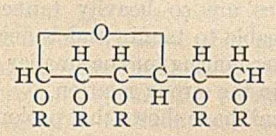
THE NATURE of tannin has been under study by organic chemists for many years, but the outstanding feature of organic chemical investigation was the synthesis of gallotannic acid (the tannin of oak galls) by Emil Fischer in 1918,[1] which rendered all previous work practically obsolete.

The study of the hydrolytic products of purified nutgalls tannin showed that 1 molecule of glucose was combined with a number of molecules of gallic acid, and that gallotannic acid was actually a pentadigalloyl glucose, with the formula



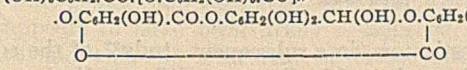
where R = digalloyl radical.

By condensing 5 molecules of tricarbomethoxygalloyl chloride with 1 molecule of glucose in the presence of quinoline (the carbomethoxy groups protecting the hydroxy groups of the gallic acid from the action of phosphorus pentachloride) and the carbomethoxy groups being subsequently removed by cold alkali, pentadigalloyl glucose, similar in properties to gallotannic acid, was obtained.

Fischer also prepared a series of acyl glucoses, many of which have tanning properties. The monacyl glucoses do not precipitate gelatin, but trigalloylglucose shows pronounced tanning properties. Trigalloylglycerol and hexagalloylmannitol precipitate gelatin in aqueous solution.

Fischer prepared penta-*m*-digalloyl-β-glucose, which was proved to be an isomer of Chinese tannin, and in the first paper mentioned he proved that the "glucogallin" isolated by Gilson from Chinese rhubarb is 1-galloyl-β-glucose.

Nierenstein[2] raises a number of objections to Fischer's formula, mainly on the ground that whereas Fischer's pentadigalloylglucose when methylated with diazomethane yields glucose on hydrolysis, methylogallotannin gives under identical conditions tetramethylglucose, showing that in gallotannin 4 hydroxyl groups are not replaced by digalloyl radicals. Nierenstein proposes a modified long chain formula based on the supposition that gallotannin is probably a glucoside of the following polydigalloylleuco-digallic acid anhydride:



or of its free acid. Five reasons in support of this formula are offered by Nierenstein, one of which is that it is in accordance with the formation of tetramethylglucose from methylogallotannin.

[1] *Ber.*, **51** (1918), 1760; **52** (1919), 829.
[2] *J. Soc. Chem. Ind.*, **41** (1922), 29T.

Nierenstein is also studying the constitution of the catechu tannins. He has recently found[3] that Paullinia tannin from *Paullinia cupana* seeds is a crystalline normal glucoside consisting of 1 molecule of dextrose and 2 molecules of gambier-catechin-carboxylic acid, forming a depside.

K. Freudenberg, formerly associated with Fischer, is continuing that great master's work on the tannins. He has shown[4] that Hamameli tannin, which has been isolated in the crystalline condition, yields on hydrolysis with tannase gallic acid and an unidentified aldo-hexose in the proportions required for a digalloylhexose.

Freudenberg's investigations[5] of chebulinic acid, which occurs in myrabolans, showed that it is a crystalline material sparingly soluble in cold water, which cannot be hydrolyzed by tannase, and that it is probably a compound of a digalloylglucose and a new phenolic acid, the latter forming a glucoside with the glucose. He showed[6] chlorogenic acid, the tannoid constituent of coffee, to be a simple depside of caffic and quinic acids. Gambier-catechin has been shown[7] to have an oxydiphenylpropane nucleus, to be related to the flavone dyes and anthocyanidins, thus disproving an older view that it was a derivative of ethyldiphenylmethane.

The tannins of the woods of the Spanish chestnut and native German oak have recently been found by this same chemist[8] to contain quercitrin, glucose, and ellagic acid.

The leaves of *Acer ginnala* yield a crystalline tannin, acertannin, $C_{20}H_{20}O_{13}$, and an amorphous mixture consisting of ellagic acid, quercitrin, an amorphous tannin, mainly galloyl-aceritols with small amounts of a flavonol glucoside, and a substance probably a phlobo-catechol tannin according to Perkin and Uyeda.[9] Acertannin hydrolyzes to 2 molecules of gallic acid and a dextrorotatory sugar, aceritol. Aceritol behaves as a polyhydric alcohol and is probably an anhydrohexitol derived from mannitol or sorbitol.

A new classification of natural tannins, more discriminating than the older pyrogallol-catechol categories, has been proposed by Perkin and Everest:[10]

1—Depsides (old gallotannins).
2—Diphenyl methoid (old ellagitannins).
3—Phlobatannins (old catechol tannins).

Freudenberg[11] has recently offered a classification much more distinctive than the above:

[3] *J. Chem. Soc.*, **121** (1922), 23.
[4] *Ber.*, **52** (1919), 177; **53** (1920), 953.
[5] *Ibid.*, **52** (1919), 1238.
[6] *Ibid.*, **53** (1920), 232.
[7] *Ibid.*, **53** (1920), 1416.
[8] *Ibid.*, **54** (1921), 1695; *Naturwissenschaften*, **8** (1920), 905.
[9] *J. Chem. Soc.*, **121** (1922), 66.
[10] "The Natural Organic Coloring Matters," Longmans, Green & Co., New York, **1918**.
[11] "Die Chemie der Natürlichen Gerbstoffe," Julius Springer, Berlin, **1920**.

1—Hydrolyzable tannins in which the benzene nuclei are united to larger complexes through oxygen atoms.
2—Condensed tannins, in which the nuclei are held together through carbon linkages.

Where both kinds of compounds are present in the molecule, *e. g.*, in ellagic acid, the classification is decided according to the genetic connection with other tannins.

Group 1 embraces (*a*) esters of phenolcarboxylic acids with each other or with other oxyacids (depsides), (*b*) esters of phenolcarboxylic acids with polyatomic alcohols and sugars (tannin class), and (*c*) glucosides. The most important criterion for Group 1 is hydrolysis to simple components by enzymes, particularly tannase or emulsin.

Tannins of Group 2 are not decomposed to simple components by enzymes. They are generally, but not always, precipitable by bromine, and when treated with oxidizing agents or strong acids condense to high molecular amorphous tannins or "reds." They are divided into two classes according to whether or not phloroglucin is present. With the exception of some simpler ketones, oxybenzophenones and oxyphenylstyrylketones, the catechines belong to the phloroglucin, class, *e. g.*, the very important quebracho, and probably oak tannin are in this class.

Freudenberg has made valuable use of the enzyme tannase secreted by *Aspergillus niger*. A recent paper by him and Vollbrecht discusses the isolation and determination of the activity of this enzyme.[12] For a complete summary of the present knowledge of the organic chemistry of natural tannins Freudenberg's very valuable book[11] should be consulted.

Electrolysis of Tannins

Extensive studies of the conduct of tannins upon electrolysis have been made by Grasser,[13] but the results are greatly confused due to oxidation, reduction, and decomposition. He found that mangrove and catechin are sodium salts, and that in some instances a separation of two qualitatively different tannins can be effected by electrophoresis.

Wilson,[14] in extension of his application of the Procter-Wilson theory of tanning,[15] discusses the reasons for the different degrees of astringency of tannins, and attributes the great difference of astringency between quebracho and gambier to the differences in the electrical charges of the particles and to the content of non-tans. He found that quebracho became mild in action when gallic acid was added to it, and suggested the mechanism for the fixation of tannins by hide substance.

Thomas and Foster[16] actually measured the electrical charge of eight different vegetable tanning materials by the U-tube electrophoresis method. They found all to be anodic in migration (at their natural reaction, *i. e.*, $-\log C_{H^+} = \text{ca. } 4.$) and that the potential difference of the Helmholtz double layer of astringent quebracho was the highest, namely, -0.028 volt, while that of mildly acting gambier was the lowest, -0.005 volt. This confirms the theory of Wilson that astringency is a function of the electrical charge.

Thomas and Foster also showed that the negative electrical charge of quebracho could be gradually reduced and finally brought to zero by addition of small amounts of hydrochloric acid, while the charge for this tanning material, as well as for four others, was raised by removal of the non-tans by dialysis: as, for example, cube gambier showed a p. d. of -0.005 volt in natural state; after dialysis for 24 hrs. it became -0.024 volt. This shows that the non-tans have a profound effect upon the p. d. of the tannin particles, and partly resolves Wilson's two explanations of astringency to one and the same thing, although it must be noted that the charge is not the sole factor in fixation by pelt, since undoubtedly one mechanism of the non-tans in reducing astringency lies in their high diffusive power and loose fixation in the pelt, thus preventing "case hardening" by the tannins and retarding and evening the fixation of the same.

The significance of H^+ ion to the charge of tannin particles was indicated in the paper by Thomas and Foster, and a continuation of the study of this question is in progress. Considerable data on the influence of electrolytes in precipitation of tannins are also given in this paper, throwing light on their colloidal properties.

Fixation of Tannins by Pelt

A study of the time and concentration factors in the fixation of tannins by pelt is being pursued by Thomas and Kelly, a preliminary paper on quebracho and gambier having appeared recently.[17] This paper shows a striking difference between the action of astringent quebracho and mild gambier. The concentration curves for gambier rise regularly and slowly like the well-known "adsorption curve," while those for quebracho rise very steeply to a maximum at 30 to 40 g. total solids per liter of solution and then drop off abruptly. They explain this action of quebracho by the fact that owing to the lack of non-tans in this astringent material the surfaces of the hide substance particles are so heavily tanned that they are rendered impermeable to tannin and hence the interiors are unaffected, thus accounting for the smaller amount of tannin fixed by the hide in the strong solution.

Wilson and Kern[18] have shown that prolonged washing with water neither hydrolyzes vegetable leather nor removes any of the tannin therefrom. They contend that the definition of tannin should be restricted to those substances which irreversibly combine with pelt. They made the valuable discovery that when completely detannized vegetable liquors are evaporated in the presence of air, tannin is generated owing to oxidation and polymerization of organic non-tans present. This is in accord with the findings of Meunier and Seyewitz,[19] that while pure phenols produce only an extremely feeble effect upon the solubility of gelatin, their oxidation products quickly render gelatin insoluble, *e. g.*, hydroquinone has no tanning properties whereas quinone has.

Wilson and Kern showed that this action takes place right in the leather, for when hide powder was drummed in various vegetable extracts and then removed, divided into two portions, one being washed immediately, the other allowed to stand in contact with air for 30 days before washing out the non-tans, the second portion showed in all cases an increased tannin content, thus explaining the importance of the time factor in the "aging" of heavy leather. Alsop's[20] statement, that sole leather tanned slowly not only contains more tannin, but actually consumes less tanning material than rapid tannage, is thus explained.

The knowledge of this chemical change was first made apparent by the introduction and use of the new method of tannin determination invented by Wilson and Kern.[21] This method is radically different from any others previously proposed and used, and as a consequence has met with vigorous opposition although it is based upon sound chemical principles.

The investigators, in a subsequent study[22] of the conduct of quebracho and gambier liquors at different H^+-ion concen-

[12] *Z. physiol. Chem.*, **116** (1921), 277.
[13] *Collegium*, **1920**, 17, 49, 137, 200, 277, 332.
[14] *J. Am. Leather Chem. Assoc.*, **15** (1920), 374.
[15] *J. Chem. Soc.*, **109** (1916), 1327.
[16] This Journal, **14** (1922), 191.
[17] This Journal, **14** (1922), 292.
[18] *Ibid.*, **12** (1920), 1149.
[19] *Collegium*, **1908**, 195.
[20] *J. Am. Leather Chem. Assoc.*, **15** (1920), 464.
[21] This Journal, **12** (1920), 465; **13** (1921), 772.
[22] *Ibid.*, **13** (1921), 1025.

trations, discovered the interesting fact that at $-\log C_{H^+}=9$, a profound change takes place upon a 24-hr. exposure of these extracts to air, because when brought back to $-\log C_{H^+}=3$, a voluminous precipitate forms. This reaction takes place to a steadily lower extent in solutions more acid than $C_{H^+}=10^{-9}$, but not at all in solutions more alkaline.

Another point brought out in this paper is the change in color of vegetable extracts with change in H-ion concentration, the color changing from a light straw at $C_{H^+}=10^{-3}$ to a very deep red at 10^{-12}, thus showing that these extracts act like indicators and explaining the long-known fact that the presence of lime in a tanned skin causes darkening of color which brightens if such a skin is treated with acid soon after tanning.

The indicator effect at different H^+-ion concentrations is reversible provided the liquors are not long exposed to air. Upon exposure to air they darken in the more alkaline solutions and the color is not changed back to the original brightness upon reacidification.

Syntans

A great deal of attention has been devoted lately to syntans. Although these are not vegetable tannins, however, because of their organic character they should be mentioned here. Syntans are condensation products of formaldehyde with sulfonated cresols and other aromatic compounds. According to Meunier[23] the tanning action of these bodies is due to the free sulfonic and free hydroxyl groups that are absorbed by the skin, thanks to their acid character. If these acid groups are neutralized, the tanning power diminishes. Syntans are now widely used as preliminary tanning agents in the preparation of heavy vegetable leathers, because they cause an increase in the rate of penetration of tannin. Wilson[14] suggests that their chief function is like that which he has described for gallic acid, or the presence of non-tans in permitting tannage in strong liquors without unevenness of fixation.

Moeller[24] points out that syntans cause hydrolysis of hide substance owing to their sulfonic acids, but that such action is materially reduced by the presence of a vegetable extract.

Hill and Merryman[25] insist that while some syntans are useful solely because of their acid character, others really do have tanning action provided they are used under carefully controlled conditions. In combination with vegetable tanning agents, in addition to the increase in rate of penetration, these authors state that syntans produce a tougher and smoother grained leather and have a bleaching action. This latter point is readily understood to be solely a function of their acidity, as demonstrated by Wilson and Kern's[21] experiments.

Hill and Merryman also point out that syntans may be used for deliming and plumping hides for sole leather manufacture. The bating properties of these agents is also discussed by Moeller[26] as a property of the sulfonic acids which they contain. Additional discussion of the uses for syntans along lines just mentioned has been published by Knowles.[27]

The term "synthetic tannins" for the agents considered above is somewhat faulty since they are not synthesized tannins resembling vegetable tannins. Emil Fischer is the only person who has prepared a *bona fide* synthetic tannin, namely, his pentadigalloylglucose. However, the name "syntans" appears to have been firmly established, and for a compact and valuable treatment of these substances the reader is referred to Grasser's new book (translated by Enna).[28]

Grasser[29] has demonstrated that the criterion of gelatin precipitation for a tanning agent is subject to error at times, because hydroxynaphthylmethane sulfonic acid precipitates gelatin but does not tan pelt, while *o*-nitrophenol tans pelt but does not precipitate gelatin.

It has been generally accepted that all tanning agents precipitate gelatin, but, in view of these new cases brought out by Grasser, it appears that actual pelt tests must be made in order to determine whether a new compound has tanning properties.

[23] *Chimie et industrie*, **1** (1918), 71, 272; *J. Am. Leather Chem. Assoc.*, **13** (1918), 530.

[24] *Collegium*, **1920**, 520.

[25] *J. Am. Leather Chem. Assoc.*, **16** (1921), 484.

[26] *Collegium*, **1921**, 232.

[27] *J. Soc. Leather Trades' Chem.*, **6** (1922), 19.

[28] "Synthetic Tannins," D. Van Nostrand Co., New York, **1922**.

[29] *Collegium*, **1920**, 234.

The Chief Chemist Remarks

A COMPARISON of efficiency of laboratories by two chief chemists led one of them to express himself somewhat as follows:

As a chief chemist, have you ever made a detailed analysis of your men? It has been proved that a man who gets two hundred a month is a better investment for a firm than one who gets one hundred and does only half the work. Do you know who in your laboratory is entitled to a raise? Do you know the weak points of your men? Are you giving them the necessary help? Are you training a man to step into your shoes when the firm gets ready to promote you? Do you give some of your men special work, which could not be given to others who are presumably of the same status? And lastly, are you a better man than your assistants?

To my mind there are ten big factors that make for success in a chemist. These vary with conditions, but for a laboratory worker each is very important: honesty, accuracy, speed, thoroughness, observation, ingenuity, loyalty, personality, health, and education.

They are arranged in the order of their importance. The first three are the most vital and refer to the physical accomplishment of the work. Most young chemists have these points well drilled into them before they leave school. It is unfortunately true that they seem to be the chief and only assets of some chemists.

The next three points are functions of the mind and usually come as the result of experience. It has been said that a man who can make an analysis is worth a hundred dollars; a man who can explain the analysis is worth two hundred dollars; while a man who can interpret and apply the analysis has no limit in value. In most lines of work, thoroughness comes first, but in chemistry, or rather in analytical or research chemistry, it must take the place indicated. The observing man is usually the wide-awake chap who can use waste material to advantage, or suggest a cheaper source of supply. The ingenious man is also the highly paid man—the inventor, or the man who can get out a new product, or cut the cost or time of manufacture.

Loyalty, personality, and health make the leader—the man for whom and with whom you like to work.

The last requirement—education—fills the chinks. It is the most easily obtained, but too often is present as a "trace only."

As an exercise in analysis, try writing these ten points in a column. Beside each point write the name of a man who, to your mind, best represents perfection in that quality. Now check yourself against this column of one hundred per cent men, and finally classify your assistants. You might even plot a curve. By doing this you will soon learn your weaknesses and those of the men working with you.

It is also a good plan to keep a monthly record. This will give you a fairly accurate idea of the men to whom the different types of work should be assigned and of those who deserve a raise. It will also afford an opportunity of checking up the "weak sister;" a heart to heart talk might give him the necessary strength. This plan might also open your own eyes; perhaps you haven't had a raise lately, and perhaps it is because of a bad habit which you have been sheltering.

While these ten points are given for analytical men, very little change will be necessary to make them applicable to any branch of chemistry. For the manufacturing chemist who has not to deal with analyses, but with men, judgment and control might be substituted for accuracy and speed.

BIBLIOTEKA POLITECHNIKI

Mineral Tannages

By F. L. Seymour-Jones[1]

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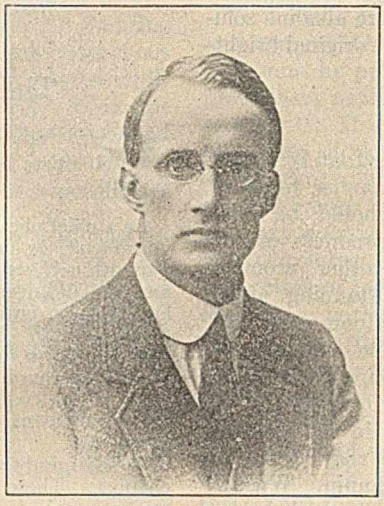
AMONG the various mineral tannages that of chrome continues to hold pride of place. Two methods are in general use. In the one-bath process the skins are treated in a solution of a basic chromic salt, usually chrome alum with soda, or bichromate reduced to the chromic state. This is followed by neutralization of the excess of free acid with a suitable weak alkali. In the two-bath process the skins are treated first in a liquor of bichromate and hydrochloric acid, then passed to a reducing bath of acid and sodium thiosulfate. Most of the recent scientific work has been concerned with the one-bath process.



F. L. Seymour-Jones

One-Bath Chrome Liquors

Acidity and Neutral Salts—The attainment of a correct basicity is important in the one-bath method. With very basic liquors tannage is extremely slow. With only slightly basic liquors the skins are abnormally plumped by the acid from the salt hydrolysis, and the resulting leather is poor. As the basicity of a chrome liquor is increased a point is reached where the chromium begins to precipitate out. When neutral salts are present in the liquor more alkali is required to bring about incipient precipitation. Wilson and Kern[2] connected this effect with the hydration of the neutral salt in solution. Thomas and Baldwin[3] found no connection between basicity as usually expressed and the true acidity determined with the hydrogen electrode. The acidity of chrome liquors decreases with dilution and with the time of standing. They also found[4] that the addition of chlorides to chromium sulfate solutions invariably increases the hydrion concentration, while sulfates at first decrease it and only increase it again at high concentrations. With sulfuric acid, chlorides increase and sulfates decrease the hydrion concentration. By adding chlorides to chromic chloride solutions Baldwin[5] again found the acidity increased. The addition of neutral salts to chrome liquors was shown by Thomas and Baldwin[6] to give a rapid increase in acidity, followed by a slow decrease. Chlorides increase and sulfates decrease the hydrion concentration of sulfuric and hydrochloric acids. Magnesium sulfate behaves irregularly, decreasing the hydrion concentration up to 0.8 M, but increasing it thereafter. Wilson[7] has shown that for chlorides this effect can be explained by the hydration of the salts in solution, but this cannot hold for sulfates, which decrease acidity. Hence, Thomas and Foster[8] extended this work, using sodium chloride and sulfate, and sucrose, the latter being chosen as a hydrating nonelectrolyte. Since sucrose did not retard tanning except at concentrations greater than 3 M, hydration seems of secondary importance, and they suggest that the chief factor is the formation of addition compounds. Burton[9] earlier considered double salt formation to be of slight importance.

Wilson and Gallun[10] find that the addition of chlorides retards tanning to an extent depending on their concentration. Magnesium chloride is anomalous, the greatest retardation occurring at about molar concentration. Burton and Glover,[11] using gelatin, find that the amount of chromium adsorbed varies with the degree of hydration of the neutral salt; chlorides increase and sulfates decrease the amount of acid taken up. In working on pelt[12] they find that chlorides retard tannage to a greater degree than sulfates. Burton[13] considers that neutral salts in chromium sulfate liquors tend to form acid sulfates. The equilibrium is thus changed and more basic chromium salts are formed with sulfates added than with chlorides.

The work on acidity and neutral salts demonstrates conclusively that difficulties will arise in practice if a chrome liquor is judged solely by its basicity and chromium content. The presence of neutral salts and the age and dilution of the liquor must also be taken into account. Further light on the exact mechanism of these effects is likely to come from a study of chromium salts and solutions from the viewpoint of inorganic, physical, and colloidal chemistry.

Concentration Effects—The effect of concentration of chrome liquor on the adsorption of its constituents by hide powder has been studied by Baldwin[14] and by Thomas and Kelly.[15] The fixation of chromium by the hide powder rises rapidly to a maximum at a concentration of 1.6 g. of chromic oxide per 100 cc., then falls to a minimum at a concentration of 14.75 g. per 100 cc., at which it remains constant up to 20.2 g. per 100 cc., the limiting value examined. The hydrogen-ion concentration for this was 0.006 M. These figures were obtained by analysis of the tanned powder. If the residual liquor is analyzed, at the higher concentrations "negative adsorption" occurs, *i. e.*, more water than chromic oxide is absorbed. The figures so obtained furnish an interesting example of the danger of determining adsorption by analysis of the residual liquor, a method implying total neglect of the role played by the solvent.

Time Effects—The effect of varying time on the fixation of chromium by hide powder has been studied over wide ranges of time and concentration by Thomas, Baldwin, and Kelly,[16] and by Thomas and Kelly.[17] Taking 750 as

[1] Goldschmidt Fellow of Columbia University 1921–2; 1851 Exhibition Scholar of the University of Leeds.

[2] *J. Am. Leather Chem. Assoc.*, **12** (1917), 445.

[3] *Ibid.*, **13** (1918), 192.

[4] *Ibid.*, **13** (1918), 248.

[5] *Ibid.*, **14** (1919), 10.

[6] *J. Am. Chem. Soc.*, **41** (1919), 1981.

[7] *Ibid.*, **42** (1920), 715.

[8] This Journal, **14** (1922), 132.

[9] *J. Soc. Leather Trades' Chem.*, **5** (1921), 187.

[10] *J. Am. Leather Chem. Assoc.*, **15** (1920), 273.

[11] *J. Soc. Leather Trades' Chem.*, **5** (1921), 183, 187.

[12] *Ibid.*, **6** (1922), 6.

[13] *Ibid.*, **5** (1921), 192.

[14] *J. Am. Leather Chem. Assoc.*, **14** (1919), 433.

[15] This Journal, **13** (1921), 31.

[16] *J. Am. Leather Chem. Assoc.*, **15** (1920), 147.

[17] *Ibid.*, **15** (1920), 487; This Journal, **14** (1922), 621.

the combining weight of collagen, on the basis of it being the anhydride of gelatin, Wilson[18] points out that for every 100 g. of collagen at least 3.38 g. of chromic oxide are necessarily fixed to produce a chromium collagenate. Thomas, Baldwin and Kelly, plotting concentration of liquor against the amount of chromic oxide fixed by 100 g. of collagen, find sharp maxima, depending on the time but at the same concentration, at amounts of chromic oxide exactly four and eight times 3.38 g., thus pointing to the formation of a tetrachrome and an octachrome collagen. The octachrome curve also shows a point of inflexion, at a higher concentration of liquor, corresponding to a tetrachrome collagen. Even if these results do not definitely prove the formation of a chemical compound, they are of great significance and must be taken into account in any theory of chrome tanning. The work certainly supports the theory of a chemical combination of the chromium and the hide substance.

Violet and Green Chrome Solutions—Chromic salts in solution are violet in the cold and green when hot, ordinary solutions being an equilibrium mixture. Two-thirds of the acid radical forms part of the cation in green solution, while in the violet all three chloride ions (in chromic chloride) are anions. The green solutions are far more hydrolyzed, and Blockey[19] showed that in green chrome alum solutions the hydrion concentration is ten times that in the violet. Burton[20] found that violet solutions tan more rapidly than green, which he attributed to the different acidity. Griliches[21] found no difference in the tanning action of green and violet liquors, but his theories of the mechanism of chrome tanning have been severely criticized by Stiasny.[22]

One curious phenomenon in the varying amounts of sodium hydroxide and carbonate necessary to bring about a permanent precipitate in a chrome liquor has been studied by Burton.[23] It is best shown by Burton's figures.

25 Cc. 3 Per-cent Chrome Alum Solution	Cc. 0.1 *N* Alkali Required to Produce a Permanent Precipitate	
	NaOH	Na_2CO_3
Green	17.8	21.8
Violet	13.2	25.0

That green solutions should require more sodium hydroxide than violet is to be expected in view of their greater acidity, but why the reverse should be true with sodium carbonate is not clear. Burton attributes it to the liberated carbon dioxide functioning as a stabilizing acid in solution, and the more acid green liquors driving more carbon dioxide from solution.

Meunier and Caste[24] with chrome alum solutions found the amounts of sodium carbonate necessary to start precipitation to be proportional to the chromium concentration at 0°, but to increase more rapidly than the chromium concentration at 100°. The amount of soda required decreases on stirring and on heating, due to the liberation of carbon dioxide and the polymerization of basic chrome salts. On aging chrome solutions the amount of soda required at first rapidly increases, then slowly diminishes to a very low value. From old or hot solutions a basic sulfate is precipitated and from fresh or cold solutions, chromium hydroxide.

Burton[25] has recently reviewed the problems of one-bath chrome tanning, and gives an extensive bibliography.

[18] *J. Am. Leather Chem. Assoc.*, **12** (1917), 108.
[19] *J. Soc. Leather Trades' Chem.*, **2** (1918), 205.
[20] *Ibid.*, **4** (1920), 205.
[21] *Collegium*, **1920**, 416.
[22] *Ibid.*, **1920**, 479.
[23] *J. Soc. Leather Trades' Chem.*, **4** (1920), 205.
[24] *Ibid.*, **5** (1921), 103, 222.
[25] *Ibid.*, **6** (1922), 157.

Two-Bath Chrome Liquors

Little work has been done on the two-bath tannage. Innes[26] studied the bleeding of leather from the first (acid-bichromate) bath. He found that most of the chromium which diffuses out is reabsorbed by the skin, and that under certain conditions bleeding is not a serious phenomenon. Schorlemmer[27] points out the disadvantage of even traces of arsenic (0.0015 per cent) in the second (acid-thiosulfate) bath, and advances a theory that the reactions of the second bath are:

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2SO_3 + S \quad (1)$$
$$5Na_2S_2O_3 + 6HCl \longrightarrow 2Na_2S_5O_6 + 6NaCl + 3H_2O \quad (2)$$

Arsenic catalyzes the second reaction, and thus impedes or prevents reduction. This view of the reactions is not in accord with the earlier work of Stiasny and Das,[28] which has met with general acceptance.

Miscellaneous Chrome Processes

Cross, Greenwood, and Lamb[29] have patented the use of concentrated solutions of chrome salts in gum tragasol jellies for rapid tanning, and Turnbull and Carmichael[30] patented starch for the same purpose. While effective and rapid, the process is messy in use, and the jelly material awkward in the drainage channels and pipes. Lamb[31] has patented the use of salts of hydroxy organic acids for stripping chrome leather scraps for glue stock, but this action of such salts in removing chromium from leather (and preventing its proper tannage in chrome liquors) had previously been demonstrated by Procter and Wilson.[32]

Theory of Chrome Tannage

The theory of chrome tannage is still obscure. Wilson[33] considers that the collagen first combines with a basic chrome salt through a single valence of the chromium atom. Further hydrolysis of the chromium compound then takes place and a second valence of the chromium unites with the collagen. Still more slowly the third valence unites with the collagen, and chromium collagenate is formed. Meunier[34] prefers to regard chrome tanning as a slow and irreversible adsorption of colloidal chromic oxide with the precipitation of a gel on the fibril surfaces, followed by a slow penetration of the gel into the interior of the fibrils.

Iron Tannage

Iron tannage is still in the early experimental stage. Pressure of war conditions forced the Germans to adopt it to some extent, and it has met with its greatest application when combined with other tannages, chrome, formaldehyde, and vegetable. Most of the work so far is embodied in the many patents which have been taken out in this connection, particularly by O. Röhm in Germany. Casaburi,[35] and Jackson and Hou[36] have described their work on straight iron tannage and have shown the question of basicity to be of great importance. The keeping qualities of the leather have yet to be demonstrated.

[26] *J. Soc. Leather Trades' Chem.*, **3** (1919), 104.
[27] *Collegium*, **1921**, 430.
[28] *J. Soc. Chem. Ind.*, **31** (1921), 753.
[29] *J. Soc. Dyers Col.*, **35** (1919), 62.
[30] Brit. Patent 110,470.
[31] Brit. Patent 132,864.
[32] *J. Soc. Chem. Ind.*, **35** (1916), 156.
[33] Private communication; cf. *J. Am. Leather Chem. Assoc.*, **12** (1917), 108, and the theory of alum tanning therein described.
[34] *Chimie et industrie*, **1** (1918), 71, 272.
[35] *J. Soc. Leather Trades' Chem.*, **3** (1919), 61, 74.
[36] *J. Am. Leather Chem. Assoc.*, **16** (1921), 63, 139, 202, 229.

Other Tannages

Very little scientific work has been done in recent years on tawing (tannage with aluminium salts), or on aldehyde and oil tannages. Moeller[37] has advanced some highly speculative theories based on peptization to account for these, but his work has been severely criticized, and the German technical journals have been occupied with the resulting polemics.

[37] *Collegium*, **1918**, 25, 61, 71, 93; **1919**, 61, 72; **1920**, 69.

The Preparation of Skin for Tanning

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BIBLIOTEKA POLITECHNIKI SZASTRIBI

John Arthur Wilson

THE apparently slow development of the chemistry of leather manufacture has been due to its extreme complexity rather than to any lack of sympathy on the part of practical tanners. This branch of industrial chemistry deals with reactions between those poorly defined groups of substances, usually colloidal, whose compositions are still matters for speculation. The raw skin is composed largely of various kinds of protein matter and is complicated by a structure which varies considerably in different animals and even in different parts of the same skin. Conversion into leather involves the removal of some of these proteins by the action of alkalies, enzymes, or bacteria, and the interaction of the remainder with tanning materials, oils, soaps, emulsions, mordants, dyestuffs, gums, resins, and other complex materials. During these reactions the structure of the skin must be carefully preserved or improved, and highly developed technic is required to impart to the resulting leather certain necessary, but almost indefinable, properties, many of which it is an art even to appreciate fully. When one considers the vast amount of energy expended by organic chemists upon the materials involved in making leather and the uncertainty of our knowledge concerning the individual substances, the complexity of the whole problem becomes more apparent.

Histology and Chemical Composition of Skin

Scientific investigations in the preparation of skin for tanning have been retarded by insufficient knowledge of the histology and chemical composition of the skins of the lower animals which have structures very different from human skin. The need has been well appreciated, but very few leather chemists have had the time, facilities, or technic required to obtain the desired information.

Recently, however, the literature on the histology of skin has been greatly enhanced by a valuable series of articles published by Alfred Seymour-Jones.[1] In addition, studies have been in progress in the writer's laboratories during the past four years of the microscopic structure of the skins of the lower animals and the changes undergone during their conversion into leather. Part of this work has already been presented[2] and its scope is gradually being extended. The importance of such studies warrants their becoming more widespread.

A review of the literature on the chemical constituents of skin has recently been made by F. L. Seymour-Jones.[3] The difficulty in making quantitative separations of the protein constituents of skin makes this type of study even more difficult than that of histology.

Many of our conceptions of the physical chemistry of the skin proteins have been derived from investigations on gelatin, particularly those of Procter[4] and his collaborators,[5] and of Jacques Loeb.[6] Loeb's work is a splendid example of the common interest which all branches of the science have in fundamental research. Although performed for its value to physiology, it has proved of great importance to leather chemistry.

Preservation and Disinfection of Skin

Raw skins are highly putrescible, and it is necessary to preserve them in some way until the first tanning operation. This is usually done by saturating with common salt, or by drying.

The attention of chemists has frequently been drawn to the appearance of stains on salted skins, usually called salt stains because their frequency of occurrence was found to be influenced by the composition of salt used and the method of its application. The staining is apparently due to a combination of the skin proteins with iron, derived either from the skin itself or from the added salt. In their natural state the iron compounds of the skin are incapable of staining, but assume this power if rendered soluble by bacterial or purely chemical action.

J. Paessler[7] found that the percentage of stains could be greatly reduced by using salt containing 3 per cent of its weight of anhydrous sodium carbonate. This retarded bacterial action prevented iron from passing into solution and served as a denaturant, in place of some more harmful material, in those countries of Europe where edible salt is taxed and salt for industrial purposes must be denatured. Abt,[8] finding some bad cases of staining were due to calcium sulfate in the salt used, pictured the reactions as follows:

[1] "Physiology of the Skin," *J. Soc. Leather Trades' Chem.*, **1917–21** (serially).

[2] "A Trip through the Tannery on the Inside of a Calfskin," presented at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 9, 1921; publication, including numerous photomicrographs, reserved for the Society's monograph on "The Chemistry of Leather Manufacture."

[3] This Journal, **14** (1922), 130.

[4] *J. Chem. Soc.*, **105** (1914), 313; **109** (1916), 307.

[5] *J. Am. Chem. Soc.*, **40** (1918), 886.

[6] *J. General Physiol.*, **1918–22**; "Proteins and the Theory of Colloidal Behavior," McGraw-Hill, **1922**.

[7] "Salting of Hides and Skins," *Ledertechnischen Rundschau*, **1912**, 137.

[8] "Microscopical Examination of Skin and Leather Applied to the Study of Salt Stains," *Collegium*, **1914**, 130.

The calcium sulfate reacted with ammonium phosphate from the nucleic acids of the skin, precipitating calcium phosphate; the ammonium sulfate thus formed rendered soluble the ferrous carbonate naturally occurring in the skin, which in turn combined with the skin, forming a stain. Becker[9] showed that the stains could be produced by pure cultures of bacteria isolated from the stains. Romana and Baldracco[10] prevented the stains by adding sodium fluoride to the salt or by washing the lymph, containing much of the iron, out of the skins immediately after flaying, but before salting.

Dried skins often come from regions infected with certain disease germs, of which anthrax is the one most dreaded. Such skins must be disinfected and apparently the best method devised is that of Alfred Seymour-Jones,[11] which consists of soaking the dried skins for from 1 to 3 days in a solution of 1 per cent of formic acid and 0.02 per cent of mercuric chloride, followed by immersion in a saturated salt solution for an hour, draining and baling for shipment. Both Abt and Seymour-Jones have pointed out, however, that hides would contain no anthrax if dried in the sun immediately after flaying.

Changes begin to take place in the skin immediately after the death of the animal. McLaughlin[12] recently found that the degree of swelling of hide in limewater depends upon the time lapse since the death of the animal. As for the practical significance of this fact, the writer has put into process together both properly preserved skins and skins taken from animals within an hour after death and could detect no difference in the finished leathers by microscopical, chemical, and physical analysis.

Soaking and Fleshing

Among the first tannery operations are washing to remove blood and lymph, soaking in cold water for several days to swell the fibers and bring them again into equilibrium with water, and the removal of the adipose tissue or flesh. The contribution of chemists in the soaking operation has been in the direction of hastening the absorption of water, in the case of dried skins, by the addition of acids or alkalies under proper control. The reason why skins must be completely wet back before fleshing or tanning is prettily illustrated in a paper on gelatin by Sheppard and Elliott.[13] Cubes and cylinders of gelatin jelly always suffer a change of shape during drying because of the greater initial rate of drying and casehardening of the edges. Skins fleshed without sufficient preliminary soaking will look smooth on the flesh side upon coming from the fleshing machine, but later, when the skin has absorbed more water, the flesh side will be so ragged and uneven as to require further treatment. If dried skins are not completely soaked back before entering the tan liquors, the distortions suffered by the fibers during the original drying will be permanently fixed by the tanning action and the leather will never have the proper suppleness.

Unhairing

Recent microscopical studies have demonstrated clearly that the loosening of the hair and epidermis by the common methods of liming and sweating, as well as by the newer methods involving enzyme action, is due to the digestion of the cell walls of the Malpighian layer of the epidermis resting on the true skin, the destruction of which leaves the hair and epidermis completely separated from the rest of the skin.

Since sterile limewater has little unhairing action on skins, it was long thought that bacteria were necessary for this action. But Schlichte[14] found that skin previously sterilized by the Seymour-Jones process could be unhaired easily after two weeks of contact with saturated limewater under sterile conditions. Wood and Law,[15] however, pointed out that the action may have been influenced by the previous swelling of the skin in the sterilizing solution. This action of swelling agents in making protein matter more susceptible to hydrolysis is now receiving increased attention.

Röhm[16] devised a process for unhairing by means of an alkaline trypsin solution. In describing Röhm's process, Hollander[17] pointed out that a skin can be unhaired by soaking for one day in a dilute solution of sodium hydroxide and then for one day in a solution of sodium bicarbonate to which trypsin is added after the swelling of the skin has been counteracted. In the discussion following Röhm's presentation of his paper, Eberle expressed doubt that the hair loosening was due to the enzyme. In a recent investigation, Wilson and Gallun[18] confirmed Hollander's findings and showed that the action proceeds slowly in the absence of the enzyme, but is greatly accelerated by its presence and by rise of temperature up to 40°; but, when the experiments were conducted under toluene to check bacterial action, there was no unhairing action at 25°, but a very marked action at 40°, indicating that pancreatin is an unhairing agent at 40° but that the action obtained at lower temperatures in practice is due to something other than pancreatin.

Ross[19] patented a process for unhairing with thrombase naturally occurring in skin. If proved sound, his view will be an important addition to our knowledge of the action of old lime liquors. J. T. Wood,[20] of Nottingham, found that formic acid will unhair a skin if sufficient time is allowed. The subject of acid unhairing has since been reviewed by Marriott.[21] Apparently anything that will hydrolyze the newly formed cells of the epidermis without injuring the rest of the skin is a satisfactory unhairing agent.

The extent to which the unhairing agent swells the skin has an important effect on the appearance of the finished leather, excessive swelling tending to produce a roughness of the grain surface. Atkin[22] was able to reason from the theories of Procter, Wilson, and Loeb[23] that the addition of arsenic disulfide to a lime liquor should cause less swelling than the addition of sodium sulfide and thus leave the skin with a finer grain surface. His reasoning is borne out in practice in the case of glazed kid leathers.

Bating

One of the greatest blessings which the industry has derived from chemistry is the replacement of the obnoxious dungs formerly used in bating by pancreatic enzymes. After liming, unhairing, and washing the skins, it was customary to put them into warm infusions of the dung of dogs or fowls until they had become very soft and flaccid. The dung appeared to be necessary to remove some undesirable constituent of the skin until Wood,[24] in 1898, discovered that the same action could be obtained by pancreatin under suitable

[9] "Salt Stains," *Collegium*, **1912**, 408.

[10] "Salting of Hides and Avoidance of Salt Stains," *Collegium*, **1912**, 533.

[11] "Formic-Mercury Anthrax Sterilization Method," London, **1910**; "Anthrax Prophylaxis in the Leather Industry," *J. Am. Leather Chem. Assoc.*, **17** (1922), 55.

[12] *J. Am. Leather Chem. Assoc.*, **16** (1921), 435.

[13] *J. Am. Chem. Soc.*, **44** (1922), 373.

[14] *J. Am. Leather Chem. Assoc.*, **10** (1915), 585.

[15] *J. Soc. Chem. Ind.*, **35** (1916), 585.

[16] *Collegium*, **1913**, 374.

[17] *J. Am. Leather Chem. Assoc.*, **15** (1920), 477.

[18] "Pancreatin as an Unhairing Agent" (not yet published).

[19] Brit. Patent 169,730; cf. *C. A.*, **16** (1922), 853.

[20] Private communication to writer in 1916; *J. Am. Leather Chem. Assoc.*, **12** (1917), 114.

[21] *J. Soc. Leather Trades' Chem.*, **5** (1921), 2.

[22] This Journal, **14** (1922), 412.

[23] *Loc. cit.*

[24] "Puering, Bating, and Drenching of Skins," E. and F. N. Spon, London.

conditions. Just what constituent was removed, however, remained in doubt for many years. Rosenthal[25] found that the material removed was a protein, and assumed that it was elastin. Alfred Seymour-Jones,[26] in collaboration with Wood, studied the effect of bating with pancreatin and concluded that bating dissolves the elastin fibers of the grain membrane. Wilson and Daub[27] examined the bating action under the microscope and showed unmistakably that the elastin fibers were dissolved away completely by the action of pancreatin. They then made an exhaustive study of the rate of digestion of elastin fibers from calfskin as a function of concentration of enzyme and ammonium chloride, time, and pH value, which has reduced the control of this operation from one of the most difficult to one of the simplest in the tannery.

The empirical method for determining the completion of the bating process is by noting when the swelling or plumping of the skin has been entirely counteracted and the skin is quite flaccid. Wilson and Daub observed a point of minimum plumping at a pH value of about 8. But Thomas and Kelly[28] and Porter[29] found the isoelectric point of collagen to be at about pH = 5. More recently Wilson and Gallun[30] made a careful study of the plumping of unhaired calfskin as a function of pH value and found two points of minimum, one near 5 and the other near 8, the one near 5 having the lower value. This seems to indicate that what we call collagen consists of a mixture of proteins of very different isoelectric point, or else that collagen undergoes some internal change, possibly tautomeric, with change of pH value that tends to shift its isoelectric point.

It has generally been thought that pancreatin is practically without action upon collagen. In fact Wilson and Daub could detect no appreciable destruction of collagen under the microscope while observing the complete solution of elastin. But F. L. Seymour-Jones,[31] experimenting upon hide powder, has found that under the right conditions and with sufficient quantity of enzyme, collagen is easily attacked and dissolved by pancreatin. Wilson and Gallun have found that pancreatin will dissolve calfskin if given sufficient time. In one experiment they found no visible destruction of collagen for the first 24 hrs., but during the second day the fibers began to dissolve comparatively very rapidly, suggesting that the fibers possess a very thin surface much more resistant to tryptic digestion than the substance in the interior. The action of enzymes on skin during its preparation for tanning offers a fertile field for further research.

[25] *J. Am. Leather Chem. Assoc.*, **11** (1916), 463.
[26] *J. Soc. Leather Trades' Chem.*, **4** (1920), 60.
[27] THIS JOURNAL, **12** (1920), 1087; **13** (1921), 1137.
[28] *J. Am. Chem. Soc.*, **44** (1922), 195.
[29] *J. Soc. Leather Trades' Chem.*, **5** (1921), 259.
[30] "Points of Minimum Plumping of Calfskin" (not yet published).
[31] Advance note.

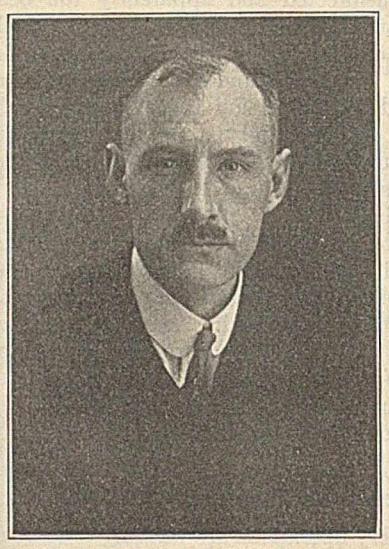
A final examination for appointment of second lieutenants in the Regular Army will be held the week beginning October 23, 1922, and appointments will be tendered successful candidates as soon as possible after December 31, 1922, in the following branches: Infantry, Cavalry, Field Artillery, Coast Artillery, Air Service, Corps of Engineers, Signal Corps, Quartermaster Corps, Ordnance Department, Chemical Warfare Service, Finance Department, and Philippine Scouts. Applicants must be citizens of the United States between the ages of 21 and 30 years. Each candidate is permitted to express his first and second choices of the branch of service in which he desires to be appointed, but the War Department reserves the right to make assignments in whatever branches of the service it may be necessary. Those interested may secure application blanks and further information from the Commanding Officer, Second Corps Area, Governors Island, N. Y., or the nearest military post.

Rare Organic Chemicals

By H. T. Clarke

EASTMAN KODAK CO., ROCHESTER, N. Y.

BY "rare organic chemicals" is here understood chemicals required in relatively small quantities exclusively for laboratory purposes, whether for chemical research, analytical work, or experimentation in medical or physical science. Certain of the chemicals employed in pharmacy, perfuming, flavoring, and other industries might reasonably be classed under this head; but in this article the above definition will be followed, to the exclusion of all industrial products.



H. T. CLARKE

The history of the progress of the manufacture of this class of chemicals in the United States really dates from eight years ago, when the supply from Germany ceased. Before that time practically nothing of the sort was made in this country, American chemists being content to draw their requirements, either directly or through supply houses, from the two important German firms which between them had built up the source from which the needs of the entire world were filled. When the pinch came, practically nothing was done during the first three years to relieve the situation, since the attention of chemical manufacturers was necessarily directed to more urgent, at any rate more spectacular, problems. The first step was taken in 1916 in the University of Illinois, when Prof. C. G. Derick inaugurated a vacation class in which, under his direction, the otherwise inaccessible organic chemicals required during the coming year were prepared. This valuable work, which did not excite imitation in other universities,[1] was continued in the same laboratory by Prof. Roger Adams, who was able to supply a certain proportion of the products of the Illinois laboratory to other universities. It was not until the latter part of 1918 that commercial firms began to enter the field. The first of these was the Eastman Kodak Co., whose action was followed by a number of concerns, in particular the Heyl Laboratories, the Special Chemicals Co., and the Synthetic Laboratories of Chicago, organized for the specific purpose of manufacturing research organic chemicals.

The success of these undertakings has of course depended largely on the coöperation of the manufacturers of those organic chemicals that are employed on a larger scale, and this has in all cases been cordially and generously accorded. Manufacturers of crudes, intermediates, and dyes, such as The Barrett Co., E. I. duPont de Nemours & Co., The National Aniline & Chemical Co., the Calco Chemical Co., The Dow Chemical Co., The Monsanto Chemical Works, The Sherwin-Williams Co., to mention but a few of the more

[1] An exception should be made in the case of the University of Wisconsin in which a considerable amount of time has more recently been devoted to the preparation of chemicals for its own use.

important, have continually furnished information as to the products they manufacture not only for sale but for their own use. The same has been the case with the firms manufacturing pharmaceuticals, perfumes, and flavoring chemicals. Some of these concerns have indeed contributed nobly by putting in the market, often without financial profit, lines of pure organic chemicals for research and development purposes. This has been done by the U. S. Industrial Chemical Co. (pure alcohols and esters), the Fries & Fries Co. (pure acids and esters), the Digestive Ferments Co. (rare sugars for bacteriology), and the General Motors Research Corporation (hydroaromatic compounds).

Valuable work has also been done by certain firms who have made readily available certain compounds that had hitherto been classed as "rare chemicals." Thus, The Dow Chemical Company now produces pure ethylene glycol, ethylene chlorohydrin and its acetate, and dichloroacetic acid; the Standard Oil Company and Carbide & Carbon Chemicals Corporation have rendered isopropyl alcohol as accessible a solvent as ethyl alcohol; while the Hirsch Laboratories have placed on the market a series of aliphatic amines and their derivatives.

With regard to the avowedly rare, and therefore generally expensive, organic chemicals, the greatest number have been prepared in the Research Laboratory of the Eastman Kodak Co., who now have a list of over 1300 different chemicals. No attempt has been made to develop any special line, for the object has been to prepare only those chemicals that are not produced commercially on a technical scale, and to build up as long a series of rare organic chemicals in as short a time as possible. During the past 12 mo., 253 new chemicals have been added to the list, of which 187 were prepared in the Eastman Kodak Laboratories. The remaining 26 per cent can be accounted for principally by the growth of the range of organic chemicals produced technically. It is interesting to note in this connection that the list of Kahlbaum contains the names of just over 2000 organic chemicals, so that to reach this number not much more than three years more should be necessary. There can be little doubt, moreover, that the manufacturers of rare organic chemicals in Germany are (or were) able to draw upon a much wider group of commercial chemicals than has yet been possible in the United States; this would explain the occasional startling differences in price between certain German chemicals and the same products listed as rare chemicals in this country.

One of the most spectacular fields of rare organic chemicals is occupied by the sugar family. The production of these compounds constitutes almost a special branch of chemistry in itself, and there are few organic chemists who would dare to enter this field without special preparation. American chemists and bacteriologists are thus greatly indebted to the Digestive Ferments Company and to the Special Chemicals Company for their fine work in making available an extensive list of the uncommon sugars in pure form. The amount of skill and labor necessary for their preparation and the urgency with which they are required for special work may be estimated from their cost, which in certain instances amounts to several dollars per gram. An allied field is represented in the amino acids required for bacteriological and physiological research. Here again valuable services have been rendered by the Special Chemicals Company and the Abbott Laboratories, as well as by certain private workers, notably Mr. H. J. Bean, who has specialized in physiological-chemical reagents of the meticulous degree of purity required for such work.

Another highly technical branch of chemistry which has collaborated with the medical sciences is the production of bacteriological and medicinal dyes, an alliance which, while already extensive, is apparently still in the infancy of its possibilities. The admirable work carried out by the Heyl Laboratories—now incorporated with the National Aniline & Chemical Company—constitutes an almost unique achievement in this domain, the quality of their products surpassing those of the European laboratories.

Closely related are the indicators employed in the modern methods involving hydrogen-ion concentration. The works of Clark and Lubs, of Acree, and of Walpole have demonstrated the great value of the sulfonphthalein family of indicators (which, by the way, are also employed in experimental medicine), and this series of dyes has been well taken care of by the Pyrolectric Instrument Co., The Coleman and Bell Co., Hynson, Westcott and Dunning, and LaMotte Chemical Products Co., all of which also manufacture the more important of the other indicators.

It is difficult for the average chemist in his laboratory to keep himself informed of the various products that are available; and to assist such workers a list of American Research Chemicals has been prepared under the auspices of the National Research Council by Dr. Clarence J. West. It would be difficult to exaggerate the value of this list, which is published annually and contains the name of every available chemical, together with an index number for the firms from which it can be obtained. Dr. West certainly deserves the gratitude of every chemist for the admirable way in which he has discharged his laborious task.

Publicity is also being given to methods for the preparation of a number of rare organic chemicals. In the organic chemical manufactures of the University of Illinois, to which reference was made above, a number of chemical reactions are studied, and reports of these have been published annually in the University of Illinois Bulletin by Roger Adams, O. Kamm, and C. S. Marvel. The information contained therein is of great value to all chemists engaged in organic research work. Another series of annual publications, also stimulated into existence by Dr. Roger Adams, dealing with the preparation of organic chemicals, is that entitled "Organic Syntheses" (John Wiley & Sons). This is a more elaborate work, in which each of the preparations described has been drawn up so as to leave no possibility of doubt and mistake in procedure, and has been carefully checked by a member of the editorial board.

The Public Health Institute of Chicago has undertaken to finance the coöperative research between the University of Wisconsin Medical School and the Chemical Department of Northwestern University, which in the past has been supported by appropriations from the U. S. Interdepartmental Social Hygiene Board. This research, which has been devoted to attempts to improve the treatment of syphilis of the central nervous system, has been directed by Dr. W. Lee Lewis and Dr. F. C. Whitmore of Northwestern University, and Dr. A. S. Loevenhart and Dr. W. F. Lorenz of the University of Wisconsin. The Public Health Institute has appropriated $21,600 for the use of both universities during the coming year.

A series of lectures on the Geology of Commerce and Industry is to be given by Dr. Ernest R. Lilley at the School of Commerce, New York University. During the fall term the commercial geology of the fuels, chemicals, and building materials will be discussed in a nontechnical manner, covering for each of the basic commodities the properties and uses, methods of exploitation and conservation, including mining and preparation for market, and the relation between market prices and production costs. During the spring term the lecturer will treat the commercial geology of the metals, dividing the subject as follows: the iron group, the nonferrous metal group, the precious metals, and the process minerals. Stress will be laid upon the nature and cost of smelting and refining.

Organic Catalysis

By E. Emmet Reid

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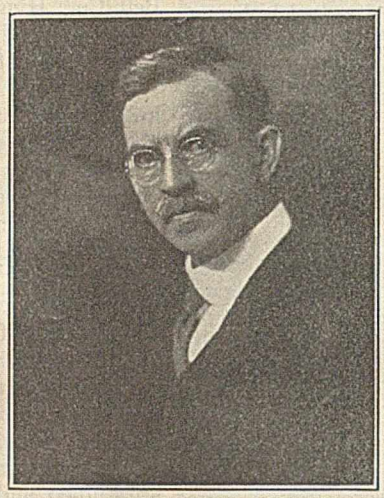
THE PAST year has seen much activity in the study of the mechanism of catalysis and a more exact study of the influence of the precise method of preparation of a catalyst on its activities, both qualitatively and quantitatively. The most striking contributions to the literature are briefly summarized in the following paragraphs.



E. Emmet Reid

The mechanism of catalysis has been studied by Langmuir.[1] Taylor and Burns[2] lay a foundation for reasoning and calculating by measuring the adsorption of hydrogen, carbon monoxide, carbon dioxide, and ethylene by nickel, cobalt, iron, platinum, and palladium. They find that adsorption is specific and that saturation is reached at low pressures. Preparations of the metals which are good absorbers are good catalysts.

Palmer and Palmer[3] make an intensive study of the hydrogenation of ethylene and explain all their results in terms of the absorption of hydrogen or ethylene on the surface of the nickel. At first the metal is covered with hydrogen and the reaction is slow. Some of this is driven off by the heat of the reaction and ethylene condenses on a part of the surface. This is the condition of maximum efficiency and the reaction slows up when too much ethylene chokes up the surface.

Rideal[4] can find no period of induction except when oxygen is present. He adopts Langmuir's view that the metal is covered with a film of hydrogen and ethylene one molecule deep and that the reaction is between the ethylene and hydrogen molecules that find themselves adjacent in this film.

Maxted[5] makes a quantitative study of the influence of poisons, lead, mercury, sulfur, and zinc, on the occlusion of hydrogen by palladium and on the catalytic power of platinum and palladium. The rate at which hydrogen is taken up is affected far more than the amount, two weeks being required for saturation with 19 per cent of lead on the palladium. With 17 per cent of lead the amount of hydrogen absorbed is reduced only 50 per cent while the rate of hydrogenation is decreased 98 per cent, which indicates that the catalytic action is confined to the surface. To cut the catalytic activity of platinum in half requires 10 per cent mercury or sulfur and only 4 per cent arsenic or zinc.

Armstrong and Hilditch[6] study the relation between the pressure of the hydrogen and the rate of hydrogenation. It appears that H_2 rather than H is the reactant, the rate being directly proportional to the pressure, provided at least 0.1 per cent nickel is present. With 0.01 per cent, the rate is too low, which seems to show that a part of the metal is combined with the ethylene groups.

Rideal[7] makes a valuable addition to our scanty quantitative data on hydrogenation by determining the dissociation pressures of the hydrogen from ethyl and isopropyl alcohols between 105° and 275° over a copper catalyst.

Matignon[8] and Herzfeld consider the formation of intermediate compounds from the standpoint of thermodynamics.

Dhar and Mittra[9] find that the oxidation of a more oxidizable substance is slowed down in the presence of the substance in which it induces oxidation. The second substance may be considered a negative catalyst. The explanation may be found in the formation of complexes.

Burrows[10] finds that the addition of sucrose, which is itself hydrolyzed, slightly accelerates the hydrolysis of methyl acetate by hydrochloric acid.

Sherman and co-workers[11] measure the influence of amino acids, copper salts, etc., on the activity of amylases.

Coffey[12] upsets tradition by showing that, under the influence of driers, oils take up only 0.6 as much oxygen as without.

Taylor and Lewis[13] study the absorption spectra of triethyl sulfonium bromide in eight solvents in an attempt to find a connection between reactions and light absorption. Most of the absorption bands were in the calculated positions.

Baly, Heilbron, and Barker[14] effect the photosynthesis of formaldehyde from carbon dioxide in water illuminated by light of short wave length, $\lambda = 200\ \mu\mu$. The formaldehyde passes into reducing sugars in light of $\lambda = 290\ \mu\mu$. In the presence of certain colored substances, the photosynthesis takes place under the influence of visible light.

Schwarz and Friedrich[15] find that Röntgen rays poison a platinum catalyst.

Rosenmund and Zetzsche[16] have made an extensive study of stopping reactions at the desired place. The following reactions occur by catalytic hydrogenation: benzoyl chloride $\longrightarrow$ benzaldehyde $\longrightarrow$ benzyl alcohol $\longrightarrow$ toluene. By adding a trace of sulfurized quinoline, 88 per cent aldehyde can be obtained.

Adkins and Krause[17] conclude that the method of preparation of a catalyst is of equal, if not greater, importance than the particular metallic element present.

Willstätter and Waldschmidt-Leitz[18] claim that hydrogenation cannot be effected with platinum or palladium free from oxygen, and suggest that catalytic poisons remove this all-important oxygen. Their experiments appear exact and convincing. H. S. Taylor explains their results by assuming that a catalyst may so cover itself up with hydrogen that the

[1] *Trans. Faraday Soc.*, adv. proof 1921; *C. A.*, **16** (1922), 864.
[2] *J. Am. Chem. Soc.*, **43** (1921), 1273.
[3] *Proc. Roy. Soc. (London)*, **99A** (1921), 402.
[4] *J. Chem. Soc.*, **121** (1922), 309.
[5] *Ibid.*, **119** (1921), 225, 1280.
[6] *Proc. Roy. Soc. (London)*, **100A** (1921), 240.
[7] *Ibid.*, **99A** (1921), 153.
[8] *Chim. et industrie*, **6** (1921), 7; *Z. phys. Chem.*, **98** (1921), 161.
[9] *Chem. News*, **123** (1921), 313.
[10] *J. Chem. Soc.*, **119** (1921), 1798.
[11] *J. Am. Chem. Soc.*, **43** (1921), 2454, 2461, 2469.
[12] *J. Chem. Soc.*, **121** (1922), 17.
[13] *Ibid.*, **121** (1921), 665.
[14] *Ibid.*, **119** (1921), 1025.
[15] *Ber.*, **55** (1922), 1040.
[16] *Ibid.*, **54** (1921), 425, 638, 1092, 2033, 2038; **55** (1922), 609; Abel, *Ibid.*, **54** (1921), 1407; **55** (1922), 322.
[17] *J. Am. Chem. Soc.*, **44** (1922), 385.
[18] *Ber.*, **54** (1921), 113.

substance to be reduced cannot get to it. Kelber[19] flatly contradicts their results so far as nickel catalyst is concerned, finding that nickel is active in the absence of oxygen and may be killed by air even at −20°, but can be revivified by treatment with hydrogen at 70° to 80°. Skita[20] took pains to exclude oxygen from the catalyst and all reactants and yet obtained rapid hydrogenations with platinum. Voorhees and Adams[21] agree that oxygen is necessary with a platinum catalyst. They simplify and improve the preparation of platinum black.

Cake[22] opens up an important field by hydrogenating glucose to *d*-sorbitol and *d*-mannitol.

Milligan and Reid[23] transfer hydrogen from an alcohol to an aldehyde.

Mailhe[24] eliminates halogens catalytically and[25] prepares cyclohexylamine by hydrogenating cyclohexanone hydrazone.

Brand and Steiner[26] hydrogenate aromatic nitro compounds to β-aryl-hydroxylamines or to azoxy and hydrazo compounds.

Schroeter[27] gives details of the preparation of tetralin and elaborates the chemistry of a multitude of its substitution products.

Wieland[28] lines up catalytic oxidation with hydrogenation by holding that the hydrogen of the compound is activated and made to combine with oxygen; what we usually call an oxidizing agent is really only an acceptor for the activated hydrogen.

Karczag[29] compares the speed of oxidation of 34 dyes by hydrogen peroxide in the presence of salts of iron, copper, nickel, manganese cobalt, and platinum. A ferrous salt acts faster than a ferric.

Clover[30] finds the autoxidation of ether to be hastened by acetaldehyde.

Conover and Gibbs[31] describe the oxidation of naphthalene by air over vanadium pentoxide at 400° to 500°. They list many other catalysts which can be used, but with poorer results. This has become an important commercial process.

Scholl and co-workers[32] have found that aluminium chloride greatly facilitates the removal of hydrogen from aromatic rings, whereby two nuclei are united as in the formation of diphenyl from benzene. With this catalyst the reaction may go well at 100° to 150°, so that products may be obtained that are otherwise out of the question. They synthesize perylene, benzanthrone, 4.5, 8.9-dibenz-pyrenequinone, 3,10, etc.

More along the usual Friedel and Crafts lines, Smith,[33] Stephens and McMullen have prepared a number of new benzoyl benzoic acids. Milligan and Reid[34] have ethylated benzene and naphthalene with ethylene, the reaction being hastened enormously by high-speed stirring. Korczynski and Mrszinski[35] find that chlorides of cobalt, nickel, iron, and tungsten may be used instead of copper chloride with aluminium chloride to effect the synthesis of aromatic aldehydes from carbon monoxide.

Gilfillan[36] compares the dehydrating power of silica, thoria, titania, and blue oxide of tungsten, on alcohols.

Vogt and Nieuwland[37] study the most effective form of mercury for catalyzing the synthesis of acetaldehyde.

Mailhe and de Godon[38] alkylate aniline by the aid of alumina.

[19] *Ber.*, **54** (1921), 1701.
[20] *Ibid.*, **55** (1922), 139.
[21] *J. Am. Chem. Soc.*, **44** (1922), 1397.
[22] *Ibid.*, **44** (1922), 859.
[23] *Ibid.*, **44** (1922), 202.
[24] *Bull. soc. chim. (Paris)*, [4] **29** (1922), 535.
[25] *Compt. rend.*, **174** (1922), 465.
[26] *Ber.*, **55** (1922), 875.
[27] *Ann.*, **426** (1922), 1.
[28] *Ber.*, **54** (1921), 2353.
[29] *Biochem. Z.*, **117** (1921), 69.
[30] *J. Am. Chem. Soc.*, **44** (1922), 1109.
[31] THIS JOURNAL, **14** (1922), 120.
[32] *Ber.*, **55** (1922), 109, 118, 324, 330.
[33] *J. Am. Chem. Soc.*, **43** (1921), 1920; *Ibid.*, **43** (1921), 1950; *Ibid.*, **43** (1921), 1965.
[34] *Ibid.*, **44** (1922), 206.
[35] *Bull. soc. chim. (Paris)*, [4] **29** (1921), 459.
[36] *J. Am. Chem. Soc.*, **44** (1922), 1323.
[37] *Ibid.*, **43** (1921), 2071.
[38] *Compt. rend.*, **172** (1921), 1417.

Oil-Cracking Patent Application of 1913 Just Granted

At the present time much gasoline is made by "cracking," which is the oil man's alias for destructive distillation. Oil is heated until it breaks down and one of the products is gasoline. A chemical process of making gasoline is described in the McAfee patent on "Process of Converting Oil," No. 1,424,574, issued to the Gulf Refining Company, August 1, 1922, on an application which has been on file in the Patent Office since 1913. Mr. McAfee says that he can make sweet saturated gasoline from higher boiling oils, such as gas oil or fuel oil, with the aid of anhydrous aluminium chloride at temperatures considerably below cracking temperatures and without the breaking down or destruction incident to cracking. The high boiling oil is heated in the presence of anhydrous aluminium chloride to a temperature corresponding to the boiling point of the mixture, and for a clean separation only the vapors at about 350° F. or less are allowed to go to the final condenser, while all vapors at a higher temperature are recondensed and returned to the condensing still. This insures returning to the still vaporized aluminium chloride and prevents it from condensing with the final gasoline formed.

In the Patent Office the progress of Mr. McAfee's application to patent was delayed by legal proceedings incident to an "interference." The contest was between Mr. McAfee and another chemist, employed by one of the large oil companies; but after protracted litigation in the Patent Office and before the Court of Appeals of the District of Columbia, Mr. McAfee was finally adjudged the inventor.

It is stated that the Gulf Refining Company has been making gasoline by the patented method for several years with entirely satisfactory results. The initial and the end boiling points of the produced gasoline can be limited within a narrow range and the material is of sweet saturated nature. The high temperatures and high pressures of the usual cracking methods are not used. The gasoline made by this aluminium chloride process, being saturated, shows practically no iodine number or heat reaction with sulfuric acid and is thus distinguished from the cracked gasolines.

The low boiling hydrocarbons found in gasoline are less complex chemically than the hydrocarbons of high boiling oils. The new process therefore contradistinguishes from various well-known building-up actions exerted by aluminium chloride by which more complex are made from less complex hydrocarbons. The elimination of building-up action in the Gulf process seems to be connected with the continual return of volatilized aluminium chloride to the still and the constant removal of gasoline as it is formed, leaving only high boiling oils to be acted on by the catalyst. The net result is the production of very little gas or high boiling material, with yields of commercial gasoline as high as 85 per cent of the original oil.

The aluminium chloride seems to act as a simple catalyst in the conversion process, since its period of utility is limited only by the carbon and heavy oils with which it combines after a rather long use. When this happens, the aluminium chloride can be revived for re-use by a process which also is patented by the Gulf Refining Company.

The Gulf Refining Company is said to be willing to license oil companies under the patented process and several improvement patents, including the so-called "recovery process" and certain patents covering inexpensive methods of manufacturing anhydrous aluminium chloride.

A meeting of representatives of various dyeing and bleaching concerns in Pennsylvania, New York, Massachusetts, and Rhode Island was held at the Hotel Biltmore, New York, N. Y., on June 21, 1922, for the purpose of considering the advisability of the formation of a national organization of dyers and bleachers.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

Chemistry of Sanitation

By A. M. Buswell

Chief, Illinois State Water Survey, Urbana, Illinois

Production of Potable Water

With the development of quantitative bacteriological technic, chemical tests for determining the sanitary quality of water lost much of their former importance. Because of increasing necessity for the use of surface supplies, all of which are more or less subject to pollution, the main question has become one of purification rather than of a test for freedom from infection, and it should be remembered that purification involves a great deal more than disinfection. Disease germs can be killed or got rid of with comparative ease, but tastes, odors, and turbidity must also be removed in order to produce a potable water.

A. M. Buswell

Water purification is, therefore, an essential chemical process and it is along the line of the investigations of the reactions involved and methods for their control that the water chemist is again coming into his own. Though it is possible at the present time to produce a potable water from almost any source, no matter how polluted, yet there is room for improvement of the product as well as of the process. Furthermore, the art is at present ahead of the theory. We can purify water with reasonable success, but we do not understand the mechanism of the reactions involved. "Who but the chemist is to fix the proper value for the dose of chemicals?" said Professor Mason[1,*] seven years ago, and we might add, "Who but the chemist can investigate the complicated reactions of these chemicals?"

The following steps represent what may fairly be considered as present standard practice in purification of municipal surface supplies for general domestic use: coagulation with aluminium sulfate or ferrous sulfate; sedimentation; rapid filtration through sand; and, finally, disinfection with chlorine. Some of the earlier "slow sand" filters are still in use, especially in Europe. In some cases chlorination without filtration is used as a more or less temporary measure and in a few instances filtration without chlorination is regarded as sufficient. Softening or iron removal is sometimes attempted, but in general such treatment is left to the private or industrial consumers.

The relation of pH to precipitation of $Al(OH)_3$ has probably been the most extensively investigated problem in the last few years. Practice had been to add lime to waters which after alum treatment showed a residuum of less than 20 p. p. m. of $CaCO_3$ (alkalinity). But Wolman and Hannan[2] showed not only that the addition of lime was unnecessary in most cases but that in some instances the addition of small amounts of acid favored precipitation. At the same time Buswell and Greenfield[3] investigated the various reactions of water purification and water softening, following the course of the reactions with the hydrogen electrode. A committee of the American Water Works Association, R. S. Weston, chairman, with the aid of a number of filter plant operators, compiled this year a considerable amount of data which will be published in the journal of that society. Clark and Theriault[4] report that hydrogen electrode experiments have shown that equilibria in aluminium solutions with the solid phase (aluminium hydroxide?) present are complex. The peculiarities nullify the value of methods previously used to estimate the isoelectric point. By taking advantage of these peculiarities the isoelectric point has been found to lie between pH 5.5 and 6.0. Experiments on time of flocculation have shown minimum time at or near pH 5.5. An empirical equation has been found relating time for first appearance of floc and pH under uniform sets of laboratory conditions. Time of flocculation is also a function of circulation, and rough relations have been found whereby small vessel experiments may be extrapolated to large volume conditions.

Buswell and Edwards[5] have shown that the unprecipitated aluminium in treated water is less than is ordinarily found in untreated natural waters even when the pH is far from the optimum. This should quiet the fears, expressed occasionally in medical circles, of the physiological effect of the "alum" used in water purification. While the pH determination has not proved the panacea some would have led us to expect, it has already proved its usefulness in the operation of certain filter plants, notably the one at Baltimore.[6] The colloidal phase of the problem is generally recognized; yet, with the exception of the work of Catlett[7] and of O. M. Smith[8] and some theoretical proposals by Pirnie,[9] little progress has been made along that line.

While the role of oxygen in causing corrosion has long been recognized, several articles[10] have recently appeared describing various devices for preventing corrosion by means of "deoxidation." These are in general of two types: (1) Filtering the water over iron or other metal turnings to "deoxidize" it, or (2) boiling out the dissolved gases. In some cases a combination of the two is used. Tillmans and Heublein[11] and later Kolthoff[12] have shown that, as would be predicted from the mass law, the presence of $Ca(HCO_3)_2$ lessens the solvent action of H_2CO_3 on $CaCO_3$. The amount of $CaCO_3$ which a water will dissolve is a measure of the "aggressive" CO_2 which is a different numerical value from "free" CO_2.

Don's[13] recent investigation of the adsorption of ammonium salts in sand filters recalls the much earlier work of Chick[14] on the same subject but from the standpoint of sewage treatment. The cause of surface shrinkage in filters has been attributed to adsorption.[15]

A symposium on tastes and odors was held at the last convention[4] of the American Water Works Association. Chlorine may be noticeable if present in excess or it may produce organic compounds which cause a "chemical" or "iodoform" taste. British operators recommend "antichlors" for the former and $KMnO_4$ for the latter.

* Numbers in text refer to Bibliography at end of this article.

The most serious recent trouble due to tastes was that produced by *Synuria* in New York City[16] supply. This taste was removed by treating with an excess of Cl_2. Another case is recorded in which an attendant attempted to dislodge by force a specimen of *Mephitis mephitis* (vulgarly known as skunk) which had perched on the water intake.

The obvious disadvantage of waiting 24 to 48 hrs. for bacteriological results to tell whether or not chlorine treatment has been sufficient, has led to the immediate popularity of the chemical "excess chlorine" test of Enslow and Wolman,[17] which can be read within half an hour. The study of filter plant loading by Streeter[18] has thrown considerable light on what may be expected from various purification plants.

No radical changes have taken place in the field of matter softening since the introduction of zeolites 10 or 15 yrs. ago. Comparatively little has been published on the zeolite base exchange[19] reactions outside the patent literature, but it is now apparent that the power to exchange bases is possessed by a large number of "alumino silicate" compounds.

Indican[20] as an indicator of pollution has been suggested. Various modifications of the hardness tests[21] have recently been proposed. Several attempts to develop a delicate test for phenols[22] in water have met with questionable success, apparently because of the interference of natural coloring matter. Scheringa[23] has recently investigated the N_2 cycle in water, and Nichols[24] has made a new study of the significance of nitrates.

The A. P. H. A. standard methods of water and sewage analysis have been revised with the coöperation of a committee from this Society and are to be published in the near future. *Public Health Engineering Abstracts*, issued weekly by the Treasury Department Public Health Service, covers American and foreign literature. The American Water Works Association has recently included an abstract department in its journal. Additional articles[25] of importance are mentioned in the Bibliography, page 842.

Stream Pollution

Probably the most important advance in this field has been along the line of analytical methods. The older tests, oxygen consumed from $KMnO_4$ and solids lost on ignition, were admittedly empirical and since there was little uniformity of technic among different workers there was small basis for comparing their results. No less than five different methods for the oxygen consumed from $KMnO_4$ are given by various authoritative textbooks. The estimation of the degree of pollution from the forms of combined nitrogen has not been found feasible. The present method, originally described by the Royal Commission on Sewage Disposal,[26] measures the amount of dissolved oxygen required to satisfy or "stabilize" the organic matter in the sample. This is accomplished by diluting the sample with an amount of aerated distilled or tap water sufficient to contain an excess of dissolved oxygen and then titrating the residual oxygen after a period of incubation (1, 2, or 5 days) at constant temperature (usually 20° C.). From the titration and the length of incubation the "biochemical oxygen demand" is calculated, or the results may be expressed as "1-day demand," "2-day demand," or "5-day demand." When first proposed this method met with some opposition in this country owing to the frequency of erratic results, and the method was not included in the 1917 edition of Standard Methods of A. P. H. A. The method had much to recommend it, however, on account of its similarity to natural conditions and was adopted for stream pollution investigations by the U. S. Public Health Service. Largely through the efforts of this Service[27] the sources of most of the troubles have been found and a satisfactory technic worked out, which will appear in the new edition of Standard Methods.

The results of the extensive investigation of the Ohio River by the U. S. Public Health Service are to be published in the near future. The report will contain much information on methods of stream study and the course of the autopurification reactions. The same organization has been making a study of the Illinois River, in which opportunity has been afforded for checking and improving their investigational methods. We may expect considerable improvement in the "tools" of sanitary chemistry as well as voluminous data on the particular problems studied as the result of these investigations.

A symposium[28] on "Stream Pollution and Sewage Disposal" held at a meeting of the American Society of Civil Engineers in New York in November 1921, together with the discussion which followed, contains considerable information of a chemical nature. Donaldson[29] has reported on the relation of coal and oil, tannery, paper, and various other industrial wastes to water supplies. The limit of 200 to 400 p. p. m. of chlorides which has been set[29,30] on the allowable pollution from oil-well wastes and sea water seems to the writer to be unjustifiably low. Several cases of ground-water supplies containing 1000 p. p. m. or more of chlorides could be cited, and there is evidence that vegetation[31] and cattle will tolerate 2000 to 3000 parts. Gould[32] has discussed the oxygen requirement of New York harbor and the various sources from which this demand may be met. He concludes that surface aeration is the principal source of O, while Purdy in the discussion calls attention to the importance of microörganisms and aquatic plants. Streeter in discussing the same paper calls attention to the fact that turbulence must be depended upon for rapid aeration.

Sewage Purification

Activity in conserving nitrogen has been largely devoted to the development of the activated sludge process which is discussed in a separate article. Richards and Weekes[33] have proposed straw filters for sewage disposal and find that the bacterial growths which occur, fix ammoniacal and nitrate nitrogen. After a time the straw is replaced and, because of the nitrogen accumulated in the bacterial growths, the used straw is good for fertilizer.

Ardern[34] has discussed sewage disposal with reference to colloid chemistry, and he gives an excellent summary of the various theories of sewage purification together with valuable lists of references. He favors a middle ground between the biochemical and colloidal theories.

Cox[35] considers that the microbial growths on trickling filters are of greater importance than they are usually deemed to be. He gives lists of organisms found and concludes that the flora and fauna of the filter determine the biochemical reactions produced. Thompson[36] has made a similar study of trickling filter biology, more especially with reference to activity of enzymes which he proved were produced.

Wagenhals[37] concludes from an extensive engineering and chemical survey of sewage treatment plants that the Gooch crucible determination of suspended matter and the five-day biochemical oxygen demand at 20° are the best tests for determining the efficiency of sewage treatment plants. The paper contains considerable chemical data. Buswell and Weinhold[38] call attention to advantages of the ultra filter over the Gooch crucible, *viz.*, portability, speed, and the fact that it may be calibrated to give a notion of the size of colloidal particles. Mohlman and Pearse[39] have reviewed the various methods for estimating colloids and have suggested the use of the nephelometer.

No attempt has been made to cover the field of disinfectants[40] or of industrial hygiene.[41]

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Activated Sludge

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IT IS conceded that the activated sludge process is the most perfect method of sewage disposal at the present time. Its growth in America and European countries has been quite widespread. Since the discovery of the process, early in 1914, the method has been adopted for several municipalities, and an exceedingly large number of experimental plants have been put in operation. The most notable ones in existence at the present time are at Davyhulme (Lancashire), Worcester, Stamford, Aeritree, Sheffield, Bradford, Tunstall, Blackpole (Worcestershire), Whitney (Blanket Co.), St. Albans, Withington, Moreton (Dorsetshire), Birmingham, Reading, Baguely, and Stoke-on-Trent, in England. In other countries, the most notable ones are at Jamshedpur (India), Sibpur (India), Holte (Denmark), Burmeister (Denmark), and Kimberly (South Africa). In the United States the best-known plants are at Houston, Texas, and Milwaukee, Wis.

EDWARD BARTOW

NEW PLANTS

Recently (April 1921) a plant has been installed at Woodstock, Ontario, to handle 1,500,000 imperial gal. per day, dry weather flow. A small plant has also been installed at Brampton, Ontario.

A plant was put in operation on October 18, 1921, at Gastonia, N. C., which treats 1,000,000 gal. sewage daily.

In October 1921, an installation was put in operation to treat the waste (600,000-gal. daily flow) from the Decker Packing Plant at Mason City, Ia.

Experimental plants have been in operation for some time at Urbana, Ill., the Calumet region of the Sanitary District of Chicago; this plant when completed will have a capacity of 1,750,000 gal., and the plant of the Desplaines River district of the Sanitary District of Chicago, when completed, will treat the sewage from a population of 30,000.

In conjunction with the Corn Products Co., Argo, Ill., the Sanitary District of Chicago has also run an experimental plant on starch wastes. This plant has a capacity of 25,000 gal.

Experimental plants using mechanical agitation have been in operation at Pasadena and Hermosa Beach, Calif. Works are in the process of construction in Milwaukee which will treat the entire sewage from that city, population 588,750, and at Indianapolis, Ind., population 314,000. Other plants in the process of construction at the present time are Brisbane (Australia), and Singapore (India).

Rotheham, Hanley, and Mansfield (England) are considering schemes along the line of the Sheffield works. Los Angeles, Calif., is also considering the adoption of the activated sludge process for the treatment of sewage of that city.

There are many other small plants and installations that could be mentioned, but lack of space does not permit.

TYPES OF AERATION

There are in general two types or modifications of aeration: (*a*) diffused air, and (*b*) mechanical agitation. The experimental plants in this country have practically all used

the diffused air treatment, which consists of blowing air through the sewage and sludge, after it has passed through filtros plates.

Intermittent aeration has been tried at Manchester, England, and elsewhere; this allows aeration for a certain length of time and then a rest, but has not proved successful in the saving of air.

Certain devices have also been tried for decreasing the amount of air necessary for the process. The Dorr-Peck process consists in aerating the sewage and sludge in a specially designed thickener, which effects distribution and circulation of the air bubbles in one chamber and causes sedimentation in another. Aeration in less time and less air required was claimed, but the company very recently announced that the process had not met their expectations and they have decided to carry the tests no further. The Trent devices consist of aeration and agitation of the sewage by drawing the sewage and air into the bottom of the activation tanks. Distribution is by means of revolving perforated arms of the rotating lawn-sprinkling principle. Tests at Pasadena, Calif., and a similar process at Hermosa Beach, Calif., showed the process to take twice the time and cost more to operate than the continuous air diffusion method.

Mechanical agitation, that is, the use of revolving paddles, has proved successful at Sheffield, England. These paddles suck the air through a tube by creating a vacuum, and rotation is carried for eight hrs. By this method the sewage is brought in contact with the air at its surface only; the power required is to mix the sewage and induce a current, and by rippling the surface increases the surface exposed to the action of the air. The Sheffield sewage may be a special type, and experiments made elsewhere indicate that mechanical agitation alone will not purify sewage in the presence of activated sludge without the expenditure of much more energy than the air-diffusion method; the original and maintenance costs also seem greater.

It is the general opinion that the continuous air diffusion method is preferred but that some aeration might be dispensed with provided some other form is used.

Settling

Certain improvements over plain sedimentation are claimed for settling sludge. Dorr thickeners have been successfully used. These sedimentation tanks are circular in diameter and have a smooth bottom with a slight slope toward the center. A revolving scraper collects the sludge continuously, scraping it toward the center of the tank, from which it is removed by a pump or by gravity without the interruption of the operation of the thickener.

Dewatering Sludge and Sludge Drying

These are the biggest problems yet unsolved, but very promising advances have, however, been made within the last few months, and complete solution is hoped for in the near future. Filter pressing and certain types of centrifuges have given promising results under varying conditions. Lagooning has also been somewhat satisfactory, but in this method the fertilizing value of the sludge is lost. Certain recent developments have been made, both in England and in this country, in filter pressing. In England it has been found possible to reduce 98 to 99 per cent moisture sludge to 75 per cent by spreading it on paper-makers' gauze or very fine screen gauze and applying a slight vacuum to the under surface; the thin cake thus produced can be readily dried in the air. In this country experiments with certain types of American filters (Oliver and American) embodying the same principle have recently given very satisfactory results.

Dewatering by plate presses and squeeze presses (Worthington or Berringan) has given promising results with sludge that has been treated before filtration. At Milwaukee by adjusting the reaction to a certain hydrogen-ion concentration with sulfuric acid, and by adding chromium or aluminium sulfate, the rate of pressing has been greatly increased.

A solid bowl centrifuge (Besco-Ter-Meer) has given much more promising results than other centrifuges at Milwaukee. This centrifuge is continuous and automatic in operation, and is devoid of all screens. It builds up a cake against a solid stationary plate and unloads it automatically. It has been possible to reduce the moisture to 72 to 75 per cent. With this machine the water does not pass through the cake but out over the top; the effluent contains a rather high percentage of the lighter and finer solids. There are those who believe that a centrifuge will be so perfected that it will solve the dewatering problem.

Another recent advance in the dewatering treatment of sludge is the Maclachlan process, or modifications of it. In this process the sludge is treated with sulfur dioxide, generated by burning sulfur, and live steam. In the Maclachlan process at Houston, Tex., the sulfur dioxide and live steam are applied to the activated sludge for 25 min., raising its temperature from 80° to 135° F. The sludge floats to the top and can be readily filter-pressed, yielding a cake with as low as 74 per cent moisture; the treated sludge may be dried on filter beds. Jackson and Doman report that the filtered sludge dries readily on hard, impervious ground when applied in depths varying from 4 to 16 in. Dehydration cracks appear in all cases within 24 hrs. At the end of the first day the moisture is reported as 77.1 per cent, in 3 days 59.7 per cent, and in 3 wks. 26.4 per cent.

The present trend in dewatering sludge seems in the direction of conditioning the sludge rather than the improvement of mechanical devices. Besides drying the sludge on beds with disposal in the lagoons, direct heat driers have been used with more or less success for the drying of filter-press and centrifuge cake. Drying experiments have been carried out with both direct and indirect heat driers, and indications are that drying in either form is an expensive process. It is generally agreed, however, that after the first 20 per cent of the water is removed the sludge more readily parts from the remainder.

Fertilizing Value

Dried sludge has been proved by various investigators[1] to have an excellent fertilizing value. The nitrogen content of the sludge has been shown to be equal in fertilizing value to the nitrogen of ammonium sulfate or dried blood, when applied to grains and vegetables. These results have also been borne out at Rothamsted. The nitrogen content of the sludge varies from about 4 per cent to 7 per cent, depending upon the type of sewage treated. It has been shown at Manchester that 21 per cent of the nitrogen of the wet sludge is immediately available for plant food, while only 8.15 per cent of the nitrogen of airdried sludge and only 4.6 per cent of that dried at 100° C. are immediately available. Heat drying lowers the percentage of nitrates considerably.

One of the new developments is irrigation and fertilization with wet activated sludge. It is possible to dispose of the sludge already in liquid form by means of a system of mains and service pipes.

The present indications are that the sale of fertilizer will partially, if not wholly, offset the cost of the dewatering and drying of the sludge, if these problems are properly solved, but no surplus applicable to the operation of the plant can be expected.

[1] Bartow and Hatfield, Nasmith, and others.

By-product Coking

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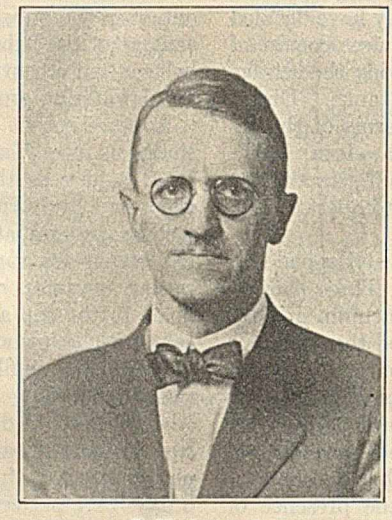
THE BY-PRODUCT coke industry has found the past two years remarkably rich in technical achievements which promise a very prosperous development as business recovers from its recent depression. It is gratifying to note that such achievements are more and more the result of planned scientific research in which chemistry has a most important part. The field of research, comprising coal and its relation to coke formation, the coking process, the properties and utilization of coke, the recovery and utilization of the by-products, and the materials of plant construction, is so large, that a review of the subject condensed to the limits of this article would amount to a mere index of the numerous important papers that have appeared. It will, therefore, be more interesting and useful to select for discussion a few subjects of investigation that may be considered typical of the general trend of research in this connection.



F. W. Sperr, Jr.

Property and Process of Coking

The various investigators who have been working on the difficult and important problem of coal constitution have contributed much toward improving our conceptions of the coking property and the mechanism of coke formation. At the best, however, any such conceptions must be regarded as working hypotheses which we must be prepared to amend or to discard altogether in the light of additional information. Coal research is still in too early a stage to formulate strict generalizations, and investigators must not lose sight of the marked individuality possessed by each and every coal.[1]

The three general methods most used in recent investigations of coal constitution are examination with the microscope, solution in organic solvents, and low temperature distillation. It may be useful to attempt a brief correlation of the work so far done.

The study of coal with the microscope has been of prime importance with respect to the direct value of the results obtained. It has shown, what is now generally accepted, that an important group of coal constituents are resinic compounds derived from plant resins that are resistant to decay. These resinic compounds are believed to have a great influence on coke formation. Regarding the nature and influence of the other coal constituents our knowledge is most unsatisfactory. There was formally a disposition to classify these as "cellulosic," but it has been pointed out that cellulose proper is unstable under the conditions of peat formation. Taking advantage of the remarkable solvent action of pyridine on coal, and of the solubility of portions of the pyridine extract in chloroform, it has been proposed[2] to classify the coal substances in the three groups—alpha, beta, and gamma compounds, without attempting to define the nature of each group. This has constituted a useful working agreement, which it is well to get clearly in mind with the following definitions:

1—The alpha compounds are insoluble in pyridine.

2—The beta compounds are soluble in pyridine, but are left as insoluble residue when the pyridine extract is treated with chloroform.

3—The gamma compounds comprise that part of the pyridine extract which is soluble in chloroform.

The gamma compounds are considered to correspond with the resinic substances. As to the nature of the alpha and beta compounds we may refer here to the hypothesis of Fischer and Schrader[3] that lignin degradation products, rather than cellulosic substances, play an important part in coal constitution.

The relation of these three groups of substances to the coking property has been investigated by S. Roy Illingworth,[4] who worked with the general idea of determining the proportion of each group in the residues obtained by heating typical coals for different periods and at different temperatures. He found the beta compounds to be less stable than the resinic compounds and that in all probability the former are the first to decompose on heating. Assuming, as the majority of investigators have done, that the resinic compounds constitute the "cementing" agency in the coking process, he developed an interesting line of inquiry into the mechanism of coke formation on the basis of determining the minimum amount of these compounds that could be present to produce a coherent coke. His results indicated a difference in the cementing properties of the various resinic substances in the different coals—the higher volatile and more poorly coking coals having, as would be expected, resins with weaker coke-producing quality than the better coking coals. Nevertheless, he took 5.5 per cent of resinic substances to be an average figure for the majority of coking coals representing the minimum amount of resinic substances capable of holding a residue together in the form of a coherent coke. He then constructed a picture of the coking process showing the formation of a plastic stage due to softening of the resinic substances, the creation of a spongy state during the period when the mass contains more than the critical amount (*e. g.*, 5.5 per cent) of resins, and the stiffening and solidification of the mass with the reduction of the resinic content below 5.5 per cent. Differences in the porosity of coke he considered to be due to differences in the stability of the beta substances. The crucial characteristic of any coal as regards porosity of the resulting coke would be the amount of volatile matter evolved when the hot mass is in its most viscous state and about to pass to a fixed structure by virtue of the destruction of the resins. He determined the rate of evolution of volatile matter during what might be considered its critical period, and obtained "porosity factors" which came in the same order as the actual porosity of the cokes from the coals investigated.

Some space has been given to this work of Illingworth be-

[1] George Charpy and Gaston Decorps, *Compt. rend.*, **168** (1919), 1301.

[2] "Monograph on the Constitution of Coal," by Stopes and Wheeler, London, 1918.

[3] *Brennstoff-Chem.*, **2** (1921), 37, 237.

[4] *J. Soc. Chem. Ind.*, **39** (1920), 111T, 133T; *Fuel*, **1** (1922), 49. See also Bone, *et al.*, *Proc. Roy. Soc.*, **100A** (1922), 582; reviewed and severely criticized by Wheeler in *Fuel*, **1** (1922), 49.

cause it is typical of that type of scientific investigation which is greatly needed in coke technology. Work of this sort should be continued to the point of enabling us to determine definitely by a laboratory examination of any given coal the quality of the coke that it will make in large-scale operation, and this should be accomplished without the necessity of large-scale tests.

The microscopic examination of coal has developed certain new terms with which coke technologists must become acquainted. Reference must first be made to the pioneer work of Dr. Reinhardt Thiessen,[5] of the U. S. Bureau of Mines, who has developed a technic of making thin sections of coal through which light can be transmitted to such a point that ordinary bituminous coal can be most thoroughly examined. The bright bands prominent in bituminous coal, he finds, represent parts of definite components of the woody parts of plants—that is, parts once pieces of logs or stems, branches, twigs, and roots, but now much compressed. Such parts of the coal he calls *anthraxylon*, meaning coal wood, from *anthrax*, coal, and *xylon*, wood. Dr. Thiessen is now making a study of the relation between the constitution of coal, as seen under the microscope, and its coking quality, and has been making considerable progress in following this relation. For example, anthraxylous constituents of Illinois coal have been separated on the stage of the microscope and subsequently coked. The experiment showed that the anthraxylon swelled, fused, and acted as a coking constituent, whereas the attritus did not swell or fuse but merely sintered, retaining the original structure that it had in the coal.

This line of investigation has been pursued in England by Marie C. Stopes,[6] who distinguishes two constituents of the bright coal bands, *viz.*, *clarain* and *vitrain*. Clarain has a bright, smooth structure but is so closely associated with fragments of the dull coal (durain) as to be difficult to separate. Vitrain occurs in brilliant, structureless, well-defined bands. It can readily be separated and is usually smaller in amount than the other constituents. The other two principal constituents she calls *fusain* and *durain*. Fusain is the familiar "mother-of-coal" or "mineral charcoal." Durain is the dull-appearing coal substance (Mattkohle) having a hard, close, firm texture and a lumpy, irregular surface of breakage across the bedding plane.

Rudolph Lessing[7] has studied the behavior of these constituents on coking. Considerable fusion and merging of particles was shown by clarain which gave cokes with a peculiar brown sheen. Vitrain produces a characteristic silver-white coke, but the consolidation of particles did not go so far as with clarain. Durain was practically devoid of coking value, but the particles adhered to each other a little more than in the case of fusain which had absolutely no coking tendency.

A study of the properties and process of by-product coking is not complete without consideration of the light shed by low-temperature distillation, in which field there has been considerable activity directed toward the development of commercial processes. So far, however, the by-product chemist is chiefly concerned with the theories of pyrogenesis and coal structure, such as are developed in the recent articles of J. J. Morgan and R. P. Soule[8] on the composition of low-temperature tar, and their reference to earlier work of the same nature.

The very important problem of the deterioration of coal in storage has been studied by William Seymour,[9] both in relation to coke manufacture and to the utilization of the coke in the blast furnace.

A brief research of an entirely new type into the carbonization of coal has been conducted by Eric Sinkinson,[10] who has shown that the electrically nonconductor coal changes to a conductor (coke) at a temperature in the region of 500° C.

Reference should be made to the investigations of F. Korten[11] into the expansion of certain types of coal during coking. Our own laboratories have done a large amount of work on this subject, and have developed a method which, on a relatively small sample, determines both the coking qualities and the contraction or expansion of a given coal. This work will be published in the near future.

By-product Formation

So far, we have been considering that type of investigation which aims at the elucidation of the coking property. Other investigations into the phenomena of carbonization have to do with the evolution of by-products and during the past two years attention has been paid principally to ammonia and sulfur. Extensive experiments in full-sized by-product ovens have been described by A. Thau.[12] The characteristics of the coke, gas, light oil, etc., produced at different temperatures were examined but the principal work was done on the conditions covering the yield of ammonia. The amount of free space above the coal in the oven did not appear to have so much influence in decreasing the yield of ammonia by secondary decomposition as has been generally believed. The hot surfaces of carbon appear to be more effective in general secondary decompositions than the hot oven walls. Air leaks were shown to diminish the yield of ammonia considerably.

H. J. Hodsman[13] refers to the work of Thau and others, and describes laboratory experiments made under his direction to examine further the decomposition of ammonia in the presence of oxygen. No destruction of ammonia was detected in coal-gas mixtures containing 1 per cent of oxygen at any temperature below 600° C. At 700° C. and higher, the loss of ammonia was very considerable. The results of these experiments agreed in general with Thau's observations.

Another laboratory research into the formation of ammonia during carbonization was conducted by A. C. Monkhouse and J. W. Cobb.[14] Cokes prepared at 500°, 800°, and 1100° C. were subjected to the action of hydrogen and nitrogen separately at three different temperatures—600°, 800°, and 1000° C. The hydrogen appeared to exercise a specific action on the nitrogen in the 500° coke, with the formation of ammonia. Another series of experiments was made on the 500° coke treated successfully at 800° C. with nitrogen, hydrogen, and steam, the action of each gas being carried to completion before the next was allowed to act. Large quantities of ammonia were obtained by the use of hydrogen when heating with nitrogen had ceased to yield any ammonia, and further large quantities were obtained with steam when the hydrogen had become practically ineffective.

Monkhouse and Cobb also obtained some data on the liberation of sulfur from the coke under the above conditions. The sulfur was evolved as hydrogen sulfide in a way similar to and parallel with that of ammonia. A much more extensive investigation of the behavior of sulfur during carbonization has been conducted by Alfred R. Powell, of the U. S. Bureau of Mines. U. O. Hutton and C. C. Thomas,[15] of

[5] *U. S. Bur. Mines, Bull.* **117** (1920), and other publications.
[6] *Proc. Roy. Soc.*, **90B** (1919), 470.
[7] *J. Chem. Soc.*, **117** (1920), 247.
[8] *Chem. Met. Eng.*, **26** (1922), 923, 977, 1025.
[9] *Blast Furnace and Steel Plant*, **1920**, 435.
[10] *J. Chem. Soc.*, **117** (1920), 839.
[11] *Stahl u. Eisen*, **40** (1920), 1105.
[12] *Brennstoff-Chem.*, **1** (1920), 52.
[13] *Gas World*, **76** (1922), 12 (Coking Section).
[14] *Gas J.*, **156** (1921), 234.
[15] This Journal, **12** (1920), 1077; **13** (1921), 33; *Gas Age*, **47** (1921), 88.

Johns Hopkins University, have also carried on a line of research in coöperation. Powell's work has been of great importance in showing the way in which different forms of sulfur decompose and the effect of hydrogen in removing sulfur from the coke, and has formed a basis for the study of methods for desulfurizing coke during the coking process which the Bureau of Mines is now conducting.

Properties and Utilization of Coke

In the work of our own laboratories in the Mellon Institute, great emphasis is placed on the study of coke itself. This has a twofold relation—first, to the conditions of coking, and second, to the conditions under which coke is consumed. A thorough knowledge of the properties of coke is essential. For some time especial attention has been given to specific gravity, porosity, and cell structure. The correct determination of the true specific gravity of coke is a problem, the difficulty of which is not generally recognized. The figures obtained vary with the method used, and since the porosity is calculated from the specific gravity, the discrepancies may be equivalent to as much as 30 to 50 per cent of the total variation in porosity found in different blast-furnace cokes. The subject has been fully discussed by H. J. Rose, of our laboratories, in a paper presented at the last meeting of the American Chemical Society. Methods of recording and comparing the cell structure of cokes have been developed, and much progress has been made toward a better understanding of this important characteristic.

Studies have also been made of the volatile matter and occluded gases in coke, in which connection the large amount of research work recently done by different investigators on the properties of charcoal has been found especially helpful. A study of the combustibility of coke is also under way. The investigation of the effect of the conditions of by-product coke oven operation on coke quality has led conversely to the development of a method that enables us to determine the maximum temperature to which a given piece of coke has been subjected.

Since 90 per cent of all coke manufactured is consumed in the blast furnace, the study of the effect of coke quality on blast-furnace operation is of prime importance. The most outstanding contribution to our knowledge of this subject has been made by Heinrich Koppers.[16] Extensive reference is made by Koppers to the work of H. P. Howland[17] on American blast-furnace practice. Koppers agrees with the general opinion of experts in this country that the most important property of coke for blast-furnace purposes is combustibility. He then shows the remarkable fuel consumption figures obtained in charcoal furnace practice and the significance of such practice with relation to the optimum coke quality. The combustibility of coke stands in close relation to the temperature of coking; the higher this temperature the less the combustibility. Good blast-furnace coke ought to be made of homogeneous coal coked at moderate temperatures in such a way that the heating is uniform at all points in the coking mass, and should be pushed out of the oven as soon a scoking is finished. Finally, it should be uniform in size. Koppers shows how the by-product coke oven structure may be modified to attain a greater uniformity of heat flow into the coking mass. Great progress has been made in this direction in recent American installations, and the Becker type ovens, which have recently been put into operation by The Koppers Company at Chicago, may be cited as the newest development that has been made with remarkably successful results in the regulation of the quality of the coke produced.

[16] *Stahl u. Eisen.*, **1921**, 1173.

[17] *Trans. Am. Inst. Min. Met. Eng.*, **56** (1917), 339.

Koppers goes much further than the regulation of coke oven conditions to produce the right sort of coke. He shows how the blast furnace itself may be improved by modifications, simple yet almost revolutionary in their conception, so as to obtain more uniform operation, increased capacity, and decreased coke consumption per ton of iron.

The relation between the physical properties of coke and its utilization in the blast furnace is being made a subject of study by the U. S. Bureau of Mines.

The various physical tests, such as shatter, hardness, porosity, and combustibility, are being thoroughly investigated at both the Southern Experiment Station of the Bureau, located at Tuscaloosa, Ala., and the Pittsburgh Experiment Station, as well as at the Experiment Station at Minneapolis, Minn. The rate of combustion of coke in various blast furnaces is being studied by taking samples of the hearth gases from a water-cooled sampling tube inserted in the tuyeres. By determining the relative percentages of carbon monoxide, carbon dioxide, and oxygen at various points in the hearth from the end of the tuyere to the center of the hearth, it is possible to note the variation in the rate of combustion in various blast furnaces using different kinds of coke. Laboratory experiments are also being made on the rate of combustion of coke of various physical properties.

Materials of Plant Construction

The most important materials in the construction of by-product coke plants are the refractories. Testimony before the Federal Trade Commission[18] shows that the by-product coke oven industry in this country stands second only to the open hearth industry in the consumption of firebrick. Modern American coking practice uses silica brick exclusively, which permits higher temperatures with consequent important decrease in coking time and increase in capacity. In this development, America is pioneer and the attention of the rest of the world is at present directed toward the adoption of this practice.

Advances in the production and utilization of other materials of plant construction have occurred during the past few years, but such advances have been shared in common with a great many other industries which also use these materials, so a detailed description is not in place here.

The Recovery of By-products and Other Developments

The preparation and utilization of the chief by-products, tar, ammonia, and benzol, each constitute an important industry in itself and the developments cannot adequately be considered in detail. In the tar industry, chief attention at present is given to the development of satisfactory processes for continuous distillation. The major attention of the ammonia industries has been directed toward the improvement of the chief product, ammonium sulfate, to give a neutral friable salt. This development is going forward mainly in England. The enormous war-time demands for benzol products have, of course, disappeared and research in this field has largely been confined to the development of a satisfactory motor fuel.

Other recent developments which give important economic aid to the advance of the by-product coke oven industry are the utilization of by-product coke oven gas as a domestic fuel, the firing of by-product ovens by producer gas (with the consequent release of a large amount of high-grade gas), and the liquid purification of gas.

[18] R. M. Howe, *Trans. Am. Inst. Min. Met. Eng.*, **62** (1919), 14.

The Anaconda Copper Mining Company has purchased a $1,000,000 phosphate rock deposit, intending to use waste smelter gases for fertilizer making.

Shale Oil

By Ralph H. McKee

PROFESSOR OF CHEMICAL ENGINEERING, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

THE DRAINING of natural resources is deplorable but the material gain resulting from their exploitation should not be overlooked. The approaching exhaustion of American petroleum has been compensated for in a large measure by the advances of American industries which this petroleum has made possible. Crude petroleum and "topped" petroleum are used as fuel in competition with coal. The present primary use of petroleum, however, is in the form of refined products, of which gasoline and lubricants are the most important. At present gasoline yields more than one-half the total revenues, though in volume it constitutes only one-fourth of the entire output.

Allman & Co.

RALPH H. MCKEE

THE GASOLINE SITUATION

The petroleum requirements of this country are closely bound up with the automobile industry. In 1900, when automobiles first became commercial, the yearly per capita consumption of petroleum in the United States was 35 gal.; in 1910 it had risen to 96 gal., in 1920 to 210 gal., and last year the increase, in spite of the financial depression, was still another 21 gal. per person. All this is in spite of a continual increase in gallons of gasoline obtained from each 100 gal. of crude oil. In 1915 each 100 gal. of crude oil gave 11 gal. of gasoline, but six years later the development of cracking had increased this to approximately 26 gal. If all the petroleum used in America were subjected to the cracking process, the amount obtained would be but about 40 gal. for each 100 gal. of crude petroleum.

In the last six years the gasoline used in the United States per automobile has decreased from 600 gal. per year to approximately 400 gal. per year, owing not to a decrease of mileage per car but to an increased efficiency of carburetors and engines. Were it not for this increased efficiency, we should already have reached our limit of gasoline consumption and with it probably a price of at least 40 cents a gallon.

Since 1921 the United States has been consuming more petroleum than it produces. This excess has been largely provided by Mexico and last year showed an importation of more than 120,000,000 bbls., that is, approximately 26 per cent of the American production. The Geological Survey and Bureau of Mines have lately shown that American production is approximately at its peak and that in a very few years the output of oil in the United States will begin to decline. Moreover, about a year ago the Geological Survey called attention to the fact that we should not expect to find any more large fields of petroleum in the United States—in other words, that practically all of the possibilities in the way of large petroleum fields in this country have been well prospected and that now we can calculate fairly closely what the production will be in the future.

On the other hand, the use of motor vehicles in this country is continually increasing. At present there are about 10,000,000 passenger cars, trucks, and tractors in use, and it is certain that the saturation point is more than 15,000,000 and perhaps will exceed 20,000,000 machines. With this expected larger demand for gasoline on one hand, and, on the other, even less petroleum available in a few years than we have at present, there arises a question as to how the motor fuel deficit is to be met. Of course, importations of oil can be made from Russia, Persia, Mesopotamia, and South America (the present Mexican fields are of short-lived type), but such an importation basis means that we shall be on the same basis as other importing countries have been, that is, the consumer will purchase his gasoline at from 60 to 75 cents a gallon. If our automobile industry and the many industries that depend on automobile transportation are to prosper, we must have a domestic supply of motor fuel and at a price more reasonable than 60 cents a gallon. Thirty-five or forty cents a gallon will probably be considered a fair price by the consumer.

Alcohol and benzene and the synthetic motor fuels having a mixture of these two as their base, will meet a small, but only a very small, portion of the needs. The total amount of these two motor fuels available in America is but a small percentage of the 20,000,000 gal. of gasoline now used daily.

OIL SHALE RESOURCES

In the last two years another source of motor fuel has begun to be considered seriously in America. In Europe oil shale has been used for nearly a century for the obtaining of petroleum. Indeed, the word "petroleum" was used for shale oil for a generation before Colonel Drake drilled the first oil well (Titusville, Pa., 1859). Oil shale does not contain petroleum, but by heating oil shale a petroleum distils from which a motor spirit similar to ordinary gasoline may be obtained.

The European oil shales yield 20 to 22 gal. of oil per ton of shale mined. In this country we have large deposits of shales that give double this yield of oil. The largest of these are the Green River deposits in Colorado, Utah, and Wyoming, but there are also deposits in Kentucky, Indiana, and Ohio, and some of equal extent in New Brunswick and Nova Scotia. Many of these will yield a barrel (42 gal.) of oil per ton of rock. For a typical oil shale view see Fig. 1. It is not commonly appreciated how large these oil shale deposits are. In the Green River section alone, there are known deposits yielding a barrel or more of petroleum per ton. These are sufficient to furnish more than five times the total world production since the commercial development of well petroleum 60 years ago.

EXPERIMENTAL WORK

In the last two years "conversations" regarding shale oil possibilities have been followed by real experimental and small-plant operations, so that to-day we have several processes in course of trial. It is as yet a question whether we have found the best method of obtaining oil from the shale. It should be

said in passing that the American shales do not work satisfactorily when retorted in the standard Scotch retort, and that, accordingly, modifications of this retort or retorts on new principles must be designed. So far the developments have been largely in the hands of mining engineers or of men without technical training. Only lately have chemical engineers taken an active hand in the industry.

It should be mentioned in this connection that perhaps the two most active nonfinancial organizations that have been

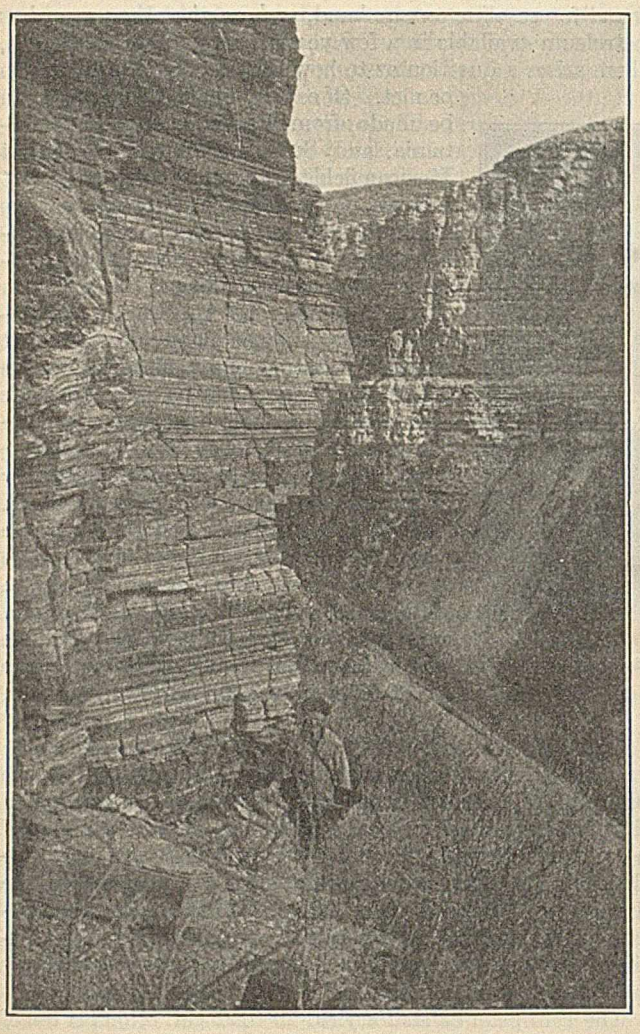


Fig. 1—Oil Shale Cliffs in Colorado

working on shale oil are the United States Bureau of Mines and the Colorado School of Mines. The first has been criticized as being too conservative in its view in connection with this new industry; the second has been equally criticized for too optimistic a view.

Patents almost without number, most of which have their prototypes in the early Scotch industry, have lately issued from the Patent Office. A number of these have fallen into the hands of promotion companies and are now being made the basis of stock-selling operations. At present, few except the inventor himself believe that any of these retorts is certain to be practicable when used on a large scale.

One plant, the Catlin Shale Products Co., Elko, Nevada, has apparently passed beyond the primary troubles in retorting, and has built a refinery to handle the crude shale oil and furnish the market with refined products. This plant has a capacity of approximately 15,000 gal. (350 bbls.) a day, a small capacity compared with commercial well petroleum plants.

About a year ago, it was shown that the organic matter in shale decomposes on heating, not to give petroleum directly but first to give a heavy solid or semisolid bitumen, and that petroleum is formed by a secondary cracking process from the first formed semisolid bitumen. This cracking process by which petroleum is formed is a liquid-phase process similar to the well-known phenomenon of the cracking of petroleum to give gasoline. Accordingly, it is not surprising that when shale oil is further cracked to give a motor spirit, the product carries 60 to 70 per cent of unsaturated hydrocarbons.

It was further found in the experimental work just referred to that decomposition of the organic material of the shale to give a semisolid bitumen occurred at a quite definite temperature (400° to 410° C.), and that the cracking process to obtain a petroleum from this took place approximately at but 20° higher.

The same investigation also showed to be incorrect the common belief that on heating, gasoline is the first product; on higher heating, kerosene; and on still higher heating, lubricating oils, etc. In other words, all these products are formed simultaneously by the cracking of the semisolid bitumen first formed.

It has not yet been possible to obtain heavy type lubricants, such as a cylinder oil, from shale oil. On the other hand, recent work has shown that excellent lubricants of light body can be made. It is worth mentioning that these lubricants, unlike ordinary well petroleum lubricants, do not decrease in viscosity rapidly on heating and, accordingly, in light use, such as in an automobile, the mileage obtained has been unexpectedly great.

Considerable gas is produced in the making of shale oil. Under the best conditions the amount of this gas is not sufficient for the fuel required in the retorting process. In Scotland they have supplemented the gas by using local coal for the shale retorts. With the American shales, which are richer in organic material than the Scotch, there is enough carbonaceous residue left (20 per cent) in the shale to permit it to be burned in a gas producer; in fact, one American plant is now regularly using this shale residue in a producer to furnish producer gas for the retorting of the shale. Most engineers would state offhand that a fuel running more than 75 per cent ash would not burn in a producer, but it does.

By-products

In the French and Scotch shale-oil plants the production of ammonia in the process is as important as the production of oil. The American shales give less ammonia, but still enough to make it worth while to recover it. If the shale is retorted at only moderate temperatures, as most American shales will be, there is obtained a large percentage (up to 20 per cent) of nitrogenous constituents in the oil. These nitrogenous constituents are largely pyridine and isoquinoline derivatives. Up to the present time, no commercial outlet for these products has been worked out. They will, no doubt, compete in the future with the nitrogen bases obtained directly or indirectly from coal tar.

Some of the western oil shales give considerable quantities of paraffin, a few as high as 30 per cent of the weight of the oil. The eastern and some of the larger western deposits have an asphaltic base and give little or no paraffin.

Irresponsible promoters have claimed that the residue from oil shale retorting carries considerable amounts of platinum, gold, and other precious metals, phosphates, and soluble potash. These claims have no basis of fact, except possibly a small percentage of potash which has been rendered soluble by the retorting process.

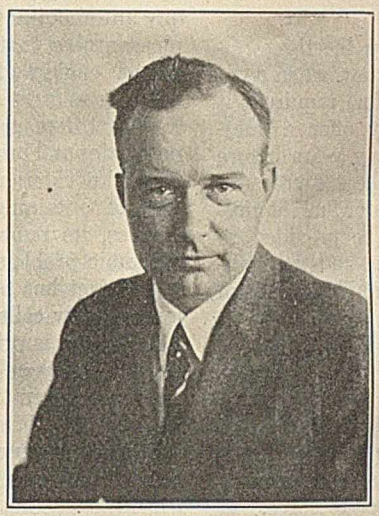
The demands for petroleum are increasing in this country at the rate of about 50,000,000 bbls. a year. We have in prospect no source of fuel oil, gasoline, or gasoline substitute other than oil shale that promises to furnish even a minor part of this demand. To meet this, even without making any allowances for the expected decrease in production from oil wells, will require each year the building of 75 shale-oil plants, each handling 2000 tons of oil shale daily, and each representing an investment of nearly a million dollars. And yet some men feel that the industrial need for chemical engineers and chemists is limited!

The Application of Chemistry to the Conservation of Motor Fuels

By Thomas Midgley, Jr., and T. A. Boyd

Chief and Assistant Chief, Fuel Section, General Motors Research Corporation, Dayton, Ohio

THIRTY years ago the first automobile had not yet been built in this country. To-day there are about 11,000,000 motor vehicles in the United States—one for every 10 persons in the country. In the early days of the automobile it appeared to be only a troublesome and very expensive luxury. But the phenomenal increase in its use, the most of which has occurred within the last ten years, indicates that the automobile is not a luxury but a necessity. It is a necessity because it meets in an admirable way one of the most fundamental needs of civilization, that of transportation. It has been said that the automobile represents the first great advance in individual transportation since man began to use the horse.



Thomas Midgley, Jr.

Need for Liquid Fuel

Automotive transportation, of which such a wide and essential use is now being made, and of which a large future expansion is assured, is dependent for its existence upon an adequate supply of liquid fuel. The use of motor vehicles has been built up around gasoline, a material which only a few years ago was a troublesome by-product of petroleum refineries. As the number of automobiles in use increased, this product, for which there had previously been very little demand, was gradually absorbed, until about 1905 there was no longer a sufficient supply of the early highly volatile gasoline to operate the motor vehicles in use.

At this point gasoline began to assume a higher place in refinery economics. It was no longer a by-product; but its production was extended in order to keep pace with the development of motor transportation, until it has now assumed prodigious proportions. In 1921 the production of gasoline in the United States was over 5,000,000,000 gal.[1] This means that the petroleum refineries in the United States are filling a 10,000-gal. tank car with gasoline every minute of the year.

Since 1909 the number of motor vehicles in use in the United States has increased over 3000 per cent, while during the same period the production of petroleum has increased only about 150 per cent. The amount of gasoline necessary to keep this rapidly increasing number of motor vehicles in operation was supplied by refineries from a production of petroleum that did not keep pace with the rising demand for motor fuel: (1) By putting an increasing percentage of the distillate from the crude oil into the gasoline fraction; (2) by cracking heavier oils; and (3) by extracting liquid hydrocarbons from natural gas.

With the possible exception of further increases resulting from the cracking of heavier oils, the limit of the percentage of gasoline that can be obtained from crude oil has almost been reached. In view of the situation that the production of petroleum has not kept, and apparently cannot keep, pace with the rapid increase in automotive transportation, this is a significant fact.

Future Supply of Motor Fuel

One of the most serious questions with regard to the future of motor transportation is that of the supply of liquid fuel. A number of producers of petroleum have expressed the belief that our reserve of petroleum will last indefinitely, and that there is every likelihood that no shortage of oil will occur.[2] In every case of this optimism that has come to our attention, however, no reason has been given for the opinion that our supply of petroleum is adequate for future needs.

A recent estimate of the petroleum reserves of the United States has been made jointly by the American Association of Petroleum Geologists and the United States Geological Survey. Their report, which was made public in January 1922, indicates that at the present rate of consumption the domestic reserves of petroleum are sufficient to meet the requirements of the United States for only about 20 yrs. Of the 15,000,000,000 bbls. of petroleum which, on the basis of this estimate, was in the ground originally, about 40 per cent has so far been mined; and over 450,000,000 bbls., or 5 per cent of the unmined reserve, are now being produced per year.

While this estimate of the geologists is necessarily based upon incomplete data and probably lacks the desired degree of accuracy, it is certain that our supply of petroleum is being rapidly depleted. If the domestic reserve of petroleum should be three times the amount of this estimate, it would last, at the present rate of consumption, only 60 yrs. It has been 60 yrs. since the Civil War. In view of this condition all possible conservation of materials that are suitable

[1] The statistics used herein have been taken from the following sources: "Gasoline," Refinery Statistics of U. S. Bureau of Mines; "Petroleum and Coal," U. S. Geological Survey; "Automobiles," *Automotive Industries*, **46** (1922), No. 7.

[2] American Petroleum Institute, *Bull.* **132** (1920); **200** (1921).

for motor fuels should be a matter of vital concern to every citizen.

Sources of Liquid Fuels, Other than Petroleum

There are three potential sources, in addition to petroleum, to which we may look for some part of our future domestic supplies of motor fuel:

1. Oils from Shale—The enormous deposits of shale in this country will undoubtedly be developed. But, even at the best, it will be many years before quantity production of motor fuel from shale can be obtained.
2. Oils from Coal—The light oils produced in the carbonization of coal make a desirable motor fuel. But, if all the bituminous coal mined in the United States in 1921 had been so treated as to yield 3 gal. of motor fuel per ton, the product would have amounted to less than 25 per cent of the gasoline produced during the same period.
3. Alcohol—Vegetation offers a source of tremendous quantities of liquid fuel, the utilization of which awaits only a proper cheapening and simplification of the process of converting cellulose to a liquid suitable for motor fuel.

The present production of liquid fuels from the three potential sources enumerated above is so small that, when compared with the enormous volume of motor fuel required, it is almost negligible. Therefore, while they offer a comforting reserve for the future, it will be many years before sufficient material can be obtained from these sources to supply any considerable percentage of the motor fuel requirements of the country. Some means must be provided to bridge the threatened gap between petroleum and the commercial production of large quantities of liquid fuels from other sources.

Increasing the Fuel Economy of Automotive Engines

The best way to accomplish this result is to increase the efficiency with which the energy of gasoline is utilized in automotive equipment, and thereby to obtain more "automobile-miles" per gallon of fuel. In itself, this is apparently a simple problem for the mechanical engineer to solve. It has been demonstrated repeatedly that large increases in fuel economy, or in number of miles per gallon of fuel, can be obtained merely by changing the gear ratio in the rear axle, so that the rear wheels make a greater number of revolutions per revolution of the motor than they did before.

But unfortunately this simple expedient is not a practical solution of the problem, because such a change in gearing produces a car that is lacking in accelerating and hill climbing ability to such an extent that people will not buy it. At the present price of motor fuel, economy is secondary to performance in the estimation of the public. Such a change in the rear axle gear ratio not only transforms the car, but it also converts what was a problem of mechanical engineering to an unsolvable one of salesmanship.

Nevertheless, this change is the correct first step toward better fuel economy. So the problem must again be referred to the engineer—not to the mechanical engineer, for he has done his part; but to the heat power engineer and the physicist. It is their problem to increase the torque delivered by the engine so that the car with the reduced gear ratio may regain its accelerating and hill climbing ability, and thereby become a product that the salesman can sell.

The solution of the problem again appears very simple. According to the laws of thermodynamics, both the torque and the fuel economy of an engine are increased as its expansion ratio (in automotive practice, called compression ratio) is raised. Logically, then, the next step is to increase the expansion ratio of the motor. This is accomplished by reducing the clearance volume above the piston, which in turn increases the pressure at which the fuel mixture undergoes combustion.

These changes, *viz.*, increasing the gear ratio at the rear axle, and increasing the expansion ratio of the engine, should theoretically produce an excellent automobile, one giving such high fuel economy that the salesman should have no trouble in marketing it. But the salesman's problem is still unsolved.

The "Knock"

This super-product of the mechanical and heat power engineers does not function properly; but, when running on gasoline, it gives a very objectionable and disturbing noise. This noise, which is metallic in sound, is called by motor mechanics a "knock," the term usually being qualified by an adjective such as "carbon," "spark," "heat" or "fuel." The knock, as it occurs in the automobile engine of the present, when it is laboring at wide open throttle, is familiar to everyone who has driven an automobile. But the degree of intensity of this knock increases with the pressure at which the fuel mixture is burned. So that, while in present-day automobiles the knock is so slight as to be merely an unpleasantness that does no harm, its intensity in this redesigned engine of considerably reduced clearance volume becomes so great as to result not only in loss of power but also in actual damage to the engine, such as cracked spark plug porcelains and broken piston tops. Because this phenomenon of the knock stands as an apparently effective barrier in the way of obtaining better fuel economies from automotive engines, its remedy is the key to the solution of a great economic problem.

The fact has been noted previously that this disturbance is frequently called a "fuel knock." This has arisen because its intensity is primarily a function of the chemical structure of the fuel used. Thus, the disturbance that is present in an engine when the fuel has the paraffin structure (gasoline) entirely disappears if benzene or alcohol is used. But the chemical structure of motor fuel from a commercial standpoint is at present fixed within fairly narrow limits. The use of petroleum oils as our commercial motor fuel is necessary on account of the enormous volume required, and because of the small amounts of other fuels available. Gasoline is an excellent fuel, except for the limitation it imposes upon economy on account of its tendency to knock. The final step in the solution of the problem, then, is to eliminate the knocking or detonating tendency of gasoline.

Elimination of the Knock

It is well known that if substantial percentages of benzene or alcohol are mixed with gasoline, the product can be used in motors of fairly high compressions without the objectionable knock. But unfortunately 40 to 60 per cent of one of these materials must be added to gasoline to accomplish the desired result; and so the amounts of benzene and alcohol available are sufficient to treat only a very small part of the gasoline that is consumed.

As the result of a large amount of work that has been done on this problem, a number of chemical compounds have been discovered which exert such an influence on the combustion of highly compressed mixtures of gasoline and air that in the presence of a small fraction of one per cent of one of these materials gasoline can be used as fuel in engines of very high compressions. Because of their remarkable effects, these compounds have been named "compressionizers" or "anti-knock materials." Their effect is to change the combustion of highly compressed mixtures of gasoline and air in such a way that no knock results, but the burn becomes entirely free from the disturbances that characterize detonating combustion. Some of these compounds are over 500 times as effective as benzene. Thus, 0.04 per cent by volume of one of these materials in kerosene is equal in effect for the

suppression of detonation to about 25 per cent by volume of benzene in the same kerosene.

A considerable number of these compounds of widely variant chemical compositions have been discovered. The results obtained in their investigation will be dealt with in a paper entitled "The Chemical Control of Gaseous Detonation with Particular Reference to the Internal-Combustion Engine," to be given at the September meeting of the AMERICAN CHEMICAL SOCIETY in Pittsburgh.

The addition of an antiknock material to gasoline makes it possible to obtain very much greater fuel economies, because it permits such changes in design to be made that the fuel can be used more efficiently. But, unless the intensity of the knock in a given engine is so great as to cut down power, the presence of an antiknock material in the fuel does not result in an increased fuel economy. Since the addition of a small percentage of such a compound makes very little or no change in the energy of a given volume of gasoline, no increase in the mileage obtained per gallon can result from its use, unless such changes are made in the engine that a larger percentage of the energy content of the gasoline can be utilized.

Some of these antiknock materials have been rather widely used, particularly in airplane engines, and their great effectiveness and value have been demonstrated thereby. In view of the remarkable effects of these compounds and the good results that have been obtained in their use, it seems certain that it will be only a matter of time until all gasoline will be treated with an antiknock material, and automobile engines having higher compressions and giving considerably greater mileages per gallon will be used. The principal effect of the use of antiknock compounds will be the much further removal of the time when the threatened exhaustion of our petroleum reserves will actually occur.

Scientific Method in Rubber Compounding

By C. O. North

THE RUBBER SERVICE LABORATORIES CO., INC., AKRON, OHIO

VERY satisfactory progress has been made during the past few years in applying scientific methods to the problems of rubber compounding. This has been made possible through the development of new and improved methods of rubber testing which in turn have furnished us with a clearer conception of the underlying principles of compounding.

The first chemists to make a study of the art of compounding had before them the picture of steel. They were of the opinion that the problems of rubber could be solved in a similar manner and consequently laid great stress on the development and application of chemical analysis. For example, they thought that coefficient of vulcanization was by far the best index of state of cure. They failed to realize that in rubber we have a mingling of both chemistry and physics. While strictly chemical problems are met in the vulcanizing reactions, yet the effects of pigments and other compounding ingredients belong within the field of physics. The coefficient of vulcanization is merely a measure of the quantity of sulfur which has become added to rubber. It is in no way a measure of the state of technical cure because of the factor known as depolymerization.

EFFECTS OF TEMPERATURE AND TYPE OF ACCELERATOR

It is now generally understood that in vulcanizing or curing we have two effects which work in opposite directions. Depolymerization or the reduction in size of the colloidal aggregates of rubber is a factor which tends to weaken or deteriorate the final product. It is influenced primarily by heat and the time of heating. For example, it is not a factor at cures made at 10 and 20 lbs. of steam pressure (namely, 239.4° and 258.8° F., respectively). This statement applies even when the time of heating is as long as from 3 to 5 hrs. As the temperature rises, the time within which depolymerization is not a decided factor grows smaller and smaller. At 40 lbs.' steam (287° F.) the range is from 1 hr. to 1 hr. 30 min. At 60 lbs. (307° F.) it has narrowed down to from 15 to 30 min. The higher the temperature, the shorter becomes the time within which rubber may be heated without serious deterioration.

Another factor which affects depolymerization is the type of accelerator employed. For example, *p*-nitrosodimethylaniline is a violent depolymerizer, as are several softeners or fluxing materials which are sometimes added to a compound for the purpose of making it easier to handle in the factory. Some softeners are powerful depolymerizers, others have little effect. For example, paraffin is quite pronounced in its action, but castor oil is quite inert.

Opposed to the depolymerizing action of heat and certain substances, we have vulcanization which ordinarily means sulfur addition. While we know many ways of reducing the size of the colloidal aggregates of rubber, yet we are limited to sulfur and sulfur chloride for commercial methods of linking them into larger units. Since vulcanization by sulfur chloride has such a small number of applications, it may be practically disregarded. Sulfur then is the principal depolymerizer. It counteracts the effects of heating and other depolymerizing influences. As will be readily appreciated, the more sulfur which must combine with rubber to produce technical cure, the poorer the product. For example, reclaims whose poor quality are well known will seldom be found to have a coefficient of vulcanization under 5. In other words, the combined sulfur will be more than 5 per cent of the rubber present.

On the other hand, Whitby's compounds vulcanized with various dithiocarbamates and cured in from 3 to 5 min. at 287° F. (40 lbs. steam) showed remarkably high tensile strengths with a coefficient of vulcanization seldom over 1.5 and ordinarily less than 1. It is therefore generally realized that the larger the colloidal aggregates in rubber vulcanized to the point of commercial cure, the greater the tensile strength, the resistance to tearing and flexing, and the more pliable and stretchy the article. Certainly when properly vulcanized such compounds have longer life and stand up better in service.

Aside from the advantage and more rapid turning over of equipment, shorter cures at moderate temperatures are very desirable because of the increased service and durability of the product so prepared. It will be remembered that a few years ago 3000 mi. was considered a remarkable record for

pneumatic tires. In those days the cures were from 3 to 5 hrs. long. To-day a record of 10,000 mi. is considered only average. The curing time has been shortened from 3 hrs. to approximately 1 hr. for the small sizes. The large sizes have been reduced in proportion.

While there are other factors which have had a bearing on this problem, the fact remains that rubber cured with the aid of organic accelerators has a lower coefficient of vulcanization than formerly and a higher degree of polymerization than was ever met with in the old days.

Regardless of the advantage of shorter cures, the compounder is limited by the slow heat flow in stocks and fabricated articles. The heat conductivities of both rubber and fabric are low and therefore a very thorough understanding of the temperature effects must be had before one can secure a uniform cure throughout an article. This requires extensive thermocouple measurements and considerable mathematics in working out the generalizations. Fortunately work on this subject is now going forward in the laboratories of several companies and it is hoped within a short time to be able to calculate the temperature at any point within the tire or other article at any time under definite temperature conditions.

Assuming that one has a very thorough knowledge of the temperature conditions, we have then the problem of securing uniform cure throughout the article. For a long time we had to place entire dependence on what is known as a rising or step-up cure. When properly worked out this method does give practically uniform effects but with the introduction of the so-called flat curing accelerators these problems have been solved much more easily. By flat curing accelerators we mean those which are capable of giving uniform physical properties over a long range of time.

An accelerator is known which has a range of from 30 min. to 4 hrs. cure at 40 lbs. or 287° F. Within this range of cures all samples of this stock have shown perfect aging to date. This is really remarkable and certainly helps to smooth off any inequalities left by an improperly gaged rising cure.

Practical Procedure in Compounding

As in other industries the application of the scientific method usually follows the rule-of-thumb experiments carried on by the first investigators. When a compounder has the task of working out compounds and structural features which enter into the construction of an article, as for example a pneumatic tire, he must first familiarize himself with the behavior of articles which have given a good account of themselves in actual service. Thus, if he is working with tires, he will study various makes, determine the average life under different conditions, the rate of tread wear and deflection under which they have been run, the type of roads, and other conditions of service. He will select those tires which have given good service, or, as is usually the case, he will pick out one tire having the most satisfactory tread, another with the better bead or another with a better carcass, and in fact will make a study of the weak points of the articles then in service.

If it is steam hose he will determine the average life both by steaming tests and actual service. His first problem is unquestionably that of service rendered and the manner in which articles of other manufacture have met this service. With the above information he will then make a more careful analysis of the conditions of service and will determine, among other things, the rapidity and extent of flexing, the maximum tensile strains which have been met, the conditions of wear, the ease with which heat may escape, whether the service is continuous or intermittent, and he will make a special investigation of all conditions which are somewhat out of the ordinary.

He will then tear down those articles which have given the best service and make a careful analysis of them, basing his decisions both on tests after service has been completed and on the freshly manufactured article. For example, he will determine the tensile strength and ultimate elongation of the different compounds which enter into the article with as much accuracy as is possible. He will determine the stress-strain curves of the different stocks and will make particular note of the load required to produce 300 per cent elongation, which figure many compounders have now come to regard as the best index of stiffness. He will study the characteristics of the hysteresis loop and particularly the ratios of energy input and output at low elongations. Moreover, he will make careful note of the resistance to tearing, to abrasion, and to flexing. These three are perhaps the most important of all, and he will measure these resistances by tests which have recently been developed but which have not yet been standardized. He will determine the rate of plastic flow and of recovery. The union of the different parts of the article to one another will also be very carefully studied. This matter is of maximum importance, particularly in pneumatic and solid tires. Many tires fail through unsatisfactory unions between the plies or between tread and breaker, or between breaker and carcass. In solids a great deal of trouble results from separation between tread and hard rubber. In fact, this is the most serious type of failure and has caused the solid tire companies much concern.

Before going any further into the development of an article to meet any definite set of conditions, the compounder must make a careful study of the conditions of manufacture. Too often are we given to the bad habit of determining what we should have without regard to what we can make. The operations through which different compounds must pass in going from the unmanufactured to the finished state must be carefully worked out. The milling, calendering, and tubing conditions must be thoroughly understood, the curing conditions must be set and the rate of heat flow measured or approximated in order to determine the minimum time and the proper temperature of the cure. Moreover, a compound cannot be considered by itself but always in relation to other stocks and the union which it must make to them. In addition to this, the compounder is limited by competition to a certain definite cost for each stock and if possible he must reduce costs, at the same time delivering a product of equal or better quality. Again, appearance is usually a very large factor. He must make a special effort to produce an article pleasing to the eye.

It will be gathered from the above that the conditions which the compounder must meet in order to develop a satisfactory article are not only numerous but difficult to handle. Much of the lack of progress along scientific lines in the past was due largely to the multiplicity of factors which had to be considered.

In compounding to meet the fine conditions of cure, a knowledge of the behavior of accelerators is required, which as yet is little appreciated. Not only must one have at hand a great mass of data obtained at normal curing temperatures, but the behavior of the various accelerators with different sulfur and accelerator ratios to rubber in the presence of various activators, such as zinc oxide, lime, etc., must be known for various temperatures. As a rule it is perfectly satisfactory to work with the temperatures of 50, 40, 30, 20, and 10 lbs. of steam. Certain accelerators will not function below 30 lbs. of steam and there is at least one which is said not to function under 50 lbs. of steam.

After working out the effects of various accelerators and sulfur ratios in simple mixes, it becomes imperative to know the influence of various rubber fillers, oils, greases, and sub-

stitutes on such compounds. The principal difference will be found in the fact that oils, etc., require slightly higher sulfur ratios. With this information as a basis, it is possible to work out compounds which will cure within the desired range or time, and the average compounder will make a special effort to have this range as wide as possible. Certainly there are few purposes for which at least a 2-hr. range cannot be obtained; in other words, a compound which will give equivalent physical properties within a range of 2 hrs. For example, it should be possible for a stock which has certain definite characteristics at 1 hr. to be cured to 3 hrs. without serious change in physical properties. This does not mean of course that one should cure at 3 hrs., but in practically all cases we are much safer in the aging properties of the compound, if, having this range, we then cure to the optimum cure or slightly beyond it.

The next step is arriving at the proper plasticity in the raw stock. This plasticity enters into every phase of the fabrication of the article. For example, a tire friction must be soft enough to run directly on cord fabric without spreading the cords. It must thoroughly penetrate the cords and it must maintain a certain tackiness all the way through to the tire building operations, and at the same time it must not be so sticky as to stick to the liner or to work out badly on the bias cutters. This plasticity is also of importance in making a proper contact with other stocks, which is the first requisite in securing good unions. It also enters into the readiness with which stocks may be run on the calender and tube machines. This requires a very thorough study of softeners and their effects.

Influence of Fillers

From a study of articles and their constituent elements, one can usually arrive at the approximate physical characteristics of the compounds employed. Outside of cure and plasticity, the development of a compound for a certain purpose requires a thorough knowledge of fillers, which may be divided into the active and inert types.

This is hardly the place to go into the reasons for activity or inertness in a pigment but briefly it is now generally understood that activity is very closely tied up with fineness of division and the condition of particle surface. For example, micronex carbon black, which is by far the finest product commercially available at present, has a fineness of division of less than 0.1μ. Moreover, it is reasonable to suppose that its surface is not merely that of a spherical particle but probably is something of the nature of a feather. Regardless of the reason, carbon black continues to be our most important filler and the one which has the greatest toughening effect upon rubber. Within the last few months, however, certain new types of zinc oxide have been brought out which are much finer and carry lower impurities than the older grades and therefore are more reactive and show greater activation effects on accelerators and give higher tensiles and better stiffening action. To date there are no competitors of carbon black and zinc oxide. Clay has been advanced and has been found of value when used in small quantities. While it does have some of the desired stiffening action, yet because of the fact that there are many agglomerates and large particles present which do not disperse well in rubber, it has as yet only limited application in high-grade compounds. Not only must one pay special attention to the fineness of division and surface effects of fillers, but the degree of ease with which these fillers can be dispersed in rubber must be well understood. Dispersion experience in paint, glycerol, water, and other media does not necessarily hold and has little bearing on the ease with which a pigment may be dispersed in rubber. Methods of milling and the softeners employed have a great bearing on the subject and there is hardly a compounder who cannot improve his compounds by improving his milling characteristics.

Of the inert fillers none are very finely divided and consequently they cannot be dispersed very thoroughly in rubber. To this class belong certain grades of whiting, clay, barytes, and others which are used chiefly because they are cheap. In high-grade stocks where severe conditions of service must be met, it is unusual to find them present in any high percentage.

In reference to the rubbers which find the widest application at present it may be stated that one of the outstanding features of our present compounding is the wide use of brown crepe. This rubber mills nicely and furnishes desirable plasticizing properties to the resultant compounds. It is true that it does vary in rate of cure but in the presence of organic accelerators this variation is so masked that it is of little importance. A much more important problem is its variation in plasticity. Many companies are now making plasticity tests by milling a definite weight of rubber under carefully controlled conditions and determining the time required for breaking down to a desired degree.

There was a time when compounding and design were widely separated and there was very little coöperation between the two ends of the business. Fortunately, to-day the designer has taken up compounding or the compounder has taken up design. It has now become a recognized fact that the success or failure of any rubber article depends not only on the stocks employed and the technic of factory production, but also upon how well the mechanics of the articles have been worked out in perfecting the design. For years we have been putting too much fabric in our tires. This year has seen a decrease in the number of plies and we are soon to decrease the number of cords per inch in the plies. Sea Island and Egyptian cotton were formerly employed exclusively. To-day much karded and combed peeler will be found in many of the best tires.

Conclusion

In outlining the above, the writer has made no effort to go into detail on any of the big problems of compounding. His whole aim has been to point out the conditions which confront the compounder and the vast amount of information which he must have at hand in order to successfully meet the conditions of service and competition. It is hoped that this paper will serve as an illustration of the application of the scientific method to one of the most difficult branches of applied engineering.

Meeting of the American Electrochemical Society

The Forty-second General Meeting of the American Electrochemical Society will be held at Montreal, Quebec, and will be opened by President Schluederberg on Thursday morning, September 21.

The recently organized Division on Electrodeposition will be well represented. One of the papers of the Thursday morning session will deal with the physical properties of electrolytic iron—a product which is being prepared commercially, contrary to all predictions of ten years ago. There will also be papers on zinc, brass, and other electrodeposited metals.

The Thursday afternoon and Friday morning sessions of the Electrothermic Division will be given over to a symposium on "Industrial Heating," which will include the following papers:

History of Industrial Heating; Principles of Design of Furnaces; Comparison of Fuel Costs in Different Types of Electric Furnaces, and with Combustion Furnaces; Resistor Materials; Specific Heats; Electric Conductivity of Insulating Materials at Industrial Furnace Temperatures; Heat Emissivity; Heat Transfer.

A popular lecture on the Progress in Physical Science is scheduled for Thursday evening. Section Q will be in charge of an old-fashioned Smoker on Friday evening. A special train will be furnished for an all-day trip to Shawinigan Falls. Hotel Windsor will be headquarters for this meeting.

Physics of Rubber, 1920–1921

By W. B. Wiegand

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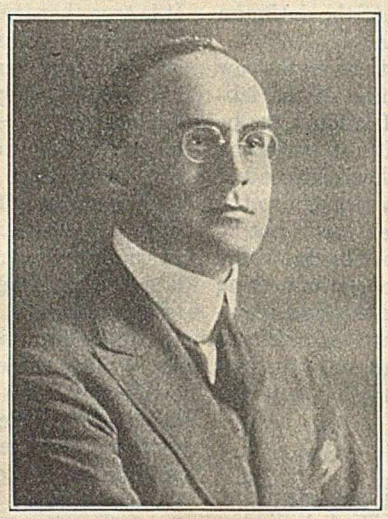
PERHAPS the most valuable publication of the period is "Plantation Rubber and the Testing of Rubber," by G. S. Whitby; Part II of which includes a review of the work on rubber by some of the master physicists of the nineteenth century. Nothing could be more fruitful than the repetition of much of this work, with with due regard to composition and life history of the mixings employed.



W. B. Wiegand

Physical Structure

Unstrained—The spatial distribution of discrete ingredients in vulcanized rubber has been admirably studied by Mr. H. Green,[1,*] whose photomicrographs show clearly the phenomena of dispersion and agglomeration. The extension of his work to uncompounded rubber may add to our knowledge of its ultimate colloidal structure and so supply visual confirmation or otherwise of the net work hypothesis of C. O. North,[2] and of the spheroidal theory of R. W. Lunn.[3]

Strained—The development of vacuoles at the poles of particles in strained rubber, predicted on theoretical grounds by H. F. Schippel,[4] has been visually confirmed by H. Green.[5] This phenomenon has deep significance in connection with the theory of reinforcement.[6]

Mechanical Properties

The physical testing of rubber has been actively carried on but with no important contributions to testing technic.[7] Standardization as to equipment, procedure, and representation is beginning to receive the attention it deserves.[8]

Stress-Strain Curve—The attention of rubber workers continues to be directed less toward breaking values and more toward the complete curve. The "conchoid" analogy of Schidrowitz and Goldsborough has been shown to be inadequate;[9] and Shields,[10] and somewhat later, Hatschek,[11] have published new formulas based on curves distorted by calculation to actual cross section; the former, who seems to use only the early part of the curve, arriving at a complex logarithmic expression, the latter deriving in elegant fashion a rectangular hyperbola for the same curve. The present writer finds that when the Hatschek method is applied to curves for stocks representing a range of typical factory mixings the construction is inapplicable. Moreover, neither author has established any physical significance for the parameters that appear in their equations.

Vogt[12] has described a modified method of recording stress-strain data, which facilitates the closer study of reversion phenomena.

Energy Relationships—Of the many physical constants used to described the properties of a sample, perhaps the most comprehensive single index is the energy of resilience as measured by the area subtended by the s.-s. curve on the elongation axis. Proposed in June 1920,[13] this quantity has been widely adopted. Gurney and Tavener[14] describe the energy absorption of various mixings subjected to repeated stresses, emphasizing the superiority of high-rubber compounds for work (such as in airplanes) requiring a slow rate of energy absorption. An important application to automotive equipment is the use of rubber spring shackles.[15] Hysteresis losses, as influenced by cure, pigment loading, and cyclic elongation, are described by Wiegand.[16]

An interesting fact is the very large increase in resilience induced by the addition of a highly dispersed nonelastic phase such as carbon black.

Volume Changes—The outstanding contribution is H. F. Schippel's[4] paper showing the enormous increases in volume (as much as 100 per cent) when highly pigmented stocks are strained. This has a vital bearing on elastic theory. Sanderson[17] has studied the thermal expansion of various mixings, finding no discontinuity at the vulcanizing point.

Grain—Van Rossem[18] has described calender grain, including its disappearance through heating, which he assigns to the Joule effect. In this opinion he is opposed by Wiegand[19] and Lunn[3] who regard the phenomenon as essentially due to viscosity-temperature relationships. (See also Skellon.[20])

Hardness tests have been thoroughly studied by Gurney,[21] particularly as applied to the manufacture of rubber-covered rolls.

Effect of Compounding Ingredients—The connection between fineness of subdivision and reinforcing action has been definitely established.[2,6] Further work is necessary to clear up the role played by adhesional forces as distinguished from specific surface. The mechanical properties of vulcanized rubber have been shown to be controllable over very wide ranges through the intelligent use of various fillers. The remarkable reinforcing properties of carbonate of magnesium have been well established by Greider.[22] Mineral rubber has been the subject of a masterly study by C. O. North.[23]

The important bearing of particle shape upon the phenomena of grain, set, and hysteresis demands further study.[24]

Measurement of Particle Size—The importance of subdivision as a guide to pigment reinforcement has stimulated H. Green[25] to develop to great precision the direct microscopic method. Using violet light, this worker has been able to measure particles down to 0.2 micron in diameter. H. A. Gardner[26] has described a very novel method of estimating the fineness and texture of pigments by rubbing them on a phonograph record. W. W. Vogt[27] favors the obscurometer method of measuring average particle size. This has had strong criticism from the standpoint of refractive index.[28]

Those who favor clay as a compounding ingredient will find the paper by Comber[29] very suggestive.

The race for superfine rubber pigments has led to intensive research, working both from the atomic state (sublimed litharge, zinc oxide, magnesium carbonate), and from the coarse condition.[30]

Thus we may soon come upon the ideal pigment, one

* Numbers in text refer to References at end of paper.

which unites colloidal fineness with freedom from entrained air and is at the same time light, cheap, and easily dispersed on the mill. The production of such an ingredient in the standard colors will mark a new era in rubber compounding.

PHYSICAL EFFECTS OF ACCELERATORS—Reinforcement is, however, attainable by means other than the introduction of a highly dispersed phase. The organic accelerators, besides shortening the cure, greatly improve the mechanical properties. Schidrowitz and Burnand[31] have shown that piperidine piperidyldithiocarbamate increases energy of resilience and ultimate tensile and decreases (improves) the "slope"—facts well known in the art.

Lack of space precludes detailed reference to other papers bearing on the physical aspects of acceleration.[32] Especial importance, however, attaches to the scholarly work of Twiss and his collaborators in which, *inter alia*, is described the interesting pseudo-reversion of accelerated mixings containing only small percentages of zinc oxide.

OTHER PHYSICAL PROPERTIES—The thermal conductivity of rubber and the more common ingredients has rightly attracted attention, and during the period under review two papers have appeared, Somerville,[33] and Williams.[34] The results arrived at by these two workers differ so radically as to leave the reader in complete ignorance. The subject deserves clearing up.

Hitherto the reversible heat (Joule effect) involved in deformations has been left entirely unrecognized in physical testing. Isothermal or nearly isothermal conditions have been chosen, whereas service conditions (as in tires) are in many cases adiabatic.

Thus the present writer feels that rubber deserves better from the thermodynamicians, and looks to the day when a Willard Gibbs or a van't Hoff will formulate for rubber the laws so carefully worked out for gases and solutions. In this connection the impact test (by Schob pendulum, for example) offers possibilities for adiabatic research.

The physical conditions attending the action of light on rubber have been carefully studied by Porritt.[35,36] An interesting commercial development is the "Rubber Glass,"[37] being developed by Fordyce Jones by means of the Peachey cure. It will be interesting to observe the light aging properties of this substance.

The variability of crude rubber as regards cure is becoming relatively less important than its variability as regards milling properties and behavior in cements. We hope for more papers on this problem. The difficulty has been to develop clear-cut technic for the quantitative expression of these differences.

Permeability to gases has been carefully studied by Edwards and Pickering.[38] Accelerated heat aging tests have become a definite part of testing technic, owing chiefly to the work of Dr. W. C. Geer.[39]

It is to be hoped that an increasing number of graduate physicists will be attracted to rubber, a subject in which they will find ample scope for work of the greatest theoretical as well as practical importance.

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Fatal Explosion at Harvard College

On May 19, 1922, an explosion and fire occurred at the Jefferson Physical Laboratory at Harvard College, which was fatal to two and injured several others.

According to the evidence, Mr. A. K. Dunbar, one of those killed, was compressing oxygen from a balloon situated just outside of the building into a steel gas cylinder that was standing on the cement floor of the basement. Compression was effected by means of a Whitehead, two-stage compressor with water-lubricated cylinders, of about one-half cubic foot per minute capacity, driven by an electric motor. The gas, after passing through the two stages of the compressor, was conducted through a small water separator and thence into the cylinder where, at the time of the explosion, it had reached approximately 1500 lbs. per square inch.

Mr. Dunbar was in an adjoining room conducting gas analyses and hastened to the compressor upon hearing a slight pop in the safety valve. The motor had stopped and he went to the main switchboard to ascertain the cause, after which he returned to the compressor room, started the compressor, and was evidently standing near the apparatus when the explosion occurred.

The primary explosion was evidently in the lower part of the steel cylinder into which the gas was being compressed, and the flying fragments exploded the separator and a partly filled cylinder of illuminating gas. The probable cause of the explosion was oxygen gas under high pressure coming in contact with oil in the lower part of the cylinder.

In the compression of hydrogen gas into steel cylinders, oil is used for lubrication, some of which finds its way into the cylinder or upon the valve thereof. In compressing oxygen gas, water or soapy water is used for lubrication, since whenever oil comes in contact with oxygen under high pressures an explosion generally follows. To avoid such accidental explosions, all cylinders used for hydrogen compression are fitted with screw connections having left-hand threads. The cylinder that exploded had a left-handed connection, and the evidence seems to show that at some previous time it had been used for the storage of hydrogen under pressure, and probably contained oil which caused the explosion.

It is reported that a new process for making colored motion pictures has been perfected by the Technicolor, Inc., of which William Hamlin Childs is the head. A plant is to be built near New York with a capacity of 1,000,000 ft. of film weekly.

The Chemistry of Rubber Vulcanization and Acceleration

By C. W. Bedford

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IT IS NOW generally conceded that the vulcanization of rubber is a chemical process, while physical chemistry plays a secondary, although important part. The addition of sulfur to rubber has long been recognized as greatly facilitated by the presence of inorganic accelerators such as litharge, lime or white lead, the latter having been first used by Charles Goodyear himself, but only within the past few years has it been shown that these inorganic accelerators are dependent on the presence of resins, proteins, organic accelerators or other organic substances, and that their action is secondary in character. While the accelerating action of ammonia had been observed in 1881,[1] it was not until 1906 that the organic nitrogenous accelerator was discovered. Since the publication of the Bayer patents on piperidine in 1912 the number of known organic accelerators has increased into the hundreds.

C. W. Bedford

The mechanism of the vulcanization process is each year becoming more fully understood through the efforts of rubber chemists the world over. The following is a brief summary of the results of their latest work.

The relative reactivity of different forms of sulfur is a fundamental question which has recently been investigated further by D. F. Twiss.[2] His work indicates that there is little difference in activity between soluble and insoluble sulfur at temperatures from 68° to 188° C. The Peachey process of vulcanization by hydrogen sulfide and sulfur dioxide[3] gases at ordinary temperatures liberates a form of sulfur which may be isolated[4] and used for vulcanizing rubber at low temperatures. This form of sulfur quickly changes through the insoluble or plastic variety to ordinary rhombic sulfur, thereby losing its extraordinary vulcanizing power. The question of "nascent" sulfur and its possible reaction with rubber is still an open one. Peachey has relied on this explanation for his cold vulcanization by gases. Others have called attention to the inactivity of nascent sulfur liberated in rubber cements by the action of hydrogen sulfide on aromatic nitroso compounds.[4] This question is of great importance for the ultimate explanation of the mechanism of vulcanization.

Vulcanization by organic disulfides without the use of elemental sulfur has recently been reported from several sources. Romani[5] cites tetramethyl thiuram disulfide and Caldwell[6] mentions oxybutyl thiocarbonic disulfide (butyl xanthic disulfide). The disulfides are said to revert to monosulfides, giving up the other atom of sulfur to the rubber. Bloch[7] had previously vulcanized rubber with hydrogen disulfide, and Kratz[8] used ammonium hydrosulfide without free sulfur but in the presence of air (ammonium disulfide). Vulcanization with disulfides seems to be related to the vulcanization without sulfur by benzoyl and other peroxides, according to Ostromuislenskii.[9]

Closely related to the action of disulfides is the action of higher polysulfides. The use of antimony persulfides is well known. Gerard vulcanized with zinc[12] and calcium polysulfides,[10] Bourquin[11] used the polysulfides of hydrogen, sodium, and calcium, Esch[12] worked with magnesium polysulfide, and C. O. Weber[13] states that zinc sulfide has some vulcanizing action. Erdmann,[14] in 1908, proposed a polysulfide theory of vulcanization through the formation of thiozonides, a theory that was later expanded by Ostromuislenskii,[15] Kratz,[16] Bedford,[17] Bruni,[18] and their co-workers. Organic polysulfides of meta-toluylene diamine disulfide, mercapto-benzothiazole disulfide, and other disulfides are also used for vulcanization purposes. Their action, however, is greatly aided by the presence of zinc oxide.

A further advance in rubber chemistry was made by Ostromuislenskii[19] by the discovery of the rapid vulcanization of rubber at ordinary temperatures. The dithiocarbamates of piperidine, methyl amines and many other organic bases cause sulfur to vulcanize rubber at room temperatures in a comparatively short time. Later it was shown that this vulcanizing power is available only in the presence of metallic oxides and that metallic salts of dithiocarbamates function in the process of vulcanization. Ostromuislenskii[20] also found that zinc alkyl xanthates are equally strong in their accelerating power although they contain no nitrogen, an element which for many years was considered necessary for vulcanization. Zinc thiophenols[21] have also been added to the list of nonnitrogenous accelerators.

Most organic accelerators rely on the secondary action of metallic oxides to bring out their full vulcanizing power, while some, such as aniline and aldehyde ammonia, are retarded thereby. Scott and Bedford[17] have divided organic accelerators into two classes: (*a*) hydrogen sulfide polysulfide accelerators, (*b*) carbosulfhydryl polysulfide accelerators. The first class includes compounds such as aniline which do not need the aid of inorganic accelerators, and are supposed to form polysulfides by first reacting with hydrogen sulfide to form derivatives of ammonium sulfide, then dissolving sulfur to form polysulfides similar to ammonium poly-

[1] Brit. Patent 787 (1881).
[2] *J. Soc. Chem. Ind.*, **40** (1921), 48T.
[3] Brit. Patent 129,826 (1919).
[4] This Journal, **14** (1922), 25.
[5] *C. A.*, **16** (1922), 854.
[6] Brit. Patent Application 174,915 (1922).
[7] Ger. Patent 219,525 (1908); *C. A.*, **4** (1910), 2211.
[8] This Journal, **13** (1921), 67.
[9] U. S. Patent 1,249,181 (1917).
[10] Gmelin, "Handbook of Chemistry," **17**, 349.
[11] *Gummi-Markt.*, **4** (1910), 408.
[12] *Ibid.*, **9**, 68 and 125.
[13] *Z. angew. Chem.*, **1893**, 631, 661.
[14] *Ann.*, **362** (1908), 133.
[15] *C. A.*, **10** (1916), 1944, 3177.
[16] This Journal, **12** (1920), 317.
[17] *Ibid.*, **13** (1921), 125.
[18] *C. A.*, **15** (1921), 3915.
[19] *Ibid.*, **10** (1916), 1943.
[20] *Ibid.*, **10** (1916), 3176.
[21] This Journal, **13** (1921), 1034.

sulfide. The second class either contains carbosulfhydryl groups or forms them by reactions during vulcanization. This class includes mercaptans, dithiocarbamates, thioureas, xanthates, etc., and is said to function through the formation of the metallic salts which are described as forming mercaptide polysulfides that contain per-sulfur sufficiently active to react with rubber at ordinary temperatures. In support of this general theory there has been prepared an active type of zinc sulfide[4] which forms polysulfides and is an active accelerator. Thiocarbanilide is comparatively inactive in the absence of zinc oxide and has been found to form zinc and lead mercaptides through its tautomeric mercapto form.

Twiss[21] energetically disagrees with this theory of the action of zinc mercaptides, dithiocarbamates, xanthates, etc., calling attention to the fact that the zinc salts still need the presence of zinc oxide to bring out their full vulcanizing power. Bedford and Sebrell[22] found that their action was also increased, in rubber cements, by the presence of aniline, and Cadwell[6, 22] finds the same action of aniline and other amines, not only on zinc dithiocarbamates, xanthates, etc., but also on thiuram disulfides and xanthic disulfides:

$$(R_2N—CS—S—S—CS—NR_2 \text{ and } RO—CS—S—SCS—OR)$$

Bruni[18] offers a second theory for the action of zinc oxide, which parallels the above-mentioned theory up to the formation of the zinc salt of the thio acid or mercaptan. He states that sulfur reacts with the zinc salt to form a disulfide and zinc sulfide according to the equation:

$$(R_2N—CS—S—)_2\,Zn + S = (R_2N—CS—S)_2 + ZnS$$

This disulfide is then believed to vulcanize the rubber by reverting to the monosulfide, which in turn reacts with elemental sulfur to reform the disulfide. Twiss[23] again calls attention to the need of zinc oxide for bringing out the full effect of the disulfide, even when the disulfide is formed outside the rubber mix and compounded as such, under which conditions Bruni's theoretical need for zinc oxide should be absent. Twiss believes that there is some reaction product common to disulfides, dithiocarbamates, zinc oxide, and sulfur, which forms the true accelerator or vulcanizing agent.

Further in regard to the thiuram disulfides, it has been shown that they do not vulcanize rubber-sulfur-zinc oxide mixes at room temperature as do the zinc salts described below, while the action of hydrogen sulfide,[4] even at ordinary temperatures, changes the disulfide to a dithiocarbamate, and in the presence of zinc oxide starts the process of rapid vulcanization without the application of heat. The above-mentioned action of aniline in causing thiuram disulfides to vulcanize rubber at ordinary temperatures may be explained in the same manner according to Fromm[24] who showed that aniline and other primary amines easily react with these disulfides to form dithiocarbamates. Thiuram disulfides as well as dithiocarbamates, derived from secondary amines, are found by Twiss to be much more active than those from primary amines.

In general, the study of the mechanism of vulcanization seems to be concentrating on the action of accelerators which need the aid of zinc oxide. Little has been published on the effect of litharge, lime or magnesia. The action of aniline, aldehyde ammonia, para nitroso-dimethyl aniline, and many other accelerators still remains practically untouched. The important factor of temperature, the nonactivity of certain accelerators at temperatures where others are violently active, has been commented on as due to the relative stability or instability of the reaction products, but a satisfactory explanation has not yet appeared.

[22] Brit. Patent Application 177,493 (1922).
[23] *J. Soc. Chem. Ind.*, **61** (1922), 81T.
[24] *Ann.*, **348**, 144.

This, in brief, is the present status of the chemistry of rubber vulcanization. The advent of the organic accelerator has furnished the rubber chemist definite chemical compounds for use in vulcanization and provided a means of throwing some light on the mechanism of the process. In general, the polysulfide theory is fairly well accepted; in detail there are many differences of opinion and many unsolved problems. History, in connection with rubber chemistry, is being made at a rapid rate and we await with extreme interest the developments of the immediate future.

D. H. Killeffer Succeeds R. T. Stokes

Following the sudden death of the former secretary of the Biscuit and Cracker Manufacturers' Association, the position was offered to and accepted by Mr. R. T. Stokes who had but recently become associate editor of THIS JOURNAL.

Mr. D. H. Killeffer has been appointed associate editor to succeed Mr. Stokes. Mr. Killeffer is a graduate of the University of North Carolina. After graduation he became a member of the staff of the Brown Laboratories of Nashville and served in the department of tests of the Nashville, Chattanooga, and St. Louis Railway. Subsequently he was research chemist on plant development for the Calco Chemical Co., and since January 1920 has been a member of the editorial staff of Drug and Chemical Markets.

Mr. Killeffer will have headquarters in New York but our readers will meet him frequently in other parts of the country, particularly in industrial chemical fields.

D. H. KILLEFFER

Meeting of Chemists at Utrecht

At Utrecht on June 21 to 23 there was held the first gathering since the war at which chemists from Germany and Austria have met chemists from England, America, and other countries.

America: L. M. Dennis, D. A. MacInnes, W. A. Noyes.
Austria: E. Abel, J. Billiter, F. Emich, A. Kailan, A. Klemenc, F. Pregl, A. Skrabal, R. Wegecheider.
Czechoslovakia: J. V. Dubsky, A. Simek.
Denmark: N. B. Bjerrum, J. N. Brönsted, J. Petersen, Chr. Winther.
England: E. C. C. Baly, F. G. Donnan, W. C. McLewis.
Germany: M. Bodenstein, G. Bredig, O. Hahn, P. Pfeiffer, R. Schenck, W. Schlenck, A. Stock, P. Walden, H. Wieland.
Holland: J. Backer, J. J. Blansma, Ernst Cohen, A. F. Holleman, F. M. Jaeger, H. R. Kruyt, W. Reinders, P. van Romburg.
Lithuania: M. Centnerschwer. *Russia:* N. Schilow. *Switzerland:* J. Piccard.

The original suggestion of the meeting was made by Professor Donnan of London, and the preliminary plans were made at a meeting in the home of Professor Cohen of Utrecht in June 1921. The details were carried out by Professor Cohen.

The following scientific papers were read and discussed:

E. C. C. BALY. Photochemical Catalysis.
P. WALDEN. Free Radicals.
W. A. NOYES. Positive and Negative Valences.
W. SCHLENCK. Contributions to the Chemistry of Free Radicals and the Varying Affinity of Carbon Compounds.
M. BODENSTEIN. The Photochemical Structure of Phosgene.
L. M. DENNIS. The Preparation and Properties of Metallic Germanium.
H. WIELAND. Free Radicals.
N. SCHILOW. Distribution Equilibria.
J. PICCARD. Absorption Colors of the Second Class.
E. ABEL. Direct and Indirect Esterification in Absolute and Aqueous Glycerol, According to Experiments of Karl Heidrich.
A. KLEMENC. Vapor Pressures of Isometric Benzol Derivatives.
M. CENTNERSCHWER. A Proposal for the Introduction of a Small Unit of Measure (Radion).

At a reception in Hotel Pays-Bas on Wednesday afternoon, there were addresses of welcome by G. L. Voerman, President of the Chemical Society of Holland; Professor Went, President of the Royal Academy of Science of Amsterdam, and a response by W. A. Noyes. [*W. A. Noyes*, Urbana, Ill.]

Recent Advances in Pulp and Paper

By Clarence J. West

Chairman, Committee on Bibliography, T. A. P. P. I., 1701 Massachusetts Ave., Washington, D. C.

Raw Materials

One of the most interesting questions in the pulp industry to-day is the future source of its raw materials. The forests are rapidly disappearing and only a few of the more enterprising mills are taking any precautionary measures with regard to reforestation. It is true that paper can be made from practically any fibrous material known, but it is also true that, in the majority of such raw materials, the process is far from being satisfactory, as far as the yield of pulp is concerned. It is not possible, in the United States at least, to prepare pulp from annual plants and similar materials, under conditions that make the process economically feasible.

C. J. West

The most promising raw materials, other than wood, thus far studied are bamboo and cotton linters. The early difficulties encountered in the treatment of bamboo have now been overcome and one or two methods are known to be quite successful.

India appears to offer an inexhaustible supply. According to Raitt, India, with its supply of bamboo, and the Savannah grasses, can produce pulp for the whole world. Raitt further estimates that the cost of production of bamboo pulp would not exceed half that of the manufacture of wood pulp. Many years ago the Department of Agriculture tried to cultivate bamboo in the southern states, but their experiments were not very successful. It still remains to determine whether bamboo can be grown in this country. If so, this would offer one solution of the problem of raw materials.

Cotton linter pulp has attracted much attention since the war. The great demand for cotton during the war period made it necessary that the cotton attached to the seed after the usual ginning process (about 200 lbs. to the ton of seed) be removed as far as possible. At the conclusion of the war the demand for this material dropped practically to zero, and successful efforts were made to convert this into pulp for paper. The manufacturers claim that this pulp may be used to advantage in place of old rags, and also in certain proportions in place of new rags. Because it is a new cotton fiber which has not been worked or processed, it gives somewhat greater bulk to paper for the same unit of weight. There is, naturally, still some question in the minds of certain paper manufacturers as to how far this pulp will be successful, but it is felt that it can be mixed with other pulps even if it cannot be used alone.

Papyrus has been proved as a paper-making material but the source of supply (Zululand and the Sudan, as well as other parts of Africa) would seem to make it unimportant as a raw material for American manufacturers.

Processes have been developed for utilizing the Jack pine, which will make available large tracts of this hitherto little-used species. Very interesting developments are reported along the line of the use of southern pine waste. Some of the claims of the promoters are questioned and only large-scale operations can settle the question.

Improvements in Processes

Rue has raised the question why a greater yield of pulp should not be obtained in the chemical processes. Fifty-five to 60 per cent of wood is true cellulose, yet less than 45 per cent of the wood is obtained as high-grade pulp; this represents a loss of about 25 per cent. The solution of the problem will necessitate a fundamental research into the various processes of pulping wood. The further need of economical utilization of other woods than spruce, hemlock, and balsam fir is also a pressing problem.

The Forest Products Laboratory has suggested that one solution of these problems may be obtained through a preliminary impregnation of the wood before digestion. The initial results indicate an appreciably shorter cooking time at lower temperatures. It is probable that the method will require a change in the usual acid composition to take care of the increased speed of the chemical reaction. The results will be increased yield, decreased screenings, and stronger pulp. Another innovation in digesting practice consists in fractional digestion, introduced by Aitken in the cooking of esparto. He proposes to remove members of the starch and pectose groups in the first treatment, using a 1.5 per cent sodium hydroxide solution, and then remove the ligneous material by a more drastic treatment with 14 per cent alkali. This method gives a cleaner and more easily washed stock, greater economy of bleach and reduction in costs of recovery. No mention has been made of comparative yields.

The process of rag boiling has been studied by Grimm. It is stated that the mechanical treatment to which the stock is subjected in the washer and in the hollander modifies the chemical constituents of the fibers very considerably. His conclusion is that the present proportion of chemicals and rags is correct. This is the first time the commercial practice has been checked by scientific studies in the laboratory.

The possibility of using decayed pulp wood has been studied by Bates and by Sutermeister. Bates concludes that infected wood may be used for sulfite pulp production if decay is limited to discoloration, and believes that chipper dust pulp might be satisfactorily blended with ordinary sulfite pulp and so utilized. Sutermeister has found that by using wood permeated with threads of dry rot but still quite hard and firm, the yield was considerably lower, the fiber weaker and practically unbleachable. Stained wood had little effect upon any quality other than that of bleaching. Bleach consumption in the case of stained pulp was about 15 per cent as compared with 10 per cent for an ordinary pulp.

Analytical Methods

Methods of control in the pulp mill continue to be a subject of investigation. Various analytical methods for sulfite liquors have been proposed and reviewed. While the analysis of the raw acid seems to be a comparatively simple one,

the analysis of the liquor produced during the digestion of the wood is complicated by the presence of the decomposition products from the ligneous portions of the wood, and the analysis of the sulfite waste liquor seems an almost hopeless task.

Another interesting field of research is in methods of differentiating the various pulps, sulfite, sulfate, soda, and mechanical. The whole procedure, from the preparation of standard samples of known pulps to the actual determination of the composition of unknown mixtures, is in need of standardization. Various stains have been proposed for this purpose but it seems a difficult matter to obtain a sufficiently marked differential staining of some of the pulps to enable even an approximately accurate determination. Lofton and Merritt have recently proposed the use of Malachite Green and Basic Fuchsin for determining the amounts of unbleached sulfite and sulfate pulps in a mixture of the two. The sulfate fibers are stained a blue or blue-green while the sulfite fibers assume a purple or pink color.

The need of standard methods is thoroughly recognized by the Technical Association of the Pulp and Paper Industry, which has a committee actively engaged in the preparation of a set of methods which it is hoped will prove so satisfactory that they will be adopted by the whole industry.

Beating

The most important questions in the beating of paper pulp are methods of accelerating the process, thereby decreasing the cost and methods for the control of the process. It is believed that a possible improvement in the manner of beating consists in the use of higher concentrations of stock moving through the beater at a higher rate of speed. This suggests that it is not the length of time which the stock is in contact with the water in the beater but the total distance that the stock travels that determines the degree of beating. The question of chemical hydration of pulp has been discussed by McKay. He claims that the process introduced by Meigs, Bassett and Slaughter will give an increase in strength of the finished sheet with no reduction in the paper-making qualities of the pulp, a decrease in beating time and a reduction in caustic, time of digestion, amount of bleach, and time required for bleaching with every grade of stock. One of the most interesting parts of McKay's contribution is the fact that he has introduced the copper number and viscosity as means of controlling the degree of beating. Much more work is necessary before it can be said that these methods will or will not answer the problem of control. It does seem to be certain that the so-called slowness test does not.

Bleaching

The bleaching of paper pulp, in the case of rags, may be readily carried out by the use of liquid chlorine. In this process no special equipment is necessary, for the liquid chlorine may be injected directly into the beater or washer where the bleaching is done. This avoids the handling of bleach drums and solutions and tends to cleanliness in the mill. The only danger is from the fumes of chlorine gas, and with properly designed control apparatus this should be very slight. The use of liquid chlorine is, it is believed, gradually displacing the electrolytic bleach in many paper mills. Because of the higher concentrations necessary, it is not possible to use liquid chlorine with chemical pulp as in the case of rags. It is first transformed into calcium hypochlorite solution, which solution is claimed to have quite different physical properties from that prepared from dry bleaching powder. Much of the success of this application depends upon the apparatus developed by the Wallace and Tiernan Company for controlling liquid chlorine. This makes possible the production of an absolutely uniform liquor. This liquor has a lower alkalinity than that prepared from bleaching powder which, under some conditions at least, is an advantage.

Wolff has proposed a new form of bleaching tub which permits the circulation of pulp concentrations of 10 to 15 per cent; naturally this gives a greater efficiency of operation. An important advantage is the saving of steam in bleaching at lower temperatures, while there is also less loss of fiber and cleaner pulp.

Wells has studied the bleaching of soda and sulfate pulps, prepared from coniferous woods, by the action of bleaching powder solutions. He finds that the alkali-solubility of the pulps increases with the strength of bleaching liquor employed and that considerable degradation of the cellulose takes place before the color is removed, indicating the unsatisfactory nature of this type of bleach. He obtains slightly more satisfactory results with regard to color removal by carrying out the bleach treatment in two stages with an intermediate washing. The pentosan contents of the pulps were found to be unaffected by bleaching, but on the other hand their methoxyl contents were reduced by the treatment.

Sizing

Little advance has been made in the study of sizing materials. The most important study is that of Blasweiler on the use of water glass (sodium silicate). He made a large number of tests with water glass alone and in combination with soaps, fats, animal size, starch, casein, etc. He draws the following conclusions, which may or may not be warranted: good suction on the paper machines; no sticking at the press rolls; rapid and complete setting of the suspended matter in backwater; greater strength and better rattle to the paper with a higher retention of clay or loadings; good color and dyeing results. Vail has also discussed, in various trade journals, the uses of water glass in the paper industry.

One of the interesting questions of the present day is the difference between gum and wood rosin in the sizing of paper, and especially in the color imparted by the latter. That there is a difference even the manufacturers of wood rosin admit. We have still to discover the reason and to remedy it, if possible.

Another question that is engaging the attention of some of the technical men of the industry is that of the real meaning of sizing quality of paper and a method of measuring it in terms of a definite, absolute unit. There are many tests for sizing quality. Recently the Valley Size Tester has appeared. This machine claims to give an accurate unit for sizing and to enable the manufacturer to keep his sizing constant during a run and from run to run. The test, however, is a relative one, and does not give us a fundamental unit for sizing quality. Such a unit is really necessary before a careful study of the factors influencing the sizing quality of paper can be made. The Paper Section of the Bureau of Standards is studying the general question of the testing of the sizing and it is hoped that they may be able to solve the problems involved.

Much interest has been aroused in the announcement of the Englishman, Kaye, that the application of rubber latex to paper-making appears to improve the texture and the strength of the paper so treated. The paper possesses the property of folding without serious permanent cracking along the line of fold. It is also claimed to be more water-repellent than paper not treated with rubber. Many other claims are made, based in part on commercial tests. If these results are substantiated by other mills, it would seem that this was an important contribution to the industry.

The Flintkote Company has reported a process for the emulsification of asphalt by means of a highly colloidal clay, so that it may be introduced into the paper-making process

in the beaters or at the paper machine. By the use of this agent it is possible to produce either waterproof or moisture-proof boards of various stiffness or pliability. The results with this method give a higher degree of resistance to water than results when raw paper or felt is saturated in a bath of hot asphalt, in accordance with the usual practice obtaining in a saturating plant.

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This brief review indicates that the pulp and paper industry is not without its own problems. Many others purely mechanical and having no place here, also confront it. The depression of the past two years has made progress in the solution of these problems almost impossible. It is anticipated, however, that the coming years will see the proper recognition of the place of the technical man in the industry and that many changes, some of them almost revolutionary in character, will be made, which will increase the efficiency of the various processes, conserve our raw materials, and give us an improved product. Not the least of these advances, we hope, will be the adoption of the standardization program now being developed through the coöperation of the manufacturers of paper with the Paper Section of the Bureau of Standards.

Hardwood Distillation

By Harry C. Merriam

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THE HARDWOOD distillation industry is carried on in the United States by 80 different concerns, operating 93 plants, with a total daily capacity of 5530 cords, 600 of which are in by-product recovery kilns and 4930 cords in ovens and retorts.

During the last ten years great progress has been made in the methods employed in the wood distillation industry, and it is the object of this paper to touch upon the most important.

Ovens have practically replaced smaller retort types and the tendency of the modern plant is toward large units. The largest oven plant operates twenty-two 10-cord ovens, with a total capacity of 220 cords, which can be increased to practically 294 cords per day on a carbonization period of 18 hours.

H. C. Merriam

The larger plants are used in conjunction with charcoal pig-iron blast furnaces and it is on this account that such large units are desirable. Most of these plants are situated in Michigan, although during the war four were built in the south.

The obtaining of sufficient quantities of cord wood has always been one of the vital problems of the wood distillation plant. During the recent war, with the scarcity of labor, this factor was very pronounced, and made most manufacturers abandon the cutting of cord wood in the woods and ship the logs direct to the plant, where they were handled in a sawmill. Some of the original sawmills were cumbersome and costly, but modifications and improvements have been carried out so that to-day the wood mill of a modern wood distillation plant will supply at reasonable cost wood suitable for distillation purposes. It has, moreover, been found fairly easy to procure log-wood cutters when previously cord-wood cutters could not be obtained.

The green logs are brought directly to the wood distillation plant, put through the wood mill, cut into approximately 49-in. lengths, and split with band or circular saws to the required size. These pieces, of the same general character as ordinary cord wood, are then passed through block mills and cut to 12-in. lengths. At this point any cord wood available is introduced and also cut to blocks. These blocks, freed of sawdust, are elevated to bins and from there dumped by gravity into the retort cars, the sides of which are carried to the top. The cars are then run into the predriers, which are of ordinary tunnel construction, either of reinforced concrete or brick, through which the waste stack gases from the ovens are circulated countercurrent to the wood and in direct contact with it. The driers vary in size, allowing from one to three carbonizing periods for drying. The two-period drying is now considered good practice.

Savings effected by this system include: decreased labor due to the mechanical handling of the wood; interest on the investment in cord wood in the drying yards; insurance, taxes, etc.; decrease in fuel consumption, with the advantage of uniformity in the character of wood entering the ovens under all weather conditions; an increase in the output of the plant by shortening the carbonization period; and the elimination of brands from the charcoal.

The application of strict temperature control to the ovens has been recognized as of great importance, and the installation of recording pyrometers for accurate control has resulted. This control not only stabilizes the yields of by-products and increases them in many plants, but prevents the overheating of the ovens, thereby eliminating in large measure the replacement of burned bottoms and costly repairs to the oven settings. It also assures the turning of the ovens in the proper cycle of time, this being a most important factor where the charcoal is used directly in a blast furnace requiring a constant supply.

The importance of large scrubbers for the efficient scrubbing of the retort and kiln gases previous to burning of the same has finally been recognized, and scrubbers of adequate size are now a standard installation in many plants.

In retort practice it has been found that approximately 1 gal. of 82 per cent of alcohol per cord of wood can be recovered, and in the case of kilns where a much larger volume of gas has to be handled, due to air leakage, etc., around the kiln, an increase in yield of from 2 to 3 gal. per cord has been reported. In fact, one kiln plant by efficient scrubbing has

obtained an alcohol yield very close to that of the ordinary oven plant.

The distillation of hardwood chips, sawdust, etc., has occasioned considerable research work to develop a successful commercial process. The difficulties encountered, such as in the drying of this waste, because of its own insulating qualities, the control during exothermic reaction, charcoal dust during decomposition, the stabilizing of the fine charcoal so that it will not ignite spontaneously, and the final briquetting of the charcoal, have all been trying problems.

A number of patents have been taken out in conjunction with this work. Three plants have been built on a commercial scale carrying out the various ideas, but only one of these plants, using the Stafford process, has proved a success.

The principle of this process makes use of the hitherto known, but not commercially utilized, heat of exothermic reaction of cellulose when at the carbonizing temperature. By predrying and preheating the material, and introducing it into a retort in which material already undergoing carbonization is present, the exothermic heat is sufficient under properly maintained conditions to bring the additional material up to the carbonizing point, when this material in turn will be carbonized and liberate heat, which will serve to bring further material to the carbonizing temperature. The Stafford process requires no heating of the retort; in fact, the retort is thoroughly lagged to prevent escape of heat. The material is previously dried in contact with the air, and is introduced continuously into the retort from which the charcoal is also continuously removed.

The continuous distillation of hardwood waste produces the same yields in methanol and charcoal and about 50 per cent more in acetic acid than the yields from ovens utilizing cord wood of similar species.

The drying of the wood to a 1 per cent or 2 per cent moisture content is carried out in large rotary driers in direct contact with the hot flue gases, and efficient drying of the wood is thus accomplished. The pyroligneous acid obtained from this dried wood is therefore in a concentrated form and subsequent treatment in the stillhouse is accomplished with a minimum of evaporation and distillation.

The advantages of the mechanical handling of all products, low fuel consumption, large capacity for small units operated continuously, higher yields, etc., make it possible to even hog cord wood and handle in a commercially successful manner. All these advantages point toward the development of this process and a gradual substitution for present practice.

Stillhouse operations have undergone many changes, and to-day the continuous treatment of the pyroligneous acid and other liquors is universally employed in the more modern plants, as against the discontinuous method in the smaller and older type plants.

The use of multiple-effect evaporators has proved a great economy factor. Early designs of multiple-effect evaporators did not take into consideration the fact that when pyroligneous acid is distilled under multiple-effect conditions the vapor on condensing deposits carbon on the surface of the tubes of the next effect, cutting down materially the transmission of heat and necessitating the dismantling of the tube bundles for the removal of the carbon. This fouling of the surface varies with different woods and is more pronounced in the case of southern hardwoods.

The use of triple effects in the evaporation of acetate of lime is a success and gives no particular operating difficulties. It is the consensus of opinion among operators who have used triple effects that double-effect economy in a combination evaporator is all that is desirable in this industry, because of the operating difficulties before mentioned. In the latest designs the pyroligneous acid is evaporated in one effect and the acetate of lime in the other. With proper design this combination gives accessibility to the tube surfaces and permits of the easy removal of the carbon coating without dismantling. Such a double effect gives an easily controlled unit for continuous operation.

In the production of acetate of lime the conversion of the concentrated acetate liquor from the evaporators to the mush state by means of steam-heated rotating rolls, and the final drying of the acetate on screen belt driers traveling in hot waste flue gases, have solved the question of low-cost production of acetate in modern plants and eliminated the troublesome labor problem so often encountered in acetate drying. The elimination of the old acetate pans, which are notorious steam eaters, has been a welcome change.

A recent innovation utilizes the acid vapors from the primary stills as a source of heat in the second effect, operating under a vacuum for the evaporation of acetate of lime liquor, the primary stills being operated under atmospheric conditions and the vapors condensed in separate tube chambers in the second effect. This keeps the distillate from each primary still separate and a visual control of each still is possible. This scheme will undoubtedly result in a considerable saving in steam, and, if adopted by old plants having primary stills, will give double-effect economy.

The application of continuous stills for the production of high-grade crude methanol of around 92 to 95 per cent (Tralles) direct from the neutralized liquor has become the standard practice. Where there is an excess of exhaust steam available, kettles have been eliminated, the steam being introduced directly into the base of the continuous still. This has considerably simplified the apparatus.

The grade of crude alcohol produced in a plant of this type is not to be confused with the crude 82 per cent produced in old plants using older methods.

The use of low pressure steam in the stillhouse has been so perfected that two plants are now operating all of their apparatus, both evaporating and distilling, on 5-lb. pressure exhaust steam.

The successful production of glacial acetic acid from carbide has been a serious blow to the wood distiller, and in his search for some way to meet this menace the production of glacial acetic acid direct from pyroligneous acid has been attempted. It is the writer's understanding that this has been successfully demonstrated on a semicommercial scale. This being so, it will give the distiller a new lease of life by again making his acetic acid a source of income, whereas at present it is a problem to dispose of it, at a profit.

In the past the refining of crude 82 per cent methanol has been carried out in central refineries, because of the difficulties encountered and the type of apparatus necessary. With the advent of the modern four-column continuous refining still, conditions have changed and the crude alcohol producer is enabled to instal his own refining unit and manufacture direct the highest grade of refined methanol. The increasing demand for pure methanol in the dye industry, and particularly in the manufacture of formaldehyde, has caused this type of apparatus to come into its own. Chemical treatment was necessary under the old system to separate the alcohol from last traces of methyl acetone, but with the new type of continuous still this is done by fractionation in the distillation process and pure methanol with a Messinger test of less than $^1/_{20}$ of 1 per cent acetone is produced direct from the crude 82 per cent. There is, too, a simultaneous production of high-grade methyl acetone, together with a small amount of oils and allyl alcohol. The production of pure methanol has enabled many of the smaller plants to instal their own formaldehyde apparatus and by this means place their alcohol on the market converted to its highest value.

The manufacturers of crude alcohol had heretofore only one outlet for their alcohol, namely, the sale of the crude to the refiner. With the modern refinery, he has his choice of a number of markets. In the modern refinery, with its steam regulators, extension stem-recording thermometers, recording pressure gages, and other accessory equipment, one operator can care for a number of stills with more perfect control than was ever possible under the old hand-controlled systems. Furthermore, strict chemical control is possible at all times, and such control is essential because of the chemical specifications that have replaced the old tests, such as odor, color, specific gravity, etc.

The production of pure acetone by the destructive distillation of acetate of lime was worked up to a high degree of efficiency during the war, because of the enormous demand for this product in the manufacture of cordite for the British government, and once again the continuous distillation of the crude acetone into the finished product showed the efficiency and low cost of this method of refining.

In order to meet the recent more stringent requirements for various grades of acetone oils, vacuum distillation has been employed, making possible closer cuts through the use of fractionating columns, with the resultant saving in steam.

The distillation of creosote oils and wood tars has been stimulated by the great demand for these oils in the flotation industry, and this demand will undoubtedly increase as the flotation process grows in favor. There seems to be a preference for hardwood oils on the part of flotation engineers.

The future of many wood distillers, following the decline in prices of by-products, is problematical, and undoubtedly only those plants equipped for low-cost operation will survive. The smaller plants of, say, under 50 cords daily capacity, will be handicapped when compared with the larger plants and these smaller plants may find it necessary to consolidate to carry on.

The Ferro-Alloy Industry

By B. D. Saklatwalla

General Superintendent, Vanadium Corporation of America, Bridgeville, Pa.

THE FERRO-ALLOY industry has come to the front within the last few years, its importance being recognized during the strenuous times of the World War. Advancement in steel metallurgy has been probably the greatest factor toward the rapid strides of our civilization within the last decade or two, and when we scan the field of improvements in the mechanical, electrical, and transportation industries for the purposes of peace or war, we cannot help but feel that all such strides have been due to the developments of newer and better types of steel, produced by the metallurgist of the present day. While this fact is obviously apparent, it is not generally recognized that these developments have been dependent on the ferro-alloy industry.

Trinity Court Studios
B. D. Saklatwalla

The function of ferro-alloys in the manufacture of steel has been twofold. Certain alloys have been used for the purpose of deoxidizing and cleansing, whereas others have been used to impart to the steel certain necessary and desirable physical properties, the alloying element forming an integral constituent of the steel.

The most commonly used ferro-alloys, ferro-silicon and ferro-manganese, function as deoxidizers in the ordinary course of steel-making. They play a double role, however, in the case of high silicon and high manganese steels, where these elements are allowed to remain in the steel in appreciable percentages, in order to obtain certain requisite properties. The electric furnace has practically replaced the blast furnace or the crucible method of production. There also appears to be a tendency to develop mixtures of silicon and manganese in the same alloy, whereby several advantages have been claimed. Several compositions of these two elements, together with aluminium and titanium, have been recommended for the purpose of deoxidation. The use of such deoxidizers appears to have gained favor in continental Europe, but does not seem to have been taken up in American practice.

As a less commonly used deoxidizer may be mentioned ferro-titanium. This alloy is manufactured in the electric furnace and also by the alumino-thermic process, according as a carbon-containing or a carbon-free alloy is desired. As to the superiority of the one or the other grade there is yet considerable controversy between the different users and makers.

The main metallurgical developments in the manufacture of ferro-alloys within the last couple of years have been in connection with those alloys that form true alloy steels and persist as a constituent of the finished metal. Among such alloys may be mentioned: ferro-chrome, ferro-tungsten, ferro-vanadium, and ferro-molybdenum. The greatest and most recent phase in the development of these alloys is the application of the electric furnace to their production, and the working out of the chemical reactions in the electric furnace, whereby an alloy of suitable purity and carbon content can be directly manufactured from the natural raw ores.

At the beginning of the ferro-alloy industry, the electric furnace was in its infancy, and consequently the field was largely usurped by the alumino-thermic process of reduction. This process has the advantage of convenience and simple equipment, but necessitates the use of more or less pure oxides for reduction, which have to be chemically prepared by an intermediate operation. Such an operation is costly and wasteful, and the aluminium required for reduction is a big item of expense. Recently, however, these deficiencies have been overcome by a very marked development in the art of alumino-thermic reduction. The preparation of pure oxides has been rendered superfluous. Owing to a systematic study of the chemical and thermal nature of the reactions, it has been possible to reduce a complex ore by means of aluminium in conjunction with suitable fluxes, whereby the desired metal or metals are carried into the

regulus and the undesirable constituents into the slag. This is accomplished by taking into consideration not only the necessary chemical factors, but also the physical ones, as size of the granules and rate of feeding of the mixture. These factors are technically important when we consider that we are dependent only on the chemical reaction of the mixture for the necessary temperature to obtain a fluid slag and a molten metal, and have no means whatever to control this temperature from any other source. Another marked improvement in the practice of alumino-thermic reduction is the fact that this operation is carried out on a very extensive scale, as a continuous one, in a shaft furnace, tapping the slag and metal at regular intervals. This continuity of operation has not only enlarged the quantity from a few pounds produced in small crucibles to several tons per day out of each shaft furnace, but has helped to produce higher temperatures, owing to large quantities reacting exothermically and storing the heat energy developed in the walls of the furnace, and thus promoting slagging reactions for the undesirable constituents, which was not possible in the small crucibles. This alumino-thermic development has been largely in connection with the production of ferro-vanadium.

The recent developments in the electric furnace for the production of ferro-alloys have been very marked. In the case of ferro-vanadium, for instance, in spite of the great strides of alumino-thermic reduction, the field is now practically dominated by the electric method. The most marked improvements in electric furnace operation have been in the development of a control mechanism, whereby the energy input is held constant by using a true watt regulator. Much higher temperatures have been produced by the use of higher current density, high voltage, and very close electrode spacing. The open-top furnaces have been replaced in several instances by furnaces with closed tops, water-cooled in some cases to conserve the heat energy. The advent of the electric furnace in the ferro-alloy industry has made many low-grade ores available for reduction at a reasonable cost, and thus has not only played a great part as an economic factor in lowering the prices of several ferro-alloys, but also made discarded mineral deposits usefully available, thus increasing our natural resources.

Another direction, in connection with the electric furnace, in which rapid progress has been made, is the refining of ferro-alloys containing undue percentages of carbon and silicon. Activity in this field has been mainly in connection with ferro-chromium. With the development of the so-called "stainless" steels there suddenly appeared a demand for a ferro-chromium very low in carbon content. The amount of chromium present in such steels is high, approximately 12 to 14 per cent, and consequently any appreciable carbon content of the ferro-alloy would cause an undue rise in the carbon of the finished steel. Several patents for refining carbon containing ferro-chromium have been recently granted, and special publicity has been given to some claiming to remove the carbon by bessemerizing the molten alloy with an oxidizing gas. Several processes have also been suggested for oxidizing the carbon content by means of iron ore or chrome ore together with fluxes.

The development of high-chromium, low-carbon steels has also led to processes for introducing the chromium without the necessity of first manufacturing a ferro-chrome. In such processes, the reducing agent, either metallic or nonmetallic, is placed in the bath of molten steel, together with the raw chrome ore, with suitable fluxes, the reduction of the chromium taking place in the molten bath of steel. In this way the reducing agents present in the bath, such as carbon or silicon, are eliminated by oxidation, and the chromium reduced during this reaction enters the steel. This process has the advantage of not introducing carbon with the chromium, and so produces a more homogeneous steel free from segregation, as the chromium reduction takes place uniformly over the entire bath and is absorbed in the nascent state of formation by the steel.

In the ferro-tungsten industry there have been no radically new developments, probably owing to the lack of demand and demoralized condition of the tungsten market.

Another alloy that has gained prominence commercially is ferro-phosphorus. In its manufacture the electric furnace is supplanting the blast-furnace method. Its principal use is to raise the phosphorus content of sheet bars in order to diminish the loss involved in stripping or tearing apart plates or sheets.

Of less importance are the alloys ferro-boron, ferro-zirconium, and ferro-cerium. Ferro-cerium has been used as a pyrophoric alloy and also as a deoxidizer in steel.

In conclusion, it may be mentioned that the United States can claim the furthest advances in the metallurgy of ferro-alloys within the last few years, and to be the largest producer in the world of a commodity on which the progress of our steel metallurgy is so vitally dependent.

Publicity for Chemistry

During the past year the *Yale Alumni Weekly* devoted an issue to chemistry. It was well planned and served to emphasize the part which Yale intends to play in chemistry in the future. Other educational institutions might do well to follow this example.

In *Current Affairs* the Boston Chamber of Commerce has placed before its members an article on the organization of the chemical and dyestuff industry in New England. This cannot fail to bring home to New England manufacturers a realization that the industry is worth keeping and deserves all possible encouragement.

In addition to sending our articles on chemical subjects to papers in nearby towns and cities, the Publicity Committee of the Rochester Section obtained during the last year the equivalent of seventy columns of space in local papers. By assigning each of the local papers to a member of the committee a great deal has been accomplished, and the experience of the committee goes to show that publicity can be obtained for the activities of chemists as an organization and for the accomplishments of individual members, if the material is presented in good form and care is taken to place it in proper hands.

The Michigan Agricultural College Section was the guest at a banquet of the Kiwanis Club in Lansing. The chemists were responsible for the principal addresses, and two hundred and fifty business men were brought into close contact with a large number of chemists. This appeals to us as a good precedent. Such a gathering does more to bring about an *entente cordiale* between chemists and business men than could be accomplished by any number of meetings where one chemist addresses a group of business men or a business man addresses a group of chemists.

Chemical Equipment Manufacturers Petition Congress

Eighty-nine firms, whose names will appear in our next issue and whose business is specifically that of supplying equipment necessary to the American chemical manufacturer and industry, believing that they are in position to have an intimate knowledge of the needs of the chemical industry, have sent the following petition to Congress:

1—That the Chemical Manufacturer requires an endless variety and enormous volume of special equipment, the production of which in this country has progressed in step with the developing needs of the Chemical Manufacturer;

2—That the Chemical Equipment Industry before the War was very small as compared with to-day;

3—That this equipment field represents millions of capital and thousands of employees, both now unemployed to a great extent and, in our judgment, certain to remain so unemployed unless the American chemical industry is properly safeguarded and maintained in a flourishing condition.

4—Therefore, we respectfully urge that you not only support personally all just provisions for the welfare of our Chemical and coördinate fields, but that you use your good judgment and effort in bringing your colleagues to do likewise, by voting for the Amendment extending the Dye and Chemical Control Act, in accordance with the report and vote of the Finance Committee.

Recent Progress in Magnesium Alloys

By John A. Gann

Dow Chemical Co., Midland, Michigan

MAGNESIUM alloys are now being widely advertised under trade names such as Dowmetal, Magna Metal, M. W. Metal, and Elektronmetal, the last named being a product of the Chemische Fabrik Griesheim-Elektron. All of these alloys are characterized by their high magnesium content, which exceeds 80 per cent and may run as high as 100 per cent. The term "Dowmetal" is a generic one covering an entire series of magnesium alloys, as made by The Dow Chemical Company. Their chemical composition and physical properties vary according to the use for which the alloy is intended. "Elektronmetal" is likewise a generic term. Magna Metal has the same composition as the German Elektron casting alloy. The writer knows very little concerning M. W. Metal beyond the fact that the literature distributed by the M. W. Metal Company is a direct translation of parts of the German Elektron catalog. The commercial production of Elektronmetal dates back to 1912, Dowmetal to 1918, while Magna Metal and M. W. Metal have not yet reached the commercial stage. The Magnesium Corporation of America at Niagara Falls, however, is producing extruded magnesium alloy parts on a quantity production basis.

The published literature relative to magnesium and its alloys is somewhat meager on account of the comparative newness of the subject and the necessity for secrecy on the part of the investigator and manufacturer during the development period and until after they are fully protected. The most recent work on the constitutional diagrams of magnesium alloys is that of Hanson and Gayler[1] which deals with the magnesium-aluminium series. These investigations are quite complete, and confirm in general the earlier finding of Grube. The main difference likely to be of any practical importance is that magnesium is capable of holding about 10 per cent of aluminium in solid solution as contrasted with 6 per cent previously given. The magnesium-rich part of this series has been discussed more in detail by Gann.[2] The relationship between chemical composition, physical properties, microstructure, and equilibrium diagram of these alloys is here shown and some of their industrial applications briefly indicated. Elektronmetal[3] has been described at various times, some of its physical properties given and commercial uses discussed. The most complete report, however, is given in the Elektron catalog, which includes methods of melting, casting, and coloring four of the alloys they are now producing.

The physical properties of magnesium alloys necessarily vary with the chemical composition and method of treatment. Pure cast magnesium, for example, has a tensile strength of only 14,000 to 15,000 lbs. per sq. in. The addition of 6 per cent aluminium practically doubles this value, that is, it increases the tensile strength to 28,000 lbs. per sq. in., while it increases the specific gravity only 2 to 3 per cent.

Heat treatment of these alloys results in up to 25 per cent increase in tensile strength, while mechanical working may increase the strength 50 to 100 per cent.

The general characteristics of standard products of the different manufacturers are given in Table I, the figures being taken from published scientific literature or, where necessary, from advertising material. Corresponding values of No. 12 aluminium casting alloy and gray cast iron are given for comparison.

Table I—Comparative Physical Properties of Cast Alloys

Properties	Dowmetal No. 1630	Dowmetal No. 217	Elektron Zl	Magna Metal	Aluminium Alloy No. 12	Gray Cast Iron
Tensile strength lb./sq. in.	22,000	28,000	19,000	19,300	20,000	30,000
Yield point lb./sq. in.	14,000	11,000	13,000	6,500	13,000	Indeterminate
Specific tenacity	12,000	16,000	10,400	11,000	7,000	4,200
Per cent elongation (2 in.)	2.0	6.0	2.0	8.5	2.0	Negligible
Brinell hardness	58	50	48	..	70	125
Scleroscope hardness	28	24	13	..	15	30

Table II—Physical Properties of Dowmetal Alloys

	Dowmetal No. 220	Dowmetal No. 1045	Dowmetal No. 1630	Aluminium[1] Alloy No. 12
Tensile strength lb./sq. in.	22,000	22,000	22,000	20,000
Yield point lb./sq. in.	14,000	14,000	14,000	13,000
Per cent elongation (2 in.)	2.0	2.0	2.0	2.0
Brinell hardness	58	58	58	75
Scleroscope hardness	28	28	28	15
Single blow impact[2]	26	32	40	26
Impact fatigue blows[3]	1,300	2,800	3,200	200
Maximum fiber stress, lb./sq. in.[4]				
200,000 reversals	6,000	8,900	11,000	
40,000,000 reversals		8,050	9,800	

[1] Sand cast in our own foundry.
[2] Dow machine.
[3] Eden-Foster machine.
[4] Farmer alternating stress machine.

Probably the most recent advance in magnesium alloys is the production of new Dowmetal piston alloys, in which the toughness and fatigue endurance have been very materially increased without any sacrifice whatsoever in other desirable properties. An exhaustive study of this subject is now in progress, and although this program is still in the elementary stages the results are of interest (see Table II). Our results on No. 12 aluminium alloy are again given for comparison.

Within the last two months a new alloy especially designed for use in high-speed motors and in racing cars has been developed. This alloy has a thermal conductivity nearly 70 per cent higher than the usual magnesium-rich alloy, thereby insuring a cooler running motor, while the toughness and impact fatigue endurance are fully as high as that of the alloys listed in Table II. The excellent results obtained in actual service from these various Dowmetal pistons indicate great possibilities in the future development and use of magnesium alloys.

[1] *J. Inst. Metals*, **23** (1920), 201.
[2] *Trans. Am. Soc. Steel Treating*, April 1922.
[3] Adolph Bergman, *Metal Ind.*, **20**(1922), 1; Felix Thomas, *Stahl u. Eisen*, **40** (1920), 290; *Selve Z. Metallkunde*, **13** (1921), 474; *Ibid.*, **316** (1921).

The Second Annual Report of the Scientific and Industrial Research Council of Alberta, covering work done during the year 1921, has just been printed. The greater part of the work was done in relation to various types of fuels, although considerable attention was given to road materials, forest products, and a geological reconnaissance in Alberta.

Nonferrous Alloy Progress in 1921

By H. W. Gillett

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THE YEAR 1921 was one of business depression in which the nonferrous metal industry was hard hit. Prices of nonferrous metals were low, and production and consumption were at a minimum. Such conditions do not make for rapid commercial progress. In the general retrenchment, research laboratories in this field had to let many workers go, so that the scientific output fell off somewhat in quantity, though not in quality.

Light Aluminium Alloys

The light aluminium alloys received much attention. Cast alloys of the general type of 85 Al: 15 Si began to be tried out commercially, one automobile firm trying out one hundred crank-cases for an 8-cylinder car, and smaller castings of this alloy being used by various firms. This alloy bids fair to rival and perhaps to supplant the long-established No. 12 alloy of 92 Al: 8 Cu, as it has a lower specific gravity, a higher tensile strength, and a decidedly greater ductility. In the foundry it appears to behave as well as No. 12, though it requires some variation of foundry practice. If service tests bear out the improved physical properties shown by laboratory tests, we may expect quantity production and use of the new alloy to follow slowly.

In that case, the interesting problem will arise of the direct production of Al-Si alloys from lower grade ores, possibly from clay. At least some simplification of the process of purification of bauxite might become possible, perhaps resulting in a lowering of the cost of production of this alloy and its more extended use. Wrought alloys of the Duralumin type (*e. g.*, 96.5 Al, 3 Cu, 0.5 Mg) have been the subject of a good deal of work which has been timely because of the tragedy of the ZR2, which was ascribed to failure of Duralumin. Merica and his co-workers at the Bureau of Standards published several papers dealing with Duralumin.

Jeffries and Archer, in an epoch-making discussion of the theory of hardening by slip-interference, considered the mechanism of the hardening of Duralumin as previously suggested in less detail by Merica, tied it in with the mechanism of the hardening of steel, and gave the metallurgical world a well-rounded theory, which, in conjunction with X-ray crystal analysis, gives us a basis for a more plausible answer to the riddle of "What is martensite in steel?" than we have had before, as well as showing the basic requirements that the equilibrium diagram of any alloy must meet in order that the alloy may respond to heat treatment.

Merica and Jeffries and Archer ascribed the hardening of Duralumin to the precipitation of the compound $CuAl_2$. British investigators at the National Physical Laboratory, however, produce strong evidence that the hardening agent is another compound, Mg_2Si. It appears that both compounds play a role but that of the Mg_2Si is predominant. If this is true, the discovery and development of Duralumin has been due to the fact that the commercial aluminium has in the past contained as an impurity the 0.25 to 0.35 per cent Si that is required to form Mg_2Si in sufficient quantity to give a properly hardening Duralumin. The Aluminum Company of America has recently produced small amounts of aluminium of extreme purity and is working on the question of the hardening agents in Duralumin and of the effect of silicon. The purity of the aluminium available will allow them to carry the study to lower silicon contents than has hitherto been possible.

The National Physical Laboratory of England has brought out a modified Duralumin which they designate as "Y" alloy, which contains a little more Cu than the usual Duralumin and 2 per cent Ni also, the aluminium content being correspondingly decreased. This alloy is claimed to be the equal of Duralumin on all usual tests and to surpass it in resistance to repeated stress at 150° C. It is described in detail in the Eleventh Report of the (British) Alloys Research Committee, which covers also a good deal of work on ternary aluminium alloys of the type containing about 3 per cent Cu and 20 to 25 per cent Zn, with or without a little Mg and Mn in the wrong condition. These alloys, in castings, give the highest ratio of tensile strength to density of known cast aluminium alloys.

Rolling these alloys was a task requiring much patience but with suitable precautions it can be done, and material of 90,000 lbs. tensile strength per sq. in. can be produced. Another British investigation of interest was that of Carpenter and Elam on "Recrystallization of Aluminium Sheet."

Besides the work of Jeffries and Archer on the theory of hardening, they have discussed the question of grain size (a problem that has also received attention from a number of British investigators). Other contributions from the research staff of the Aluminum Company of America have dealt with the density of molten aluminium and Al-Cu alloys at various temperatures, and with the heat treatment of castings.

Anderson, of the Bureau of Mines, has continued his work on practical problems relating to the preparation of aluminium alloys, dealing with cracking of castings in the foundry-gas atmospheres in aluminium-melting furnaces, iron-pot furnace practice, etc.

The use of aluminium alloy pistons in automobile engines appears to be progressing slowly. Some cars that previously used them have gone back to cast iron, while other cars have started to use them. As a result of improved design, recent aluminium pistons appear to be giving better results than earlier ones. Magnesium alloy pistons are being tried out, but the situation on Dowmetal, electron alloy, and similar alloys of a magnesium base seems to be one of general interest but little actual use as yet.

Heavy Aluminium Alloys

Of heavy alloys into which aluminium enters, aluminium bronze is the most important. Blue discussed the heat treatment of this alloy and pointed out that he had found the alloy unreliable because of the uncertainty of getting the same results twice and the difficulty in commercial production of getting the physical properties claimed for it on the basis of laboratory tests. This drew emphatic replies from producers of the alloy, but Blue countered by showing that his arguments were based on tests of alloys produced and heat-treated by his critics themselves. A translation from the French of Grard's book on aluminium and its alloys has been published, which deals with the heat treatment of aluminium

bronze, as well as exhaustively discussing aluminium and its light alloys.

Brass and Bronze

Some attention has been paid, especially by French workers, to heat treatment of brasses and bronzes.

The research department of the Woolwich (England) Arsenal has published in the *Journal of the British Institute of Metals* three important papers, one by Genders on "The Extrusion Defect," which, with its discussion, covers many interesting points of the general subject of extrusion of metals, and one by the same author on "Casting Brass Ingots." The other, by Moore and co-workers on "Season Cracking of Brass," is extensive and has aroused much comment.

Corrosion of brass and Muntz metal has been dealt with by Rawdon of the Bureau of Standards. British investigators continued work on corrosion of condenser tubes. Another British investigation of scientific interest is that of Haughton on the copper-tin equilibrium diagram.

The American Brass Company has given a very fine paper on "Grain Growth in Alpha Brass." This firm has also made noteworthy application of spectroscopic analysis to routine laboratory work. The Scovill Manufacturing Company presented in This Journal a method for electrolytic determination of very small amounts of lead.

The General Electric Company put out its new bearing metal, "Genelite," made by mixing oxides of copper, tin, etc., with an excess of graphite, reducing and compressing, giving an alloy carrying graphite mixed all through the material and hence having self-lubricating properties. The material is probably not applicable to a very wide field, but will fit in well for some uses.

The Anaconda Copper Mining Company, producers of copper and zinc, has taken over the American Brass Company, the largest producer of brass.

The competition of aluminium and nickel alloys, more recently rolled and extruded zinc, and still more recently of the new stainless iron (low carbon steel with around 15 per cent chromium) has threatened to cut into the fields heretofore served primarily by copper, brass, and bronze. The producers of copper and its alloys have therefore formed the Copper and Brass Research Association, whose function is to combat this encroachment and to develop new fields for the copper alloys. The organization does not cover the field that its name implies to a chemist or metallurgist, as it deals so far only with commercial research," *i. e.*, propaganda and advertising (on a sane and reasonable basis), and not with chemical, physical, and metallurgical research. The field proposed by the National Research Council, which was to be covered by the Alloys Research Association but which materialized only in a limited information service on alloys, is still unfilled. The British Nonferrous Metals Research Association, with headquarters in Birmingham, appears to be getting a good start.

Notwithstanding the depression of 1921, the various brass rolling mills which had previously laid down plans for extensive installations of electric furnaces, went ahead with the installations, which is pretty good proof that electric brass melting is expected to continue to show lower melting costs than fuel-fired furnaces in the more normal times ahead, as well as under the conditions during and just after the war. Electric melting of brass and bronze has had a very rapid growth. There are to-day more electric brass furnaces installed in the United States than electric steel furnaces. While the average electric brass furnace is smaller than the average electric steel furnace, the percentage of electrically melted brass, in comparison with the total annual output, is greater than that of electrically melted steel.

Nickel

Pure nickel and such alloys as Monel metal continue to find increasing application. Madsen has described before the American Electrochemical Society notable advances in the production of ductile electrolytic nickel, and Merica, of the International Nickel Company, has published a collection of data on the properties of nickel and its alloys.

Guillet, the French metallurgist, has discussed in *Chemical and Metallurgical Engineering* the replacing powers of various elements for zinc in brass. An alloy of about 46 Cu: 10 Ni: 44 Zn is of particular promise.

Foundrymen in this country were forced to use up a good deal of cupro nickel, shell-band scrap containing a little nickel, in recent years, and much of this went into alloys as if it were pure copper, giving alloys with small amounts of nickel. The generally satisfactory results have raised the question whether intentional additions of nickel may not be quite generally useful in copper alloys, since it forms a solid solution with copper that is stronger than copper, just as it forms a solid solution with iron and strengthens the ferrite, so that one may increase the strength of almost any steel by addition of suitable amounts of nickel.

The producers of nickel are naturally interested in this, and developments on this line may be looked for in the future.

Cobalt

One interesting development in connection with the cobalt-chromium cutting alloy, stellite, is that the producers are making commercial inspection of stellite tools by the X-rays, to detect blowholes and other defects in the cast tools. The application of X-ray examination to metals is being carried farther than in the past and still further improvements are expected to be attained in the near future.

Zinc

Marked advances have been made in the application of rolled and extruded zinc to industrial use. Its cheapness and resistance to atmospheric corrosion make it useful for a multitude of uses. A paper by Mathewson of Yale and co-workers of the New Jersey Zinc Company in the *Transactions of the American Institute of Mining and Metallurgical Engineers* gives great detail on the properties and applicability of the material. One by Ingall in the *Transactions of the British Institute of Metals* on "Mechanical Properties and Microstructure of Rolled Zinc" supplements the American paper.

General

Steady progress is being made in fields that touch the interests of the chemist and metallurgist working on nonferrous alloys. Refinements and more speedy methods in chemical analysis, improvements in methods of physical testing, more knowledge of endurance testing, advances in metallography, etching practice, and photomicroscopy apply to the nonferrous as well as to the ferrous field.

Theoretical problems in atomic and crystal structure and arrangement, the study of space lattices by the X-ray spectrometer, grain growth and recrystallization, the study of colloids and the application of colloid chemistry to metals and alloys bear on both ferrous and nonferrous alloys, and to discuss them here would take us outside the scope of this review.

It is interesting to note that some of the advocates of the "amorphous cement" theory appear to be modifying their views somewhat, especially in regard to cast metals, and opposition to the theory is beginning to be expressed as vigorously as is its propagation and defense. This will incite the collection of more experimental facts and more rig-

orous examination of the explanations for them, so that ultimately we shall know a good deal more of the truth.

Meanwhile, the arguments pro and con will continue to make the discussions of metallurgical papers lively.

Conclusion

The above represents the personal "reaction" of the reviewer on the more important features of nonferrous alloy progress in 1921. Another reviewer might pass over most of these and cite many other developments, commercial and scientific. The interested reader will find the detailed nonferrous history of 1921 in the following (rated in classes according to usefulness to the writer).

Class 1—*Transactions of the American Institute of Mining and Metallurgical Engineers, Journal of the Institute of Metals* (abstracts valuable as well as papers. Most of the abstracts available in *Chemical Abstracts* but more readily used in *J. Inst. Metals* on account of being collected and classified); *Chemical and Metallurgical Engineering.*

Class 2—*The Foundry; The Iron Age* (contains many nonferrous data); *Metal Industry (N. Y.); Metal Industry (London).*

Class 3—*Revue Metallurgie; Zeitschrift für Metallkunde; Engineering (London).*

Class 4—*Brass World; Metall und Erz.*

Physical Chemistry as Applied to Foods

By Carl L. Alsberg

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THE SLOP JAR used to be the destination of most of the colloidal substances the chemical investigator encountered. What did not crystallize he stigmatized as a smear. Yet what does not occur in nature in the crystalline form is at least as important to man as what crystallizes, for it constitutes the essential portion of organized beings. Until well toward the end of the last century only the biochemist or the physiologist concerned himself with such material. It was necessary for the biochemist to pioneer in this field and for the science of physical chemistry to have developed before the study of such colloidal, not readily crystallizable material became interesting to chemical investigators generally. Solely by means of the application of the principles of physical chemistry to the study of the colloidal materials that characterize living organisms has progress in many branches of biological science become possible. Such phenomena as the acid-base equilibrium in animals and plants, the maintenance of neutrality, the transport of carbonic acid through the blood, the mechanism of secretion and excretion, cell respiration, the osmotic phenomena exhibited by living semi-permeable membranes, and the metabolism of microörganisms came to be understood only when conceptions of physical chemistry began to be applied by the biochemist in the study of biochemical phenomena. Studies upon the true character of acidity and alkalinity, upon dissociation, the phase rule, emulsions, sols and gels were necessary before some of the apparently simpler problems of biology could be studied. It is fair to say that to-day the science of general physiology is based very largely upon the science of physical chemistry. Each advance in physical chemistry is liable to be followed by a corresponding broadening of our knowledge of the behavior of living things. It is obvious that only through such knowledge can progress be made in many branches of medicine. Thus, to physical chemistry must be attributed much of what we know about the coma that may result from the disturbance of the acid-base equilibrium in the body, which the pathologist knows as acidosis, so common a cause of death, especially in diabetes.

Since agriculture and food manufacture are essentially forms of applied biochemistry, physical chemistry has made possible great advances of immediate practical usefulness. Without physical chemistry our present-day conceptions of the equilibria that prevail in soils and in the soil solution would be impossible. An increase in our knowledge of the behavior of colloids and of emulsions is destined to influence profoundly the world's methods of food production. For example, wheat owes its preëminence as a bread grain in large measure to the fact that it contains a mixture of proteins known as gluten, which, when mixed with water, forms a tenacious, elastic mass. For this reason wheat and, to a less degree, rye alone of all the grains yield dough. Because of the physical qualities of gluten—its toughness, its distensibility, and its coagulability by heat—it is possible to produce leavened bread. These qualities of gluten—elasticity and coagulability—however, are physicochemical, not purely chemical qualities in the ordinary sense. They do not depend primarily upon the arrangement of the atoms in the molecule but rather upon the physical condition of molecular aggregates. If, then, the properties of gluten which render wheat so desirable as a bread grain are physicochemical, they depend upon the physicochemical condition of the protein molecule, not upon its chemical structure. It is not too much to hope that physicochemical research upon colloids will one day enable us to control the colloidal state to such an extent that we can give to a colloid essentially those physicochemical properties that we desire. If this can be done, and there is no inherent impossibility in the idea, it may be possible to give to other proteins besides gluten the physicochemical properties of gluten. When that time comes, leavened bread will be produced from materials or grains other than wheat and rye. What this would mean to the food supply and the future of the race is obvious. Indeed, before such profound developments take place, it is probable that the application of physical chemistry to the food industries will render them vastly more efficient. To-day the milling and baking chemists are studying the hydrogen-ion concentration of milling and baking materials and are coming to realize that this is one of the most important, if not the most important, factor in determining the bread-producing qualities of flours and the behavior of doughs in fermentation. It is not improbable that in the milling laboratories of the country the potentiometer before long will be as familiar an instrument as the buret. What is likely to be true in the mill is likely to be true in the bakery, in the creamery, and in the sugar refinery. The behavior of dough and yeast is profoundly influenced by physicochemical conditions. Butter is an emulsion. The colloids of cane and beet juice play an important part in molasses formation, while the problem of decolorizing carbon is one for the physical chemist. Examples might be multiplied vastly, were space available. It is perhaps sufficient to add, in conclusion, that most of the industries that elaborate raw materials derived from living beings have to deal with colloids. Therefore they can make progress only so fast as they apply to their problems the discoveries made in that branch of physical chemistry which is known as colloid chemistry.

An Outline of the History of Chemistry Symbolically Represented in a Rookwood Fountain

By Harry Shipley Fry

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THERE are certain symbols and figures that are typically characteristic of the foremost periods in the History of Chemistry. The reproduction of some of these symbols and figures and their artistic embodiment in a fountain[1] of Rookwood faience has been accomplished in a remarkably unique and harmonious style by the master artists and ceramic craftsmen of the Rookwood Pottery of Cincinnati.

An appreciation of the symbolism of this fountain from the twofold point of view of the *history* and the *motive* of chemistry calls for a brief outline of the motives of the foremost periods in the history of chemistry accompanied by a description of the principal symbols and figures that have marked these periods. The five generally recognized overlapping periods, the predominant ideas in any one being accepted far into another, are approximately as follows:

1—*The Prehistoric Period*, from prehistoric times till 1500 B. C.
2—*The Alchemical Period*, from 1500 B. C. till 1650 A. D.
3—*The Iatrochemical Period*, from 1500 A. D. till 1700 A. D.
4—*The Phlogiston Period*, from 1650 A. D. till 1775 A. D.
5—*The Quantitative Period*, from 1775 A. D. till 1900 A. D.

The science of chemistry is defined by J. B. Mellor[2] as "man's attempt to classify his knowledge of all the different kinds of matter in the universe; of the ultimate constitution of matter; and of phenomena which occur when the different kinds of matter react one with another." Since all material transformations, physical or chemical, are accompanied by energy transformations, it follows that the extent of our knowledge of these changes and the ultimate constitution of matter determines the subserviency to mankind of both matter and energy. Accordingly, the motive of the science of chemistry as well as that of other natural sciences has been expressed in a broad and comprehensive sense by a maxim of Galileo Galilei (1564–1642) which is the motto of the fountain: "Let us remember, please, that the search for the constitution of the world is one of the greatest and noblest problems presented by nature." This applies not only to man's search for the ultimate constitution of the atom from the time of the Hindu philosopher, Kanada, 1200 B. C., to the researches of J. J. Thomson, Bohr, Rutherford, and Langmuir, but also to the past and present quests for the limits of the universe which according to the metaphysics of relativity and Einstein may be finite.

Berthelot, in his work, "*Les Origines de l' Alchemie*,"[3] writes:

> Chemistry is not a primitive science, like geometry and astronomy; it is constructed from the debris of a previous scientific foundation half chimerical and half positive, itself founded on the treasure slowly amassed by the practical discoveries of metallurgy, medicine, industry, and domestic economy. It has had to do with alchemy, which pretended to enrich its adepts by teaching them to manufacture gold and silver, to shield them from diseases by the preparation of the panacea, and finally to obtain for them perfect felicity by identifying them with the soul of the world and the universal spirit.

Egyptian hieroglyphics and picture writings show that many of these practical discoveries were the fruits of Egyptian Alchemy, but the Chaldeans were in fact the pioneers of alchemical science. Although no written record of Chaldean Alchemy has been discovered, we are aware that the number "7" was greatly respected in their philosophy and religion. They recognized seven visible planets, seven gods of heaven, seven gods of earth, and seven devils. The Chaldean philosophy also connected the properties of the seven metals with the influence of the seven planets and both in turn with the functions of the organs of the human body and the destinies of men. Now since these ideas originated in the Prehistoric Period and were maintained throughout the subsequent periods (and are even given credence by some to-day), it is appropriate that the seven Chaldean symbols, which represent simultaneously the seven planets and the seven metals, be embodied in the crowning arch of the fountain. Thus from left to right (Fig. 1) across the top are noted the symbols for the Sun or gold, Venus or copper, Mars or iron, Jupiter or tin, Saturn or lead, the Moon or silver, and Mercury or mercury.

The second and longest period in the history of chemistry, that of Alchemy, extends through thirty centuries—from 1500 B. C. to 1650 A. D. A series of books attributed to Hermes Trismegistus, a native of Babylonia, whom the Egyptians regarded as a god of wisdom, and other ancient records clearly indicate the existence of purely empirical technical arts such as glass-making, pottery, dyeing, painting, tanning, brewing, baking, the preparation of poisons and their antidotes, antiseptics and oils, expressed and distilled. While these are branches of alchemical knowledge, the word "alchemy" is more especially used to designate the manufacture, or better said, the sophistication of silver and gold.

With the development of various technical processes and the effort to transmute the metals, there was associated a great philosophical folly, namely, the search for the philosopher's stone and the elixir of life. Before considering the doctrine of transmutation, the philosopher's stone and related symbolism, it is consequential to note some contributions of the Greek philosophers to alchemical thought. They were not chemists. Few observations or experiments were made because they preferred to argue from general principles to particulars rather than from particular observations to general principles. Nevertheless, they clearly enunciated without any experimental foundation whatever the fundamental principle of all sciences—the law of the conservation of mass—and portrayed qualitatively the atomic constitution of matter.

Empedocles of Agrigentum (490–430 B. C.) divided all matter into four elements—fire, air, water, and earth—which were retained in the natural philosophy of Plato (427–347 B. C.) and of Aristotle (384–322 B. C.). It was due to the intellectual prestige of Aristotle that his idea of the transmutation of the four elements became the dominant motive of the period of alchemy. Fire, air, water, and earth were the roots of all things, endowed with the property of being without beginning, indestructible and homogeneous. From the mixtures of these four elements, which carried, respectively, the principal qualities, heat, cold, wetness, and dryness, arose all substances as we perceive them. The properties

[1] Gift of the Senior Engineering Class, **1921**, University of Cincinnati, to the Chemistry Building.

[2] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, p. 11. Longmans & Co., **1922**.

[3] Georges Steinheil, Paris, **1885**.

of substances were attributed to the fundamental properties of the elements of which they were composed. Hence, elements were transmutable one into the other by the abstraction of certain qualities and the substitution of others.

The transmission of Greek philosophy to the peoples of the west was the result of the conquest of Spain (711 A. D.) by the Arabs, who contributed enormously to the increase of chemical knowledge. Geber,[4] the 8th century Arabian chemist, developed the Aristotelian conception of the constitution of matter so as to account for the observed differences between the seven metals and to supply a theoretical basis for their transmutation. The four elements of Aristotle were retained as the ultimate constituents but the substances *mercury* and *sulfur* were assumed as the more proximate ones; mercury being the vehicle of the qualities of ducility, fusibility, and luster; and sulfur the bearer of the property of combustibility. Accordingly, the change of one metal into another should consist in the addition or withdrawal of one of the two constituents, sulfur and mercury, or in its purification.

Geber's Two-Principle doctrine held sway for seven centuries. Basil Valentine (second half of the 15th century) added a third principle or element, *salt*, representative of that which is permanent and unaltered by the action of heat. This Three-Principle doctrine became dominant for two centuries. It was accepted entirely by Paracelsus (1493–1540?) who made alchemy the servant of medicine.

The great work of Paracelsus was in effecting a breach with tradition and setting physicians and alchemists free from the bondage in which they were held by convention. He borrowed his medical treatments from barber-surgeons, old women and quacks, and employed powerful and dangerous medicines prepared from mercury, opium, and antimony more boldly and successfully than his predecessors. Paracelsus taught that the object of chemistry was not to make gold but to ameliorate disease. The art of making drugs, the motive of the Iatrochemical Period, thus became one of the original branches of alchemy, but it was frequently obscured by combined searches for the philospher's stone and the elixir of life.

Paracelsus also promulgated the Three-Principle doctrine so vigorously that it became associated with his name. It is a question whether these three principles—sulfur, mercury, and salt—were accepted by chemists instead of the four Aristotelian elements or alongside with these. Since "elaborate ambiguity, direct contradiction and studied vagueness are the characteristics of alchemical style," it would be useless to attempt to prove anything by directly quoting alchemical manuscripts. Nevertheless, the following excerpt from "A New Light of Alchymia," 1607, by Michael Svandivogius, is typical of medieval speculation relative to the interrelationships of the four elements (Aristotelian), fire, air, water, and earth, and the three principles (Paracelsian), sulfur, mercury, and salt. (Note arrangement of symbols in Fig. 1.)

We will now descend unto the Principles of things. . . . But how they are produced of the foure elements, take it thus. . . . The Fire began to act upon the Aire, and produced Sulphur, the Aire also began to act upon the Water, and brought forth Mercury, the Water also began to act upon the Earth and brought forth Salt. But the Earth since it had nothing to work upon, brought forth nothing, but that which was brought forth continued and abided in it. Wherefore there became only three Principles, and the Earth was made the Nurse and Mother of the rest. . . .These three Principles are altogether necessary because they are the near matter . . . The remote are the foure elements out of which God alone is able to create things. . . . By the due separation, and conjunction of these Nature produceth as well Metalls, as Stones in the Minerall kingdome; but in the Vegetable Kingdome Trees, Herbs, and all such things; also in the Animal Kingdome the Body, Spirit, and Soule, which especially doth resemble the work of the Philosophers. The Body is Earth, the Spirit is Water, and Soule is Fire, or the Sulphur of Gold.

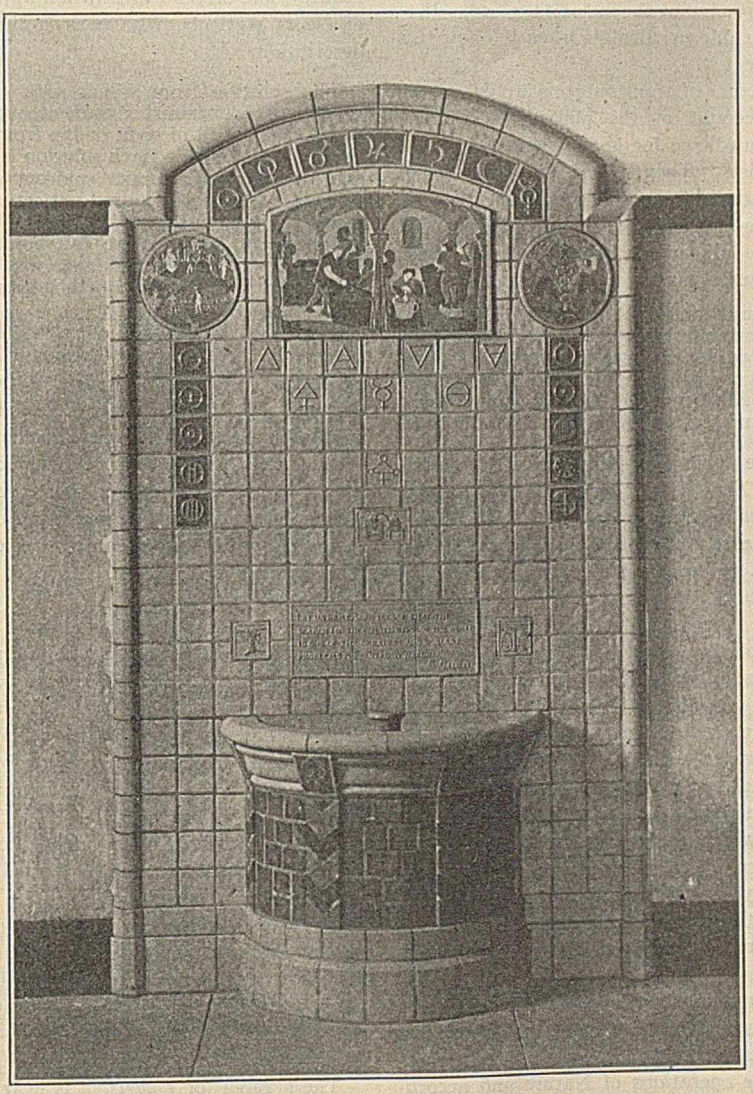

Fig. 1—The Four Triangular Symbols from Left to Right Represent the *Four Elements:* Fire, Air, Water, and Earth. The Three Underlying Symbols Represent the *Three Principles:* Sulfur, Mercury, and Salt. The Symbol for *Phlogiston* Is below That of Mercury. Dimensions: 5′ 2″ x 8′ 4″

Thus was alchemy in the 16th century complicated by religious ideas. It was even argued that the exact and natural sciences proceed by induction and deduction while the occult and spiritual sciences proceed by analogy. Following out this line of thought the alchemists produced the following remarkable triology:

Material World
- Sulfur
- Mercury
- Salt

Human World
- Body
- Soul
- Spirit

Divine World
- Father
- Son
- Holy Ghost

Each of these was a trinity in unity, and a unity in trinity. In each world was a distinct design: in the material, the perfection and the metals; in the human, the

[4] Freund's "Study of Chemical Composition," Cambridge University Press, 1904, and J. Campbell Brown's "History of Chemistry," Churchill, London, 1913, are chief sources in following descriptions.

perfection of the soul; in the divine, the contemplation of the Deity in His splendor.

The mystic alchemists interpreted the Three Principles in their own fashion. Mercury, the passive and female principle, was *matter;* sulfur, the active and male principle was *force* or *energy;* and salt, the middle term in the proposition, was *movement,* which applied force to matter. In other terms, mercury was the *subject;* sulfur, the *cause;* and salt, the *effect.* Such, in brief, was the involved philosophy of the alchemists.

Symbolism highly typical of the achemical transmutation doctrine and the philosopher's stone motive is found in the circular plaques in the upper left- and right-hand sections of the fountain (Fig. 1). The one to the left is a reproduction of a drawing taken from Kelly's medieval work, *Theatre of Terrestial Astronomy.* Its subject, the *Mutual Conversion of the Elements,* represents a black rock, on the top of which stand the variously colored figures of Saturn, Jupiter, Mars, Sol, Venus, Mercury, and Luna. On the black plain in the foreground are Mercury and Luna, labeled *Hermaphrodita,* with a crescent on her head. To the left of Mercury and to the right of Luna close observation detects the symbols of mercury and sulfur, respectively. The four elements blow from the four corners upon the place where Mercury stands with Luna. This plaque illustrates how the latter alchemists, who were astrologers as well, laid special stress, as did the earlier Chaldean alchemists, upon the influences of the seven heavenly bodies, each producing the metal it typified. Paracelsus even pretended to be able to calculate when and how this planetary influence took effect.

A description of the doctrine of transmutation would not be complete without some account of the philosopher's stone, which was "the universal medicine for giving perfection," the constant aim of the alchemists. They treated the symptoms of the metals as the doctor treats those of a sick man when he does not know the cause of his patient's illness. They tried to remove the symptoms of illness and induce those of health or perfection. As the centuries passed,

> the alchemists became more and more extravagant in their visions, and attributed unlimited powers to the philospher's stone, such as making precious stones, curing diseases, prolonging life, and controlling elemental spirits. It could preserve health, raise the dead, make the old young, turn the coward into a hero, strengthen the memory, and sober the drunkard! [BROWN]

The circular plaque of the upper right-hand corner of the fountain (Fig. 1) is a copy of *The Birth of the Philosopher's Stone* from *Der Hermetische Triumph,* Amsterdam, 1689. The alchemists assumed that the material of the stone or elixir embodied: 4 angles in its virtues: fire, air, water, and earth; 3 angles in its substance: sulfur, mercury, and salt; 2 angles in its matter: the fixed and the volatile; 1 angle in its radical principle: the *prima materia.* The sum of these angles is 10, which number in their Cabala, or mystic system, was held to express the material of the philosopher's stone. A close inspection of the heterogeneous details of the plaque reveals most of the angles just noted. There are fire, air, water, and earth. The symbol of sulfur is immediately above that of mercury which consists of intertwined serpents. The hermetically sealed flask beneath, or the philosopher's egg, in which prolonged heating operations were conducted, is above fire. The sun and the moon, *i. e.,* gold and silver, direct their rays or influence into the egg. The opinion prevailed that the philosopher's stone must be produced by the union of metals, and *a fortiori* of the perfect metals gold and silver.

The ideas of the constitution of the philosopher's stone were conflicting, and the opinions of the alchemists as to the number of operations involved in its synthesis are various, but the process was made to imitate the operations of Nature and accordingly was prolonged through seven stages, each corresponding to the influence and invocation of one of the seven planets. Thus for each planet, the philosopher's egg was heated a fixed number of days, the total operation occupying no less than 217 days, or over seven months. The perfected philosopher's stone was reputed to be a red powder which, when projected upon a quantity of molten base metal in a crucible, would transform it into an ingot of pure gold.

This survey of the alchemical period may be fittingly concluded by directly quoting the estimate of J. Campbell Brown:

> When we reflect upon . . . the philosophy and aims of the alchemists, we perceive how foolish it would be to sum them up in a single epithet. The men belonged to distinct classes. There were mystical or religious alchemists who made use of terms of art merely as parables, and alchemical processes as allegories. Their real subject was the human soul; their true object the guidance of mankind to salvation. But these were few. There were philosophical alchemists, steeped in the doctrines of Aristotle, who sought by the transmutation of base metals into gold to prove their great thesis—the unity of all things. There were scientific alchemists, whose desire was to discover the properties and combinations of metals, and the best methods for their manipulation. And there were mercenary alchemists, who hoped to find in the philosopher's stone the key to a store of unlimited riches. Unless we keep these different classes in mind, and differentiate clearly between them, we shall never understand all that is implied in the title 'alchemist.'

The mystic symbolism of these circular plaques is offset by the larger, central double-panel reproduction of a Medieval Soda Plant. The original illustration appears in the *De Re Metallica* of Georg Agricola, who records the following self-explanatory description:

> The solution from which soda (natron or hydrous sodium carbonate) is obtained is made of sweet water percolated through earth that is full of soda or lye from the same being percolated through oak ashes. Each solution is caught in tubs and poured into quadrangular copper caldrons and boiled till it condenses to soda. Then it is poured out into casks which contain copper wires, to which the soda adheres and hardens and becomes copper-green, or what we call borax, to use a Moorish name. Pliny tells us that formerly soda was mixed with copper rust and rubbed with copper in copper mortars.

The third and fourth or the Iatrochemical and Phlogiston Periods in the History of Chemistry are practically synchronous, extending from the beginning of the 16th to nearly the 19th century. The Iatrochemical Period is marked by the motive to produce and investigate medicinal substances by chemical means, and the production of chemical compounds in the search for new medicines, rather than the alchemical search for the philospher's stone which was not, however, entirely abandoned. The philosopher's stone motive became the *elixir vitae* motive. The symbolism described is typical both of the Alchemical and Iatrochemical Periods.

The Phlogiston Period is marked by a more sincere and precise search for chemical truth, and especially by the rise, development and fall of a remarkable theory of combustion which brought together as related processes a number of diverse phenomena that at first appeared to have nothing in common, namely, combustion, acidification, respiration, reduction, and the solution of metals in acids. All combustible substances were assumed by G. E. Stahl (1660–1734), the founder of the phlogiston theory, to consist of the product of combustion plus a hypothetical, inflammable substance termed "phlogiston," which corresponded to the fire matter of the ancients or to sulfur of the alchemists. Substances in burning lost the phlogiston. Lavoisier later demonstrated *quantitatively* that combustion was due, not to the loss of phlogiston, but to a direct combination of the combustible substance with the oxygen of the air, and thus at one blow overthrew the phlogiston theory and established the oxygen theory of combustion.

The symbol for *phlogiston* is near the center of the fountain, below the symbols for the four elements and the three principles (Fig. 1) and above Lavoisier's famous apparatus in which the synthesis and analysis of mercuric oxide were demonstrated.

A word of appreciation is due the phlogiston theory for the great service it rendered in effecting the correlation of diverse phenomena and promoting the development of chemistry along scientific lines. While the phlogiston theory was radically wrong, we must realize, as Whewell states, that "If our hypothesis renders a reason for the agreement of cases really similar, we may afterwards find the reason to be false, but we shall be able to translate it into the language of truth."

It was Anton Laurent Lavoisier (1743–1794) who effected this translation. His advent and achievements mark the establishment of chemistry as a science, to which he contributed more than any previous investigator through quantitative methods of procedure. Lavoisier's theories and works initiate the fifth, or the Quantitative Period, in the history of chemistry. Using the apparatus noted in the small panel at the center of the fountain—a retort, resting on a charcoal furnace, with a curved neck communicating with a bell jar—Lavoisier effected the quantitative synthesis and analysis of mercuric oxide. This work not only established the oxygen theory of combustion but demonstrated quantitatively for the first time the principle of the conservation of mass.

In relation to Lavoisier, also note the four tiles in the circular rim of the drinking basin of the fountain, which illustrate a special glass vessel of alchemical origin termed a "pelican" and used for prolonged heating operations involving the circulation and condensation of vapors. In such a vessel, formerly used as the philosopher's egg in which alchemists endeavored to generate the philosopher's stone, Lavoisier boiled a given weight of pure water for 100 days and demonstrated that the earth which appeared in this water was from the disintegration of the previously carefully weighed vessel, and not due, as was generally believed, to the transmutation of water into earth. This, of course, undermined transmutation ideas. He further proved that water was not an element, but a compound of hydrogen and oxygen, and defined an element as a substance which we have *not as yet* been able to resolve into other substances.

Brief note must now be made of the concomitant rebellion against the Aristotelian and transmutation doctrines which held sway throughout the Alchemical, Iatrochemical, and Phlogiston Periods. Pronounced instances of this rebellion became common toward the end of the 17th century and are especially noted in the works of Van Helmont, Francis Bacon, René Descartes, Pierre Gassendie, Robert Boyle, and Isaac Newton, most of which tended strongly toward the reëstablishment of the conceptions of the Greek atomistic philosophers, Democritus, Epicurus, and Leucippus. These ancient writers held a view of the constitution of matter which in most astonishing respects agrees with many of our modern views. But the fundamental distinction between the ancient and the modern doctrines lies in the fact that John Dalton (1766–1844) transformed mere *qualitative speculations* into a *practical quantitative theory* by assuming that chemical combination occurs between simple numbers of elementary atoms of fixed characteristic weight. This conception enabled Dalton to explain fully the fundamental laws of definite or fixed composition and multiple proportions.

In 1803 Dalton devised a symbolic notation for the elements and their compounds, which was both qualitative and quantitative. A circle with a dot at its center stood for one part by weight of hydrogen. A plain circle stood for the weight of oxygen (5.66 parts according to Dalton) which combined with one of hydrogen. The ten circular figures, five in each of two parallel vertical rows, one row on each side of the fountain, are Dalton's symbols for the most common elements: on the left—oxygen, iron, calcium, sodium, and potassium; on the right—magnesium, hydrogen, carbon, mercury, and sulfur.

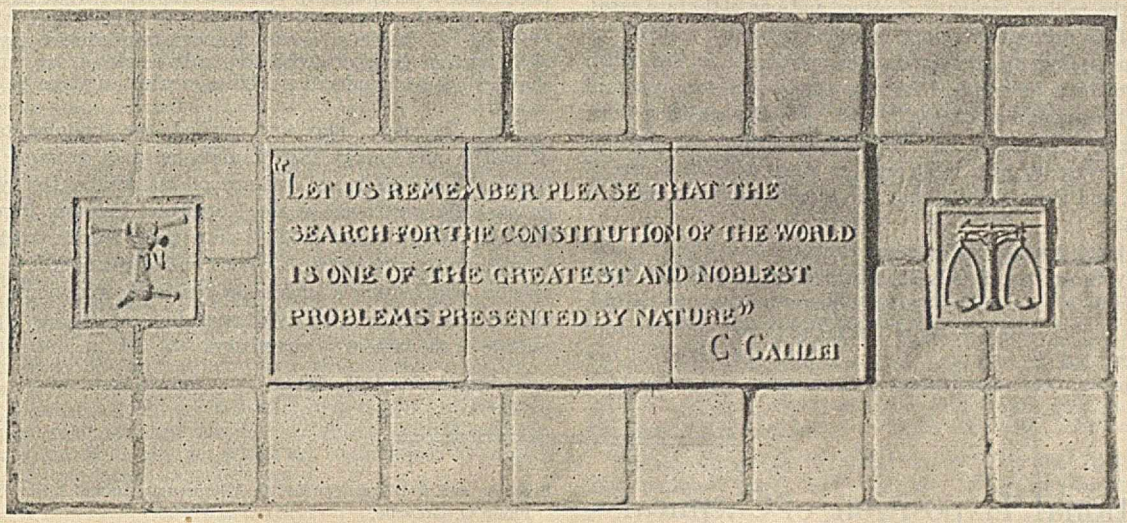

FIG. 2

A few years later Berzelius substituted for Dalton's geometrical hieroglyphic symbols, the more convenient and simple representation by letters now universally employed. Dalton's criticism of Berzelius' modification of his symbols is quaint: "Berzelius' symbols are horrifying; a young student in Chemistry might as soon learn Hebrew as make himself acquainted with them."

The achievements, both theoretical and practical, of the pure and applied chemistry of the Quantitative Period are far too numerous and extended for an outline. In fact, the chemistry lecture and laboratory courses of the universities of both hemispheres barely begin to convey an understanding of what chemistry is and what it does. Be this as it may, the fountain recognizes the function of chemistry's two foremost instruments, the spectroscope and the analytical balance, in promoting the motive of chemistry and other natural sciences. This motive, the motto of the fountain in the central horizontal panel, has been aptly expressed by Galileo Galilei, the inventor of the astronomical telescope, in the words, "Let us remember, please, that the search for the constitution of the world is one of the greatest and noblest problems presented by nature." (Fig. 2.)

To the left of this motto is the spectroscope, to the right the analytical balance. The use of the spectroscope in conjunction with the astronomical telescope reveals the constitution of the world. Practically every element known in the earth has been identified in the sun and in various heavenly bodies through spectro-photography and spectrum analysis. The deli-

cacy of the spectroscopic test is the most extreme known, since it reveals the presence of one part of sodium vapor in twenty billion parts of air. This corresponds to our being able to detect a fragment of common salt weighing 0.00000000001 oz.!

On the other hand, the advent of the analytical balance enabled chemistry to become an exact science since through its use the quantitative composition of hundreds of thousands of compounds has been accurately determined. Specially constructed balances rival in sensitiveness the extreme delicacy of the spectroscope. For instance, Ramsay and Gray attacked the problem of determining the relation between the weight of an atom of the radium emanation, niton, and one of the rare gases, argon. This necessitated their making a balance capable of displacement from the central or zero position of balance when the minute load of a hundred-thousandth of a milligram is placed on it. This amounts to 0.00000004 oz. Thus Ramsay and Gray were able to deal with a very tiny bubble of niton weighing one fourteen-hundredth of a milligram, or about two-millionths of an ounce, and thereby show that the atomic weight of niton is about 222.

These facts serve to indicate how the spectroscope and the balance, only two of the chemist's numerous instruments, aid most substantially in the search for the constitution of the world, which, as Galilei states, is one of the greatest and noblest problems presented by nature. Undoubtedly, the extent of our knowledge of the constitution of the world and of matter, which also implies energy, determines the extent of the adaptability of both matter and energy to humanity's needs.

The Alchemists sought to make gold; the Iatrochemists to make medicines; the Phlogistonists, the immediate forerunners of chemistry as a quantitative science, sought more definitely for truth itself, which search culminates in an ethics of science. P. V. N. Myers in his *"History as Past Ethics"*[5] states that

> Among the particular virtues which science has fostered is philosophical veracity or love of truth. . . The man of science must be a truth-lover, a truth-seeker, and a truth-teller. He must take every pains to find out what is the exact fact, and then make a scrupulously veracious report of what he has found. It has in the creation of this scientific conscience, which pronounced the habit of accuracy, open-mindedness, impartiality of judgment, love of truth for truth's sake a supreme virtue, that science has rendered one of its greatest services to morality.

Thus Chemistry, pure and applied, the fundamental science of matter and energy transformations, may promote both the physical and the moral welfare of mankind. Its symbolism, as partially portrayed in the Rookwood fountain herewith described, readily lends itself to an artistic creation, which, it is hoped, will commemorate the good will of the donors of the fountain in establishing a university tradition and mark a unique achievement in ceramic craftsmanship serving as a symbolic outline of the history of chemistry.

[5] Ginn & Co., **1913**, 353.

National Exposition of Chemical Industries

The following program of the 1922 Exposition supplements that given in the August issue of THIS JOURNAL and gives the plans as far as they have been completed. The dates for the meetings of the various chemical organizations are still only tentative.

Monday, September 11. 8:00 P. M.—Official Opening, Grand Central Palace Auditorium. Speakers, Wayne B. Wheeler, general counsel for the Anti-Saloon League; Charles H. Herty, chairman of the Exposition Committee and president of the Synthetic Organic Chemical Manufacturers Association of the United States; and others.

Tuesday, September 12. 2:00 P. M.—Program will probably be under the direction of the Synthetic Organic Chemical Manufacturers Association of the United States.

Wednesday, September 13. 2:00 P. M.—Program under the direction of the Technical Association of the Pulp and Paper Industry.

Thursday, September 14. 2:00 P. M.—Program under the direction of the Technical Photographic and Microscopical Society.

Friday, September 15. 2:00 P. M.—Program under the direction of the American Ceramic Society.

Friday Evening or Saturday, September 16.—A Symposium on Standardization.

All portions of the program held in the Grand Central Palace, with the exception of the dinners of various societies, will be open to all visitors at the Exposition. The annual dinners of the Salesmen's Association of the American Chemical Industry, and also that of the American Institute of Chemical Engineers, will be held on Wednesday evening, September 13. At the former, Herbert Hoover, Secretary of Commerce, will be the chief speaker. The Alpha Chi Sigma meets informally at dinner on Thursday, September 14.

The motion picture program includes the following in addition to those previously published:

The Story of Air Reduction. Courtesy of the U. S. Bureau of Mines.

The Manufacture of Newsprint Paper at the Spanish River Pulp and Paper Company Mills in Ontario. Courtesy of the G. H. Mead Company.

The Story of Natural Gas. Courtesy of the U. S. Bureau of Mines.

Dust Explosions. Courtesy of the U. S. Bureau of Chemistry.

Protozoa and Rotifers: Studies in Microscopic Animal Life. Courtesy of Philip O. Gravelle.

Extinguishing the Largest Oil Fire in the History of Casper, Wyoming.

Fire Extinguishing Tests on Blazing Oil Tanks at Port Arthur, Texas.

The All-Weather Fire Extinguisher That Won't Freeze.

An Industrial Firefoam Sprinkler System.

The last four films are the courtesy of the Foamite Firefoam Company.

Protecting Buildings against Lightning. Courtesy of Baltimore Copper Smelting and Rolling Company.

The program of the Technical Association of Pulp and Paper Industry and the Standardization program were given in full in August issue of THIS JOURNAL.

The program of the Technical Photographic and Microscopical Society is as follows:

Photomicrography in Pulp and Paper Research Problems. MISS ELOISE GERRY and E. M. DIEMER, Forest Products Laboratory, Madison, Wis.

The Photomicroscopy of Paint and Rubber Pigments. HENRY GREEN, New Jersey Zinc Co., Palmerton, Pa.

The Finishing of Motion-Picture Films. DOMINIC S. MUNGILLO, Craftsmen's Film Laboratory, New York.

Mechanics of Motion-Picture Apparatus. CLARENCE W. GIBBS, Victor Animatograph Co., New York.

The Motion Picture as an Aid to Industry. ALFRED B. HITCHINS, Director, Research Laboratory, Ansco Co., Binghamton, N. Y.

Microscopy in Leather Tanning. GUIDO E. DAUB, A. F. Gallun Sons Co., Milwaukee, Wis.

Use of the Microscope in Textile Work. ALBERT H. GRIMSHAW, Textile School, New Bedford, Mass.

Protozoa and Rotifers: Studies in Microscopic Animal Life. (Illustrated by motion pictures.) PHILIP O. GRAVELLE, South Orange, N. J.

The Federal Trade Commission has dismissed, without prejudice to its right to institute new proceedings, about forty complaints against nationally known business concerns which had been charged with maintaining resale prices similar to those in the Beech-Nut Packing Case. These cases were suspended until the determination of the Beech-Nut case, and in view of that decision and the age of the cases it has been decided to dismiss them and to institute new proceedings if new inquiries show it to be advisable.

WASHINGTON NOTES

Alleged Dye Monopoly Hearings

The much-discussed and long-awaited hearings before a subcommittee of the Committee on the Judiciary, United States Senate, pursuant to Senate Resolution 77, creating a special committee to investigate the expenditures made in behalf of various propaganda and in the maintenance of lobbies in Washington, have appeared under the caption "Alleged Dye Monopoly," and occupy 1485 pages of finely printed matter. If there exists a doubt in the mind of any chemist as to the existence of a monopoly in the domestic dye industry he should get a copy of these hearings and inform himself as to the true condition of affairs.

The hearings were begun on February 20, continued practically without interruption until May 16, and were finally concluded on June 3 when the committee met to hear some supplementary testimony. In nearly 1500 pages of testimony there is nothing to prove that there has been or is at present a monopoly in the dye and other branches of the organic chemical industry in the United States. The witnesses were examined under oath and waived any immunity under the law. The chairman of the subcommittee repeatedly invited cross-examination of the witnesses, but it is significant that in no instance was the invitation accepted.

From a study of this testimony it is evident that a grave injustice has been done the American dye industry by compelling the most prominent members of the industry to come to Washington, often at great personal sacrifice, expense and inconvenience, to answer trumped-up charges which are so obviously groundless and without foundation as to be absurd.

What Next?

The chemical industry seems to be suffering defeat all along the line, at least so far as the present tariff bill is concerned. By a vote of 32 to 30, the Senate rejected the recommendation of the Finance Committee to place a duty of 5 per cent ad valorem on chemical wood pulp and put it on the free list. Next came potash. Only one senator—Senator Shortridge—voted for a tariff. Senator McCumber then introduced an amendment which provided for a diminishing duty, similar in all respects to the tariff originally proposed except that the payment was transferred from the consumer to the U. S. Treasury. This amendment met with violent opposition on the floor of the Senate and was rejected by a vote of 32 to 27. This means that potash is keeping company with wood pulp on the free list. Now comes the vote on white arsenic which has likewise been placed on the free list. We cannot refrain from asking "What next?"

New Chemical Division

One of the chief aims of the newly organized Chemical Division of the Department of Commerce is to assist American chemical manufacturers by placing at their disposal accurate and detailed information on foreign markets for their products. The following branches of industry will be handled by this division:

Chemicals, general, organic and inorganic.
Dyes and coal-tar chemicals.
Pigments, paints, and varnishes.
Fertilizers and fertilizer materials.
Botanical drugs, pharmaceutical and medicinal preparations.
Essential oils, perfumery, cosmetics, and toilet preparations.
Explosives and fireworks.

The Department of Commerce is constantly receiving inquiries in regard to the introduction of American products into various foreign countries. The Chemical Division will serve as a medium to bring these opportunities promptly to the attention of domestic concerns. One of the first undertakings of the division will be the compilation of a list of domestic firms interested in the development of foreign trade. This list, known as the "Exporters Index," will serve as the basis of distribution of such information in foreign markets. The division also plans to organize advisory committees for each of the various branches of the chemical industry coöperating with the Department. In the case of existing trade associations, the contact with the industry will doubtless come through such associations.

The division will welcome suggestions from representatives in the industry by which it can be of assistance to domestic manufacturers.

Census of Dyes and Other Synthetic Organic Chemicals, 1921

The United States Tariff Commission has just issued as Tariff Information Series No. 26, a "Census of Dyes and Other Synthetic Organic Chemicals, 1921." There is included in this report for the first time a census of synthetic organic chemicals other than those derived from coal tar. The report shows a largely reduced output of dyes in 1921. This relatively limited production more nearly represents our domestic requirements, for the very high output of the previous year was coincident with a considerable export trade of the United States. This reduced output in 1921 may be accounted for by (1) the loss of most of our export trade, (2) the large stocks carried over from the previous year, and (3) the general business depression.

Congress Petitioned

The Synthetic Organic Chemical Manufacturers Association of the United States held a meeting in New York on August 4 for the purpose of discussing the situation now facing the American dye and organic chemical industry as a result of the action of the Senate in striking out of the tariff bill the protection proposed in the bill as submitted by the Finance Committee. As a result of an all-day discussion, the following petition was unanimously signed and forwarded to Senator McCumber, chairman of the Finance Committee, and to the other members of the Committee:

"At a meeting of the Synthetic Organic Chemical Manufacturers Association of the U. S., held at New York, August 4, 1922, the manufacturers of dyes, drugs and other organic chemicals, gave consideration to the serious danger that threatens their industry by reason of the defeat of the Dye and Chemical Control Act in the Senate, July 15. They now respectfully petition the Finance Committee to take such action as may be appropriate to reinstate the clauses in the Tariff Act stricken out by the Senate's action. They repeat what they have heretofore testified to before your Committee, that nothing less than the provisions of the Dye and Chemical Control Act will adequately protect their industry; that no specific or ad valorem rates will prevent the German Kartel from regaining absolute control of the American organic chemical market; and that the manufacture of dyes, medicinals, and other organic chemicals can no longer be maintained in this country without the legislative protection heretofore advocated by your Committee after thorough investigation of all the facts."

August 10, 1922

Calendar of Meetings

American Chemical Society—64th Meeting, Pittsburgh, Pa., September 4 to 9, 1922.

Eighth National Exposition of Chemical Industries—New York, N. Y., September 11 to 16, 1922.

American Electrochemical Society—42nd Meeting, Montreal, Canada, September 21 to 23, 1922.

American Institute of Mining and Metallurgical Engineers—126th Meeting, San Francisco, Calif., September 25 to 29, 1922.

American Society for Steel Treating—Convention, Detroit, Mich., October 2 to 7, 1922.

Paris Letter—Correction

In the letter from Mr. Charles Lormand appearing in the August issue of This Journal under the above title, the following correction is to be made on page 750:

In the paragraph on "The Commission on Chemical Periodicals" omit the expression reading, "(1) The abbreviations used by *Chemical Abstracts* are not desired" and substitute therefor the following: "For all abbreviations of titles of periodicals the abbreviations utilized by *Chemical Abstracts* are to be adopted."

BOOK REVIEWS

Fluidity and Plasticity. By E. C. BINGHAM. (International Chemical Series.) Cloth $8^1/_4 \times 5^1/_2$, xii + 440 pp., 96 illustrations. McGraw-Hill Book Co., Inc., New York, 1922. Price, $4.00.

In 1914 Dunstan and Thole could cover the relation between viscosity and chemical composition, and related subjects, in 89 pages, while Bingham, largely on account of his own pioneer work in plasticity, now needs 429 pages. Bingham's predilection for fluidity makes him less thorough in considering the technical measurement of high viscosities. Thus (p. 35) there is no reference to the change in critical velocity with the length of capillary, and (p. 69) the directions for selecting a viscometer do not apply to oils, for which the maximum viscosity must be considered. The statement (p. 233) that the rate of flow through an orifice is independent of the fluidity is evidently inapplicable to liquids of high viscosity. The conclusion (p. 29) is also open to question, that as the Couette correction has no definite value it is unnecessary to determine where it should be applied. The value has been found to vary with the conditions, although the average value may approach zero. (W. F. Higgins, "Collected Researches," National Physical Laboratory; Bureau of Standards, *Technical Paper* 112.) When the Couette correction is ignored, an accuracy of 0.1 per cent (p. 65) cannot be obtained without an excessively long capillary, even if other errors are assumed negligible.

The reader who is interested in plasticity should perhaps consult the original papers and form his own judgments. (The bibliography of 82 pages should prove of great value for this and other purposes.) Bingham's contention (p. 225) that conditions should be controlled so that all the observed points lie on a straight line, is a help as far as calculation is concerned, but may lead to misinterpretation if, as Buckingham has indicated, there are three properties of the material to be measured, just as the assumption of the one property of "viscosity" for a plastic material has caused endless confusion.

WINSLOW H. HERSCHEL

Colloid Chemistry of the Proteins. Part I. By WOLFGANG PAULI, translated by P. C. L. THORNE. Cloth, $8^1/_2 \times 5^1/_2$, xii + 140 pp. P. Blakiston's Son & Co., Philadelphia, 1922. Price, $2.25 net.

This book is the first part of a small volume developed from lectures delivered during the winter of 1912–13 and from such work of others as seemed desirable to the author in rounding off the presentation. Part II is scheduled to appear within a year.

After a brief introduction to colloid chemistry, the author treats the soluble proteins, in particular the albumins, as amphoteric electrolytes, each having two mean ionization constants, one as an acid and the other as a base, which characterize it. This view forms the basis of a very illuminating discussion on the behavior of albumins in solutions of acids and bases and at the isoelectric point. Issue is taken with Robertson's view that both ions of HCl combine with proteins in such manner that two protein ions, one positive and one negative, are formed. Electrophoresis experiments on albumin solutions show only positively charged protein ions in acid solution and negatively charged ones in alkaline solution. The changes in state undergone by alkaline solutions of proteins with lapse of time are attributed to a rearrangement of the peptide linkage from the keto to the enol form. The book closes with an interesting discussion of the migration velocity of protein ions.

With the rise of colloid chemistry, it has become evident that the reactions of the proteins follow well-known laws of physical chemistry. Since the author appreciates this, it is regrettable that he is not more thoroughly familiar with the works of Procter and Loeb, which would have enabled him to avoid dependence upon the assumption that low concentrations of electrolyte markedly repress the ionization of protein salts or that increased viscosity of protein solutions is necessarily due to the hydration of protein ions. However, the remarkably clear presentation of certain phases of the subject establishes the book as a valuable contribution to the literature on the physical chemistry of the proteins.

JOHN ARTHUR WILSON

Reports of the Progress of Applied Chemistry. Issued by the SOCIETY OF CHEMICAL INDUSTRY. Vol. VI, 1921. 625 pp. Society of Chemical Industry, Central House, 46/47 Finsbury Square, London, E. C. 2.

This publication, now appearing for the sixth consecutive year, has proved itself a most welcome friend to one who would keep himself informed of what is going on in the many fields of chemical activity. No one can hope to cover all the fields and often his own specialty is all he can hope to do in detail. But here some twenty-six subjects are covered by as many different specialists who have assembled a valuable résumé. Not only is the literature covered broadly from English, American, French, German, and other sources but references are given to the patent literature and to patents issued.

In many chapters the plan of review is systematic, broad, and comprehensive in its arrangement and execution. The extent of the field that is covered is shown by the following chapter headings: Plant and Machinery; Fuel; Gas, Destructive Distillation, Tar Products; Mineral Oils; Coloring Matters and Dyes; Fibers, Textiles, Cellulose and Paper; Bleaching, Dyeing, Printing, and Finishing; Acids, Alkalies, Salts, etc.; Glass; Refractory Materials; Ceramics and Building Materials; Iron and Steel; Metallurgy of the Nonferrous Metals; Electrochemical and Electrometallurgical Industries; Oils, Fats and Waxes; Paints, Pigments, Varnishes and Resins; India Rubber; Leather and Glue; Soils and Fertilizers; Sugars, Starches and Gums; Fermentation Industries; Foods; Sanitation and Water Purification; Fine Chemicals, Medicinal Substances, Essential Oils; Photographic Materials and Processes; Explosives.

A chapter headed Analytical Chemistry that appeared in last year's Reports is omitted this year (1922), and the heading heretofore Agricultural Chemistry has been changed to Soils and Fertilizers, although the subject matter is along the lines of the previous chapters on Agricultural Chemistry in preceding volumes. At the conclusion of the subject matter are two indexes—one a name index, the other a subject index, each apparently quite complete and correct.

Not only is the book interesting even to one with a slight knowledge of chemistry and its application to the arts and manufactures, but to the various specialists in many, if not in all, subjects there will be some hint or suggestion of a new fact or discovery.

Altogether it is a worth-while book which ought to be widely distributed in chemical libraries, and the equal of its predecessors.

R. L. EMERSON

Industrial Oil Engineering, Lubrication and Industrial Oil Section. By JOHN ROME BATTLE, B.Sc. in M.E. 1131 pp. J. B. Lippincott, Philadelphia and London, 1920. Price, $10.00.

This reference book contains a collection of tables and miscellaneous data relating to industrial oils, mainly lubricants. Although the reviewer realizes the great labor and difficulties connected with the compilation of data from numerous sources, he feels that the value of the book would have been considerably increased if more care had been used in the selection and arrangement of the material. Some of this is of very doubtful value, as, for instance, the obsolete and partly incorrect conversion table for weights and measures (p. 26). It may be interesting to know the method used by African natives to produce palm oil (p. 252), or the color of the funnels of the Cunard line steamers (p. 781); to the reviewer, however, these matters appear irrelevant to the subject of the book, and the space might have been better occupied, for instance, by a definition of kinematic viscosity, repeatedly mentioned in the book.

A good many repetitions and duplications are found in the book, which tend to swell the volume and hide its good points. Thus, the Conradson carbon test is described three times, twice at page 322 and again at page 1051. That sodium and potassium hydroxides are known as alkalies, is pointed out twice, on pages 230 and 876.

More serious than the above are some statements that are directly misleading: Temporary hardness of water is ascribed to calcium and magnesium carbonates (p. 73). Pale paraffin oil (mineral soap oil) is declared on page 876 to be capable of neutralizing an amount of caustic or carbonate in the soap kettle.

The book will be found useful in many respects, despite shortcomings of the kind mentioned above, which should be eliminated in a future edition. The printing and other mechanical features of the book are excellent.

Synthetic Tannins: Their Synthesis, Industrial Production and Application. GEORG GRASSER, Lecturer in Tanning Chemistry at the German Technical College, Brunn. Translated into English by F. G. A. ENNA. viii + 143 pp. D. Van Nostrand Co., New York, 1922. Price, $4.00.

The German edition of this useful book was written in 1920 by Grasser, who should be an authority on syntans as a result of his work in this field for the Badische Anilin und Soda-Fabrik.

Syntans have received considerable attention since the Great War. There is no doubt that syntans were "life-savers" to German leather manufacture when the Central Empires were cut off from sources of vegetable tanning materials. In the author's German preface is stated, "Just as in the case of the coal-tar dyes, the synthetic tannins will make us independent of foreign supplies, and thus keep within our borders the vast sum of money required in former days for the purchase of foreign tanning materials."

The book is divided into two parts. Part I, consisting of 77 pages, deals with (*a*) synthesis of vegetable tannins and depsides, (*b*) synthesis of tanning matters by condensation of phenols, hydroxybenzenes, naphthalene derivatives, and the anthracene, and di-, and triphenylmethane groups, (*c*) tanning effects of mixtures and natural products, and (*d*) methods of examination of tanning matters. Part II, 60 pages, deals with syntans, predominately Neradol D, their industrial production, application, and properties.

A number of syntans are not mentioned, but it is natural, in view of the author's connection, that Badische products should be discussed to the exclusion of other manufacturers' products.

This book contains much information that is useful for the practical tanner as well as for the tannery and organic chemist.

A. W. THOMAS

Fuel and Refractory Materials. By A. HUMBOLDT SEXTON, F.I.C., F.C.S., completely revised and enlarged by W. B. DAVIDSON, D.Sc., PH.D., F.I.C. 382 pp., 111 illustrations. D. Van Nostrand Co., New York, 1921. Price, $4.00.

Whoever undertakes to write a book on industrial chemistry in any of its phases must meet squarely the task of describing up-to-date practice, for by so much as he fails in this his labor is in vain. In "Fuel and Refractory Materials" the reviser seems to have had indifferent success in this respect. Though a Briton and stressing British methods, he strives, apparently, to be eclectic in the treatment of his subject, and the best general practice must therefore be the basis for judging his book.

American charcoal manufacture is discussed from the standpoint of a method used in 1876 employing the bee-hive type of oven; no reference is made to the modern continuous retort oven with its extensive plant for the treatment of by-products. The only journal reference is dated 1883.

The subject of powdered fuel is given a short paragraph in description of experimental work done between 1873 and 1896. Is it possible that the author has not heard of the tremendous development of this branch of fuel technology since that period? With one exception the methods of coal calorimetry given are obsolete, or should be at least. The Berthelot-Mahler is illustrated with a cut of one of the crude early forms of this instrument.

Shale oils and distilled petroleums are given half a page each, mention being confined to Scotch shales and to Pennsylvania and Baku crudes, respectively, while under the head of motor spirit nothing is said of cracking processes. Recent views of the constitution of coal and some modern theories of the chemistry of coking "have not been incorporated, as it is felt that these subjects are still in their infancy."

In spite of many excellent features of the book, the reviewer feels that without liberal use of the blue pencil in the hands of the instructor it cannot be used as a textbook for students; as a reference book for the industries, it is on the whole too superficial to be of great value.

H. L. OLIN

Metric System for Engineers. By CHARLES B. CLAPHAM, Lecturer in Engineering, University of London. 181 pp. E. P. Dutton & Co., New York, 1922. Price, $6.00.

This book, as the author states in his preface, is designed to offer a thorough exposition of the metric system, particularly as it is met with in engineering calculations and measurements. After an introduction, in which the fundamental principles of the system are explained, the measurements of length, area, volume, and weight are fully treated in separate chapters. Well-arranged tables of equivalents are given in each topic, together with numerous practical problems, showing how the metric system is employed in a great variety of engineering calculations. A chapter is devoted to measurements of energy and work, acceleration, power and heat, in which appear the less common units of measurement, which are often confusing to those who are unacquainted with their derivation. The last chapter presents an impartial review of the controversy which has arisen in England and the United States over the adoption of the metric system. Such topics as the complexity of the present English system, the origin and growth of the metric system, its present position in Great Britain and in this country, and the important question of the practicability of its adoption are treated in a very interesting manner. In spite of the apparent painstaking effort of the author to present both sides of the question from the viewpoint of an engineer, this chapter as a whole presents one of the best general arguments for the adoption of the metric system which the reviewer has seen. A careful reading of the book reveals very few typographical or other errors. It will be especially useful to all who are not fully acquainted with the system and who have occasion to apply it in engineering or other industrial lines of work.

ROBERT E. SWAIN

CURRENT PUBLICATIONS

NEW BOOKS

American Fuels. RAYMOND F. BACON AND WILLIAM A. HAMOR. Mellon Institute Technochemical Series. Vol. I. 630 pp. Vol. II. 615 pp. Illustrated. Price, $12.00 per set, net. Not sold separately. McGraw-Hill Book Co., Inc., New York.

Analytical Chemistry: Calculations of Analytical Chemistry. E. H. MILLER. 201 pp. Price, 9s. Macmillan & Co., Ltd., London.

Analytische Chemie der Alkaloide. K. H. BAUER. 425 pp. Price, $4.80. Gebrüder Borntraeger, Berlin.

Adhesives: First Report of the Adhesive Research Committee. 129 pp. Price, 4s. 2½d. H. M. Stationery Office, London.

The British Association. A Retrospect 1831–1921. O. J. R. HOWARTH. 318 pp. Price, 7s. 6d. The British Association for the Advancement of Science, London.

Chemistry for Beginners and Schools. C. T. KINGZETT. 237 pp. Price, 5s. Baillière, Tindall & Cox, London.

Chemistry: A First Book of Chemistry for Students in Junior Technical Schools. A. COULTHARD. 156 pp. Price, $1.25. Isaac Pitman & Sons, New York.

Chemistry: Second Year College Chemistry. A Manual of Laboratory Exercises. WILLIAM H. CHAPIN. 122 pp. Illustrated. Price, $1.50. D. Van Nostrand Co., New York.

Coal: Mitteilungen aus dem Schlesischen Kohlenforschungsinstitut der Kaiser-Wilhelm Gesellschaft. FRITZ HOFMANN. 180 pp. Price, $3.50. Gebrüder Borntraeger, Berlin.

Coal-Tar Colors in the Decorative Industries. A. CLARKE. 166 pp. Price, 6s. net. Constable & Co., Ltd., London.

Colloids: Les Colloides. J. DUCLAUX. 2nd edition, revised and enlarged. 305 pp. Price, 10 fr. Gauthier-Villars et Cie, Paris.

Copper: Les Progrès de la Métallurgie du Cuivre. A. CONDUCHÉ. Encyclopédie Léauté. 254 pp. Price, 14 fr. Masson et Cie., Paris.

Dictionary: Werkstoffe: Handwörterbuch der Technischen Waren und ihrer Bestandteile. PAUL KRAIS ET AL. 3 volumes. 529, 784, and 728 pp. Price, paper, 450 mk.; bound, 540 mk. J. A. Barth, Leipzig.

Fats: Die Losungsmittel der Fette, Oele, Wachse und Harze. H. WOLFF. Monographs on the Chemistry of Fats, edited by K. H. BAUER. 118 pp. Price, 9s. Wissenschaftliche Verlagsgesellschaft, Stuttgart.

Fuel: Report of the Fuel Research Board for the Years 1920, 1921. Second Section. Low Temperature Carbonization. DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. 73 pp. Price, 2s. H. M. Stationery Office, London.

Fur Dyeing and Fur Dressing. WILLIAM E. AUSTIN. 191 pp. Price, $4.00. D. Van Nostrand Co., New York.

Handbook: A Pocketbook for Chemists. T. BAYLEY. 425 pp. Price, $3.15. Spon & Chamberlain, New York.

Intermediate Chemistry: Smith's Intermediate Chemistry. JAMES KENDALL AND E. E. SLOSSON. 566 pp. Price, $3.25. The Century Co., New York.

Intermediate Chemistry: A Laboratory Outline of Smith's Intermediate Chemistry. JAMES KENDALL. 127 pp. Price, $1.25. The Century Co., New York.

Minerals: Essentials for the Microscopical Determination of Rock-Forming Minerals and Rocks, in Thin Sections. ALBERT JOHANNSEN. 53 pp. Illustrated. Price, $2.00. University of Chicago, Chicago.

Modern Chemical Lecture Diagrams. GEOFFREY MARTIN. 88 pp. Price, 3s. 6d. Sampson Low, Marston & Co., Ltd., London.

Nitrogen Fixation: L'Azote: La Fixation de l'Azote Atmosphérique et son Avenir Industriel. L. HACKSPILL. Encyclopédie Léauté. 271 pp. Price, 14 fr. Masson et Cie., Paris.

Organic Analysis. E. de BARRY BARNETT AND P. C. R. THORNE. 168 pp. Price, 7s 6d. University of London Press, London.

Organic Chemistry: Theories of Organic Chemistry. FERDINAND HENRICH. Translated and enlarged from the 4th revised German edition by TREAT B. JOHNSON AND DOROTHY A. HAHN. 620 pp. Price, $6.00 net. John Wiley & Sons, Inc., New York.

Perfumes and Cosmetics; Their Preparation and Manufacture; a Complete and Practical Treatise for the Use of the Perfumer and Cosmetic Manufacturer, Covering the Origin and Selection of Essential Oils and Other Perfume Materials, the Compounding of Perfumes and the Perfuming of Cosmetics. GEORGE WILLIAM ASKINSON. Revised edition. 392 pp. Price, $6.00. Norman W. Henley Publishing Co., New York.

Photography: Abridged Scientific Publications from the Research Laboratory of the Eastman Kodak Co. No. 4. 319 pp. Eastman Kodak Co., Rochester, N. Y.

Petroleum: Handbook of the Petroleum Industry. DAVID T. DAY, *et al* Two volumes. 2070 pp. Price, $15.00, net. John Wiley & Sons, Inc., New York.

Quantitative Analysis: Calculations of Quantitative Chemical Analysis. L. F. HAMILTON AND S. G. SIMPSON. 191 pp. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

Relativity: The Theory of General Relativity and Gravitation. LUDWIK SILBERSTEIN. 141 pp. Price, $2.00. D. Van Nostrand Co., New York.

Steel Foundry. JOHN HOWE HALL. 2nd edition, revised and enlarged. 334 pp. Illustrated. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

Tanning: Manuel du Tanneur, Mégissier, Corroyeur. P. HUC. Bibliothèque Professionnelle. 402 pp. Price, 12 fr. net. J. B. Baillière et Fils, Paris.

Textiles and Their Manufacture. A. F. BARKER, W. M. GARDNER, R. SNOW, AND F. BRADBURY. 386 pp. Illustrated. Price, 15s. net. Constable & Co., Ltd., London.

RECENT JOURNAL ARTICLES

Ammonia: Transformation Industrielle de l'Ammoniaque en Urée, Engrais de Haute Concentration. CAMILLE MATIGNON. *Chimie et industrie*, Vol. 7 (1922), No. 6, pp. 1057–70.

Blast Furnace: The Development of the Blast Furnace. J. HENDERSON. *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, Vol. 22 (1922), No. 10, pp. 178–83.

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MARKET REPORT—AUGUST, 1922

[Supplied by Drug & Chemical Markets]

Chemical prices generally are extremely nervous and several important items have been sharply advanced during the month past. The gradual absorption of the government surplus stocks of phenol has finally resulted in an acute shortage and prices are extremely firm. Nothing better than 15 cents per pound could be done after August first for carlots of large drums, which is the price asked by the refiners of natural on the same quantity of material. No synthetic phenol has been made for the past two years and the government surplus has been the sole dependence of consumers. The virtual demolition of this surplus has left the market in an extremely tight position, with little prospect of relief until it is possible for makers of synthetic to get their plants back into operation, which will take some time, according to reports now current in the trade. Following this condition makers of salicylates advanced their prices sharply and are now looking forward to a real shortage for lack of raw material.

An advance of 35 cents per hundred was made by the makers of calcium acetate late in July, making the new price $2.35 per hundred at the works. This, following as it did an advance early in July, forced a further advance in acetic acid, and thus greatly discouraged buyers, who were already none too insistent. The present prices of acetic acid are based on $2.67^1/_2$ for 28 per cent in carlots of barrels at makers' works, and many of the consumers of this product consider this level too high for safe buying. The consequence has been a general reduction of purchases throughout the market. Acetone and methyl ethyl ketone were advanced correspondingly.

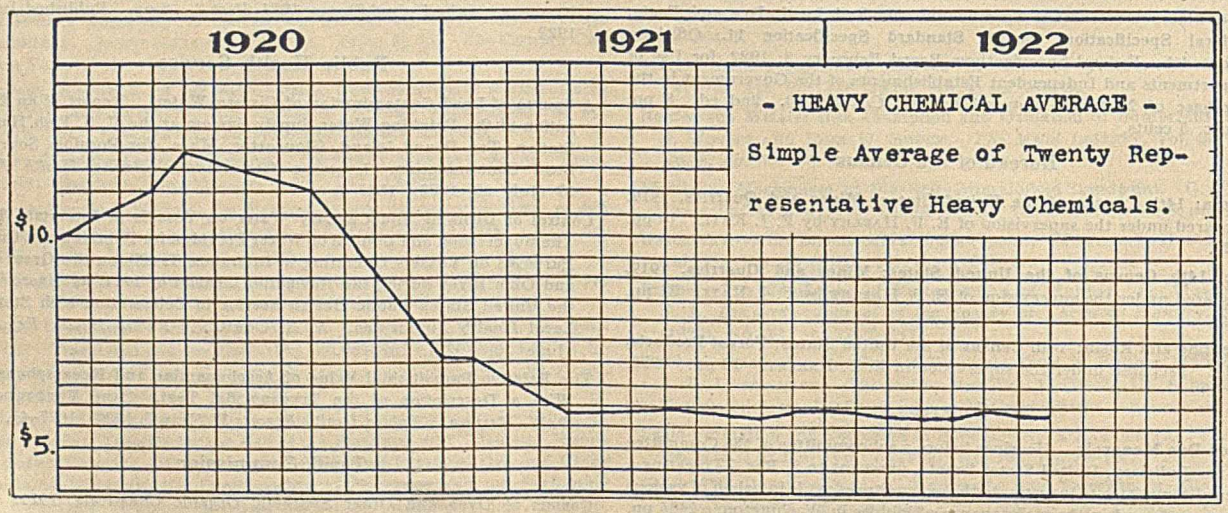
Glycerol has been advanced by makers during the period and is firm at the higher level. Camphor has been firmer and higher from Japan. Oxalic acid has been in good demand throughout the period and has been twice advanced by makers to a present level of 16 cents at their works. In one direction it has been found possible to shade this figure somewhat, but the general attitude is one of firmness.

In the inorganic list, interest has been centered largely in the insecticide situation. Copper sulfate continues extremely scarce, and few firm offers are available, even at the nominal price of 7 cents named in a few cases for odd lot business. Arsenic is becoming increasingly attractive to many speculative and consuming interests. Reports from the cotton-growing districts state that the demand for insecticides for the present season has not been satisfied yet, on account of the coming of a veritable plague of the cotton leaf worm from the Mexican border. The call from the affected districts is for any arsenical compound that can be used for checking its spread. This demand comes at a time when makers have practically nothing to offer in either calcium arsenate, lead arsenate, or Paris green, and when the white arsenic market is attracting speculative buyers in such numbers as at present. The coming of real consuming demand is forcing prices rapidly higher. So far there have been few sales above 8 cents, but many indications point to further advances. The lack of activity in the copper-producing areas, from which the domestic arsenic supply comes, the higher prices asked from Japan for shipments, and the dearth of supplies in any of the other markets of the world, are taken as the basis of extremely bullish reports which are being widely circulated in the market.

Many of the large consumers of chemical materials have established rules that no supplies shall be taken on under any circumstances which are not immediately needed in plant operations. This has led to frequent irregular telegraphic orders for rush shipments to be delivered within a few hours at most, and has greatly confused the situation. Indications point to sharp advances on the slightest provocation. Declines may be caused in a similar way by the forced release of any considerable quantity of material by speculators or others who are not in position to hold for favorable sale.

The coal-tar product situation generally has attracted little additional interest from the trade during the past month. Plans are being made by the larger interests in intermediates and dyes to continue operations whether the licensing feature of the tariff bill is included or not. Consumers in the meantime are taking on only such limited supplies as are required for their present requirements. Less tendency is noted among manufacturers to cut prices on this small lot business and there are many features of firmness in the situation, but the total amount of business being done is small.

Fertilizer materials are stronger in all markets on short supplies in the face of increasing demand for export. Vegetable oils have shown little strength during the month on declining prices on cottonseed oil. Prospects in this oil indicate a heavy yield from the present crop and consequently lower prices. Fish oils are firm. Menhaden oil is particularly firm and scarce on account of the low yield from the poor catch caused by poor weather conditions during the fishing season. Animal oils are little changed and have shown a fairly steady trend. Turpentine has reached a steady level after the sharp speculative advances of a short time ago. The trend of the metal markets has been upward, although the actual net increases have not been large.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

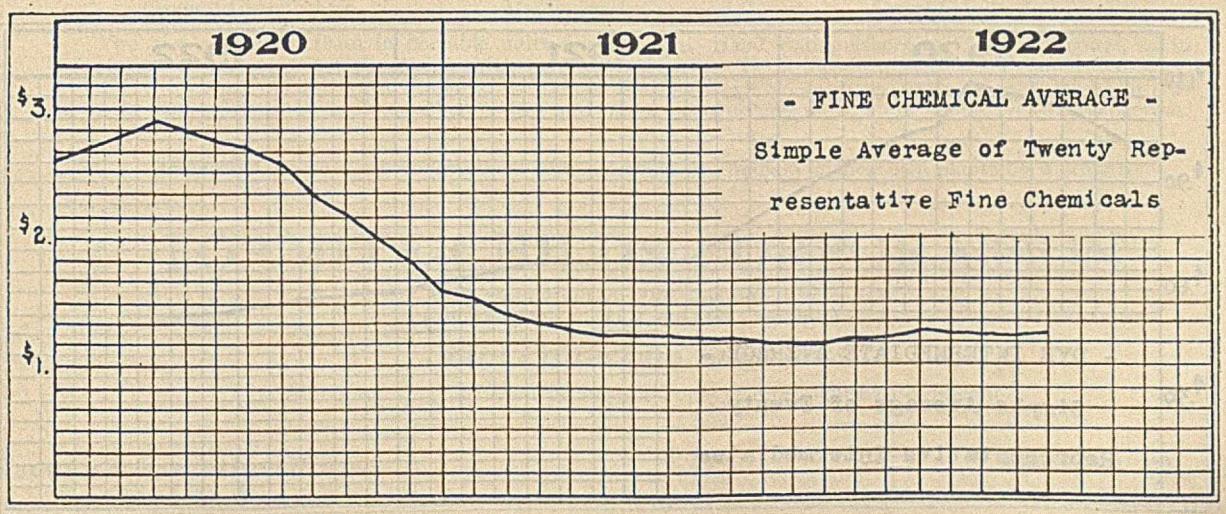
	Aug. 1	Aug. 10	Jan. 1922
Acid, Boric, cryst. bbls.....lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20°lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.07	.07	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.06	.06	.06
Phosphoric, 50% tech.....lb.	.08	.08	.10
Sulfuric, C. P.....lb.	.07	.07	.07
66° tks. wks.....ton	16.00	16.00	16.00
Oleum 20%.....ton	19.00	19.00	19.00
Alum, Ammonia, lump.....lb.	.03½	.03½	.03½
Potash, lump.....lb.	*.03	*.03	*.03½
Chrome.....lb.	.06½	.06½	.07
Soda, ground.....lb.	.03½	.03½	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.07	.07	.08
Chloride, white gran.....lb.	.07¾	.07¾	.07½
Ammonia, anhydrous .....lb.	.30	.30	.30
Ammonia Water, drums, 26°...lb.	.07½	.07½	.07½
Arsenic, white.....lb.	.07½	.08	.06½
Barium Chloride.....ton	*85.00	*85.00	*53.00
Nitrate.....lb.	*.06	*.06	*.07
Barytes, white.....ton	33.50	33.50	28.00
Bleaching Powd., 35%, works .....100 lbs.	1.60	1.60	2.25
Borax, cryst., bbls.....lb.	.05½	.05½	.05¾
Bromine, pure, wks.....lb.	.25	.25	.23
Calcium Chloride, fused, f.o.b. N. Y.....ton	24.50	24.50	28.75
Chlorine, liquid.....lb.	.06	.06	.06
Copper Sulfate.....100 lbs.	7.00	7.00	5.55
Iodine, resublimed.....lb.	4.20	4.20	3.80
Lead Acetate, white crystals...lb.	.10½	.10½	.11
Nitrate.....lb.	.15	.15	.15
Red.....lb.	.08	.08	.08
White (Carb.).....lb.	.07¼	.07¼	.07¼
Lime Acetate.....100 lbs.	2.35	2.35	1.75
Magnesium Carbonate, tech...lb.	.06	.06	.06
Magnesite, calcined.....ton	55.00	55.00	55.00
Phosphorus, yellow.....lb.	*.25	*.25	*.27
Red.....lb.	*.26	*.26	*.30
Plaster of Paris.....bbl.	4.25	4.25	4.25
Potassium Bichromate.....lb.	.09¾	.09¾	.10½
Bromide, imported.....lb.	*.15	*.15	*.13
Carbonate, calc., 80–85%.lb.	*.04¾	*.04¾	*.04½
Chlorate, cryst.....lb.	*.06½	*.06½	*.05½
Hydroxide, 88–92%.....lb.	*.05¾	*.05¾	*.06
Iodide, bulk.....lb.	3.30	3.30	2.90
Nitrate.....lb.	.08	.08	.08
Permanganate, U. S. P....lb.	*.14	*.14	*.15
Prussiate, red.....lb.	*.90	*.90	*.29
Yellow.....lb.	*.32	*.33	*.24½
Salt Cake, bulk.....ton	21.00	21.00	17.00
Silver Nitrate.....oz.	.48	.48	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.60	3.60	3.80

*Resale or Imported (not an American makers' price).

	Aug. 1	Aug. 10	Jan. 1922
Sodium Acetate.....lb.	.05	.05	.04
Bicarbonate.....100 lbs.	2.00	2.00	2.00
Bichromate.....lb.	.07	.07	.07¾
Bisulfite, powd.....lb.	.04¼	.04¼	.04¼
Chlorate.....lb.	.06¾	.06¾	.07½
Cyanide, 96–98%.....lb.	.23	.23	.28
Fluoride, tech.....lb.	.09½	.09½	.09½
Hyposulfite, bbls.....100 lbs.	3.25	3.25	3.50
Nitrate, 95%.....100 lbs.	2.55	2.55	2.32½
Nitrite.....lb.	.09½	.09½	.06½
Prussiate, yellow.....lb.	.20½	.20½	.16½
Phosphate (di-sod.),tech..lb.	.04	.04	.04¼
Silicate, 40°.....lb.	.01	.01	.01⅛
Sulfide, 60%, fused.....lb.	.04	.04	.05
Strontium Nitrate.....lb.	*.08	*.08	*.10
Sulfur, flowers.....100 lbs.	3.00	3.00	2.75
Crude, mines.....long ton	14.00	14.00	16.00
Tin Bichloride, 50% sol'n.....lb.	.10½	.10½	.09¾
Oxide.....lb.	.38	.38	.37
Zinc Chloride, U. S. P.....lb.	.35	.35	.35
Oxide, bbls.....lb.	.08	.07	.08

ORGANIC CHEMICALS

	Aug. 1	Aug. 10	Jan. 1922
Acetanilide, U. S. P. bbls.....lb.	*.29	*.29	*.29
Acid, Acetic, 28 p. c.....100 lbs.	2.67½	2.67½	2.37½
Glacial.....lb.	.11	.11	.10
Benzoic, U. S. P.....lb.	.55	.55	.60
Carbolic, cryst., U. S. P., drs.....lb.	.15	.16	.12
50- to 110-lb. tins....lb.	.21	.21	.18
Citric, crystals, kegs.....lb.	*.44½	*.44½	*.43
Oxalic, cryst., bbls., wks...lb.	.15½	.16	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.....lb.	.26	.29	.24
Tannic, U. S. P., bbls....lb.	.70	.70	.75
Tartaric, cryst., U. S. P...lb.	*.28½	*.28	*.25
Acetone, drums.....lb.	.13½	.13½	.12
Alcohol, denatured, complete.gal.	.31	.31	.45
Ethyl, 190 proof, bbls....gal.	4.65	4.65	4.75
Amyl Acetate.....gal.	1.90	1.90	2.00
Camphor, Jap, refined, cases...lb.	.80	.83	.90
Carbon Bisulfide, c/l.....lb.	.06	.06	.06½
Tetrachloride.....lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.25	.25	.43
Creosote, U. S. P.....lb.	.40	.40	.40
Cresol, U. S. P.....lb.	.14	.14	.14
Dextrin, corn.....100 lbs.	3.09	3.09	2.70
Imported Potato.....lb.	.09	.09	.06½
Ether, U. S. P., 100 lbs.....lb.	.14	.14	.14
Formaldehyde, bbls.....lb.	.08	.08	.10½
Glycerol, dynamite, drums....lb.	.13½	.15	.14½
Methanol, pure, bbls.....gal.	.72	.72	.75
Methylene Blue, med.....lb.	3.00	3.00	4.00
Petrolatum, light amber.....lb.	.04½	.04½	.05¼
Pyridine.....gal.	1.75	1.75	1.75
Starch, corn, pow'd.....100 lbs.	2.47	2.47	2.13
Potato, Jap.....lb.	.07	.07	.06½
Sago.....lb.	.03½	.03½	.04



Courtesy of Drug & Chemical Markets

BIBLIOTEKA

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

OILS, WAXES, ETC.

	Aug. 1	Aug. 10	Jan. 1922
Beeswax, pure, white.....lb.	.40	.40	.33
Castor Oil, No. 3.....lb.	.12	.12	.10½
Ceresin, yellow.....lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills...lb.	.09½	.09½	.06¾
Cottonseed Oil, crude, f. o. b. mill.....lb.	.08½	.08½	.07
Linseed Oil, raw, c/l.....gal.	.88	.88	.69
Menhaden Oil, crude, mills...gal.	.43	.43	.35
Neat's-foot Oil, 20°.....lb.	.20	.20	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.30	6.30	5.30
Rosin Oil, first run.....gal.	.39	.39	.36
Shellac, T. N.....lb.	.78	.78	.66
Sperm Oil, bleached winter, 38°.....gal.	1.35	1.35	1.70
Stearic Acid, double pressed...lb.	.09½	.09½	.09¾
Tallow Oil, acidless.....lb.	.10	.10	.10
Turpentine, spirits of.....gal.	1.18	1.18	.82½

METALS

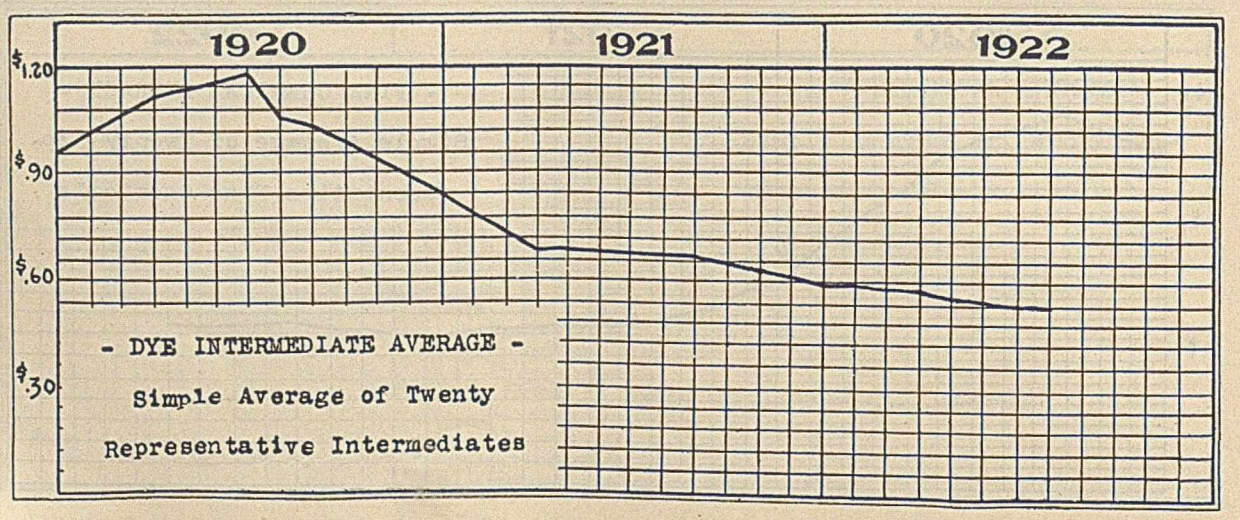
	Aug. 1	Aug. 10	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.17½	.17½	.17
Antimony, ordinary.....100 lbs.	5.25	5.25	4.55
Bismuth.....lb.	2.10	2.10	1.80
Copper, electrolytic.....lb.	.14	.14	.13⅞
Lake.....lb.	.14	.14	.13¾
Lead, N. Y.....100 lbs.	5.75	5.85	4.70
Nickel, electrolytic.....lb.	.39	.39	.45
Platinum, refined, soft.....oz.	93.00	93.00	78.00
Quicksilver, flask.....75 lbs. ea.	55.00	57.00	52.00
Silver, foreign.....oz.	.71⅜	.71⅜	.65¼
Tin.....lb.	.32	.32	.32¾
Tungsten Wolframite....per unit	2.00	2.00	2.00
Zinc, N. Y.....100 lbs.	6.25	6.60	5.20

FERTILIZER MATERIALS

	Aug. 1	Aug. 10	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.50	3.50	2.60
Blood, dried, f. o. b. N. Y....unit	4.00	4.00	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia.....	2.75	2.75	2.25
Fish Scrap, dried, wks.....unit	4.10 & .10	4.10 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	5.00
Tennessee, 78–80%.....ton	4.00	4.00	8.00
Potassium Muriate, 80%....unit	.60	.60	*.75
Tankage, high-grade, f. o. b. Chicago.....unit	4.00 & .10	4.00 & .10	3.00 & .10

COAL-TAR CHEMICALS

	Aug. 1	Aug. 10	Jan. 1922
Crudes			
Anthracene, 80–85%.....lb.	.75	.75	.75
Benzene, pure, tanks.....gal.	.30	.30	.29
Naphthalene, flake.....lb.	.06½	.06½	.07½
Phenol, drums.....lb.	.15	.15	.11
Crudes *(concluded)*			
Toluene, pure, tanks.....gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks.....gal.	.45	.45	.45
Intermediates			
Acids:			
Anthranilic.....lb.	1.10	1.10	1.10
Benzoic, tech.....lb.	.50	.50	.50
Cleve's.....lb.	1.50	1.50	1.50
Gamma.....lb.	1.80	1.80	2.25
H.....lb.	.75	.75	1.00
Metanilic.....lb.	1.00	1.00	1.60
Monosulfonic F.....lb.	2.30	2.30	2.30
Naphthionic, crude.....lb.	.60	.60	.65
Nevile & Winther's.....lb.	1.20	1.20	1.30
Picric.....lb.	.20	.20	.25
Sulfanilic.....lb.	.22	.22	.26
Tobias'.....lb.	1.50	1.50	2.00
Aminoazobenzene.....lb.	1.15	1.15	1.15
Aniline Oil.....lb.	.14	.14	.17
Aniline Salt.....lb.	.20	.20	.25
Anthraquinone (sublimed)....lb.	1.35	1.35	1.50
Benzaldehyde, tech.....lb.	.65	.65	.45
U. S. P.....lb.	1.40	1.40	1.25
Benzidine Base.....lb.	.85	.85	.90
Benzidine Sulfate.....lb.	.70	.70	.70
Diaminophenol.....lb.	5.50	5.50	5.50
Dianisidine.....lb.	4.50	4.50	4.75
p-Dichlorobenzene.....lb.	.17	.17	.15
Diethylaniline.....lb.	.60	.60	.90
Dimethylaniline.....lb.	.32	.32	.40
Dinitrobenzene.....lb.	.20	.20	.21
Dinitrotoluene.....lb.	.20	.20	.25
Diphenylamine.....lb.	.58	.58	.58
G Salt.....lb.	.65	.65	.70
Hydroquinol.....lb.	.80	.80	1.35
Monochlorobenzene.....lb.	.10	.10	.10
Monoethylaniline.....lb.	1.00	1.00	1.00
b-Naphthol, dist.....lb.	.23	.22	.30
a-Naphthylamine.....lb.	.30	.30	.30
b-Naphthylamine.....lb.	.95	.95	1.05
m-Nitroaniline.....lb.	.72	.72	.85
p-Nitroaniline.....lb.	.75	.75	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol.....lb.	.75	.75	.75
o-Nitrotoluene.....lb.	.12	.12	.15
p-Nitrotoluene.....lb.	.60	.60	.70
m-Phenylenediamine.....lb.	1.00	1.00	1.10
p-Phenylenediamine.....lb.	1.50	1.50	1.60
Phthalic Anhydride.....lb.	.35	.35	.38
R Salt.....lb.	.55	.50	.60
Resorcinol, tech.....lb.	1.30	1.30	1.50
U. S. P.....lb.	1.75	1.75	2.00
Schaeffer's Salt.....lb.	.60	.60	.70
Sodium Naphthionate.....lb.	.60	.60	.70
Thiocarbanilide.....lb.	.35	.35	.40
Tolidine (base).....lb.	1.15	1.15	1.20
Toluidine, mixed.....lb.	.30	.30	.30
o-Toluidine.....lb.	.16	.16	.20
p-Toluidine.....lb.	1.00	1.00	1.10
m-Toluylenediamine.....lb.	.95	.95	1.10
Xylidine.....lb.	.42	.42	.40



Courtesy of Drug & Chemical Markets

Modern Fire Protection
for
Modern Chemical Processes

THE use of **water** on your chemical fires, by hose line, buckets, or common "chemical" extingushers, too often **increases** the danger of conflagration.

Firefoam extinguishes fire by cutting off the supply of oxygen necessary for combustion with a thick, air-tight blanket of durable Firefoam bubbles inflated by harmless carbon dioxide gas.

Firefoam Smothers Fire

It Coats
It Clings
It Floats

It Coats and fireproofs any burning substance, liquid or solid.

It Clings wherever it is applied—the draught of the fire or outside air currents cannot carry the extinguishing element away. The carbon dioxide gas is confined in bubbles and stays where you need it.

It Floats on liquids, however volatile and inflammable. Reignition or reflash are impossible under a Firefoam blanket.

In the largest as well as the smallest risks Firefoam smothers fire without damage to materials or equipment. It has proved to be the only adequate extinguishing method for protecting 55,000 barrel tanks of gasoline, and has been adopted by all leading companies of the oil and chemical industries.

Following is a suggestive list of the many drug and chemical companies that have protected their property with Firefoam:

E. I. Dupont De Nemours Powder Co.
Barrett Co.
General Chemical Co.
Victor Chemical Works
U. S. Industrial Alcohol Co.
Dow Chemical Co.
Mallinckrodt Chemical Co.
Merck & Co.
Monsanto Chemical Works
Newport Chemical Works
Semet-Solvay Co.

You can obtain Firefoam in portable units from 2½-gal. Hand Extinguishers to 750-gal. Engines, or in stationary systems especially designed for your particular risk. By arrangement with the Grinnell Company, of Providence, Firefoam is also available in Firefoam Automatic Sprinkler form, to protect those extra-hazardous risks like coal tar intermediates where water and other extinguishing devices are ineffective and dangerous.

Interested executives may arrange a demonstration of Firefoam in their own plants by writing to

FOAMITE-CHILDS CORPORATION

(A Consolidation of the Foamite Firefoam Company and the O. J. Childs Company, Inc.)

Fire Protection Engineers

Manufacturing and Distributing All Types of Fire-Fighting Equipment

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Ethyl Acetoacetate
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Ethyl Carbonate
Ethyl Formate
Ethyl Fumarate
Ethyl Isovalerate
Ethyl Lactate
Ethyl Malate
Ethyl Maleate
Ethyl Monochloracetate
Ethyl Normal Butyrate
Ethyl Propionate
Ethyl Oxalate
Ethyl Phthalate
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Isoamyl Propionate
Isobutyl Acetate
Isobutyl Formate
Isobutyl Isovalerate
Isobutyl N-Butyrate
Isobutyl Propionate
Isopropyl Acetate
Isopropyl Formate
Isopropyl Oxalate
Methyl Acetate
Methyl Formate
Methyl N-Butyrate
Methyl Oxalate
Monacetin
Normal Propyl Acetate
Normal Propyl Isovalerate
Normal Propyl N-Butyrate
Normal Propyl Propionate
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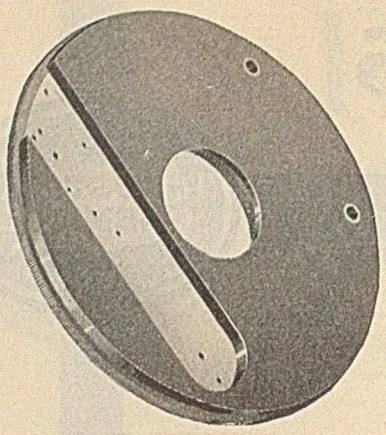

A Molded Microscope Stage

Spencer Lens Company of Buffalo, pioneer microscope manufacturers in America, have won for themselves an enviable place in the optical field.

One of the details in their search for betterments and increased efficiency is the revolving table or "stage" for these microscopes, molded complete in one operation. A phenolic condensation product supplanted the composition formerly used, because this material offers the combined advantages of mechanical accuracy, cleanliness, durability, and good appearance. Oil and reagents cannot penetrate the surface of such a stage; it does not turn brown with use, warp, crack, or deteriorate with age. The use of this material here actually simplifies manufacture, by the molding in of all necessary apertures, knurling, and metal inserts, thus obviating further machining of the piece.

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3043-B

OLD man Noah was progressive.

NO question about that.

600 years old and then built his sea-going zoo.

THE greatest thing in the world of its kind in his day.

BUT the modern liner knocks Noah's product for a row of clam shells.

JUST so.

WHEN Joachim Bishop first commercially produced Platinum Ware it was *Some* Stuff—for his day.

BUT 80 years have passed since J. B. started.

COMPARED with Platinum Ware manufactured by the modern processes developed and used by J. Bishop & Co., the original product would be crude. But the principle of progress-in-manufacture is the same.

EACH piece of Bishop Platinum is especially refined, hammered, finished and inspected so that the user is insured the maximum amount of service.

WHEN your platinum apparatus needs repair or replacement, will you give us an opportunity to estimate?

J. BISHOP & CO.
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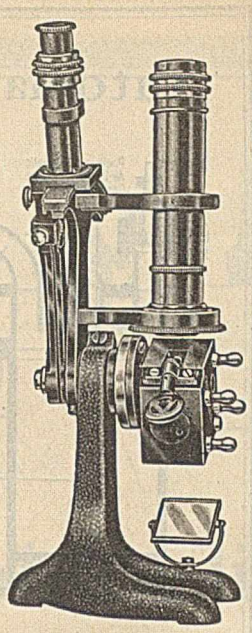
The Improved Precision Model Refractometer



The VALENTINE-ABBÉ REFRACTOMETER, which is the first refractometer to be made in America is an improvement over the original Abbé REFRACTOMETERS made in Germany more than twenty years ago.

Exclusive features in design constitute important improvements. These are the only advancement which has been made, and are embodied only in the Valentine-Abbé Refractometer, precision type, model 1921.

This instrument is fitted with heatable prisms for temperature control. The optical system is arranged to give strong illumination with sharply defined black border line when investigating relatively the darkest substances. The range of the instrument is from N_d 1.300 to N_d 1.720 and the accuracy when reading refractive index to one-half unit in the fourth decimal place.

These instruments are giving very satisfactory service in many leading laboratories investigating sugars, oils, glass, drugs, etc.

VALENTINE-ABBÉ REFRACTOMETER, PRECISION 1921 model, with thermometer, glass test plate, dispersion chart and bottle of Monobromonaphthalene, in case with lock and key.....$185.00

DITTO, but with an added scale reading directly in percentage of dry substance in sugar juices from 0 per cent to 90 per cent for temperature of 20° C. .$200.00

DITTO, with scale for reading at 28° C. for use in tropical countries.....$200.00

The spiral heater and water pressure regulator for use with Refractometers of all types.....$45.00

Certificate of accuracy from the U. S. Bureau of Standards will be furnished without extra charge unless this privilege is waived by the purchaser.

Inquiries are solicited regarding these instruments fitted with special scales for specific lines of research or factory control.

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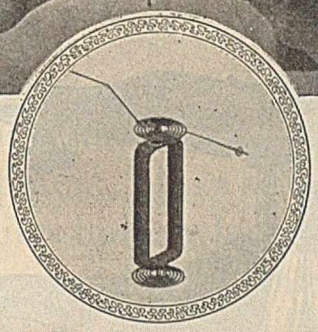
Manufacturer
HADDONFIELD, N. J.



What's "under the hood" of Brown Pyrometers

first of a series

The movable element

Watch making has no problem like this. This assembly requires 13 parts and 43 operations. It weighs the same when finished as the common pin—35 to the ounce.

Three layers of 50 turns (150 turns) of .003″ copper wire are heavily cemented together and baked and the form removed. To both ends are cemented diminutive aluminum brackets that form an anchorage for the ground steel pivots and the hair springs. The springs, pivots and the hollow aluminum pointer are then attached.

With jewel bearings at each end having a normal bearing speed almost too slow to be measured, and weighing 1/1750 oz. per ohm resistance—this is perhaps the most sensitive, most nearly dead-beat, most sturdily constructed and longest lived of all pyrometer movable elements.

THE BROWN INSTRUMENT CO.
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Brown Pyrometers
Most used in the world

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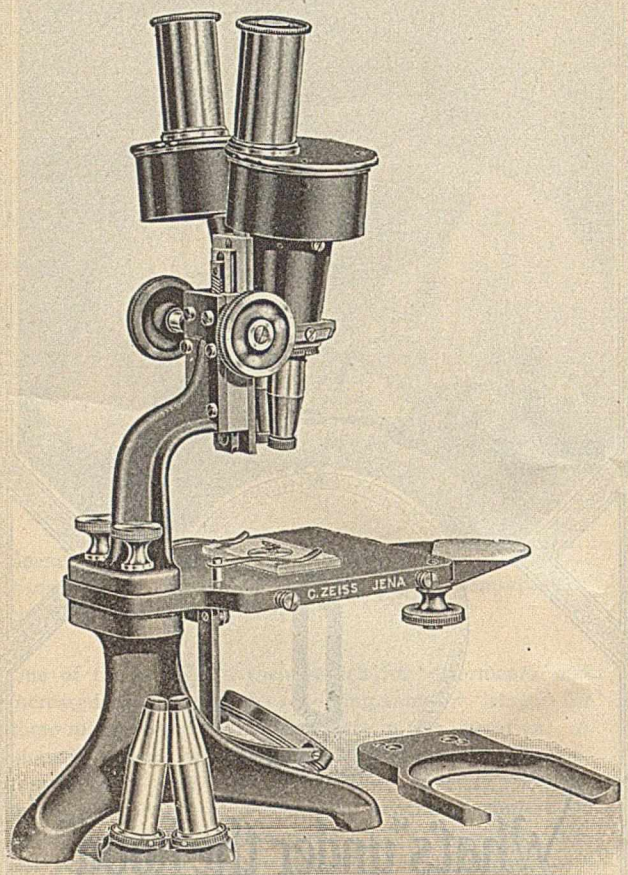

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EASE AND PRECISION
OF OPERATION

For use in Works and Laboratory.

Invaluable for examination of textiles, papers, metals, mechanical parts, precipitates, etc.

Stand XA in Case	$97.00
Paired Objectives a_0	18.00
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" oculars No. 2	5.00
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	$143.00 f.o.b. N. Y.

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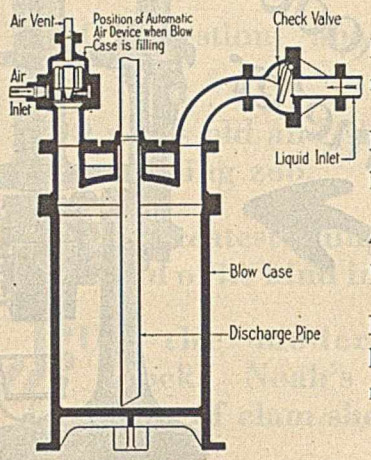

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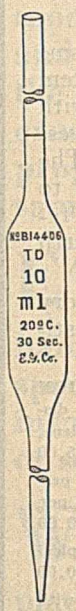

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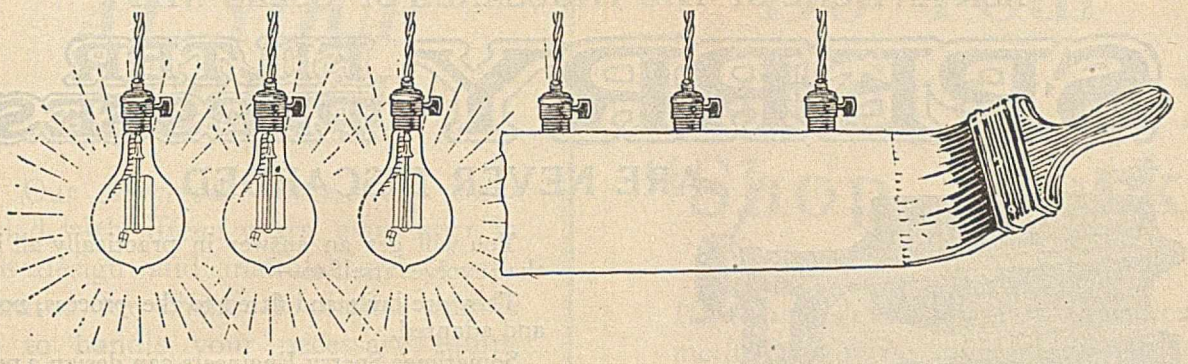

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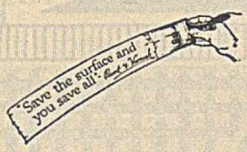
A factory-lighting paint which combines the most scientific achievements in this field is made from



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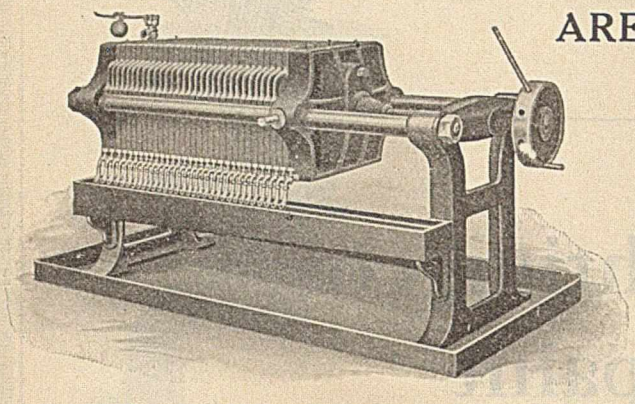

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You will get an answer in practically all instances that evolves itself to—

They are built and fitted to the process, not altered and adapted.

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In the first case the requirements are very similar to those of another press.

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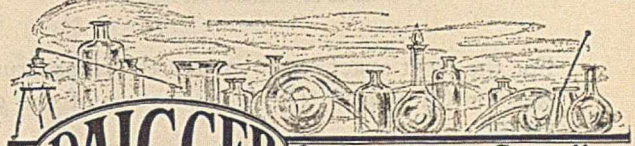

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Note Check your Requirements

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The official printed copies of this patent having been exhausted, the Gulf Refining Company on request will be glad to furnish a reprint to anyone interested.

GULF REFINING COMPANY

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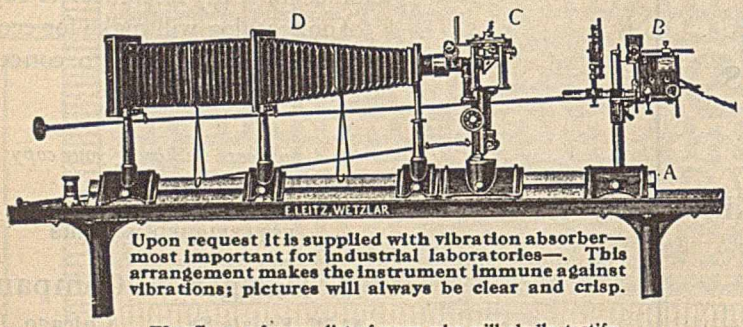
Leitz "Micro-Metallograph"

Large Metal Microscope with Camera



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We offer a reference list of users who will gladly testify as to the merits of the apparatus

The Leitz "Micro-Metallograph" is the only metallurgical equipment which received a distinct recognition at the Panama-Pacific International Exposition, due to its merits and efficiency.

It can be furnished with either of the following optical equipments:

Achromatic Objectives, for routine investigations.

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Boiling Range: 68°–75°C.
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Color: Water White
Purity: 95–100%.

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Boiling Point: 200°C under 29" Vacuum.
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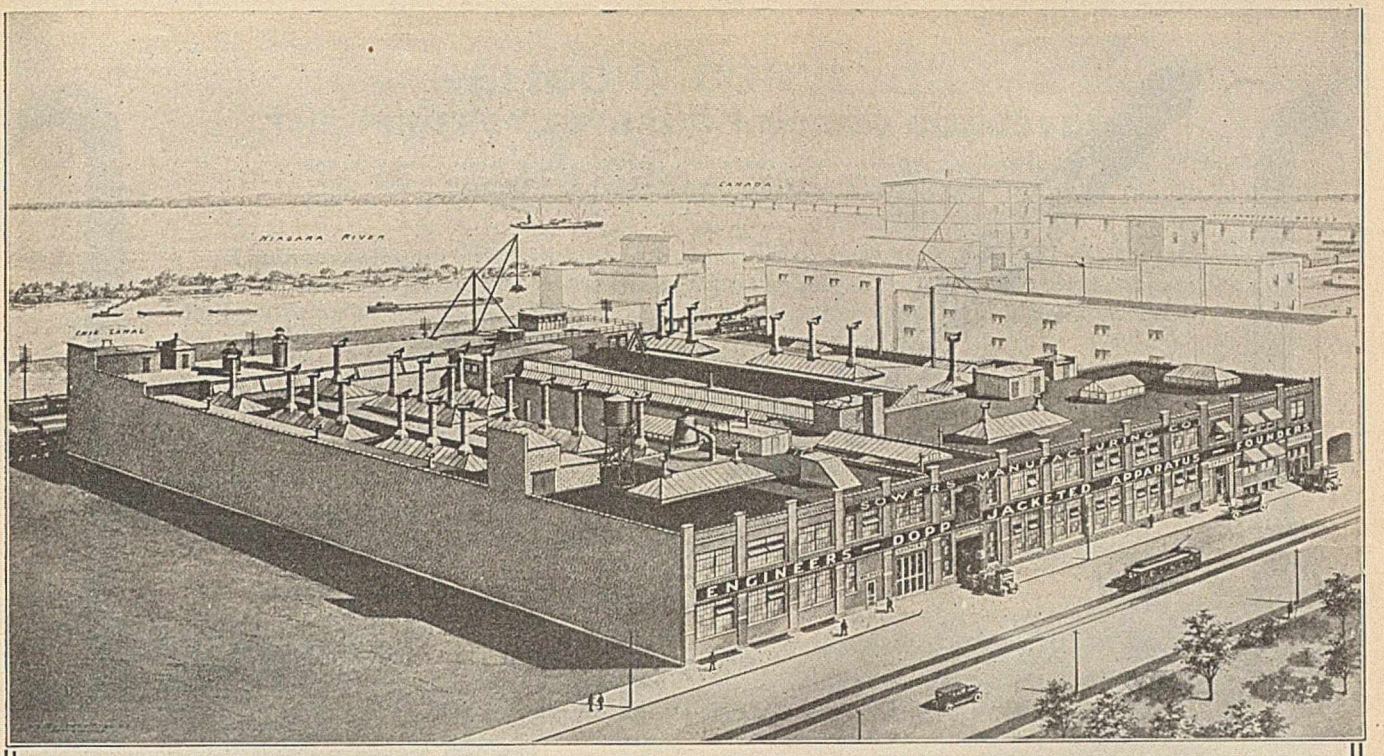

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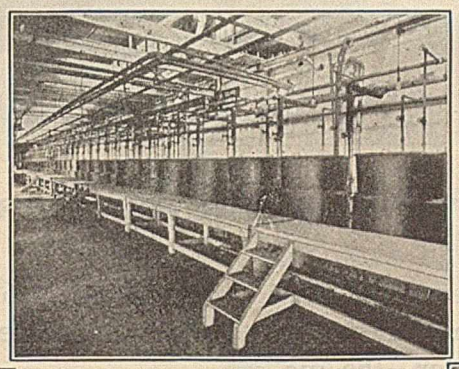

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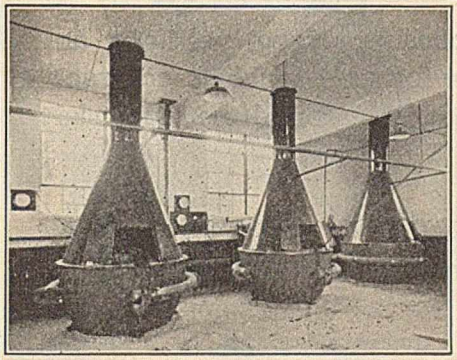

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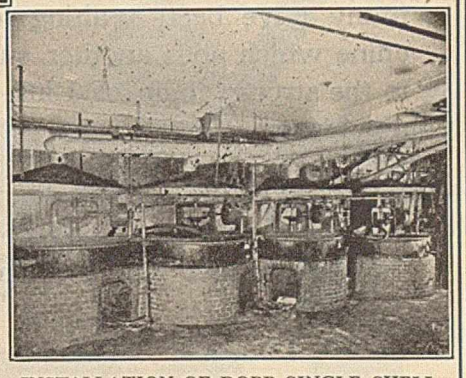

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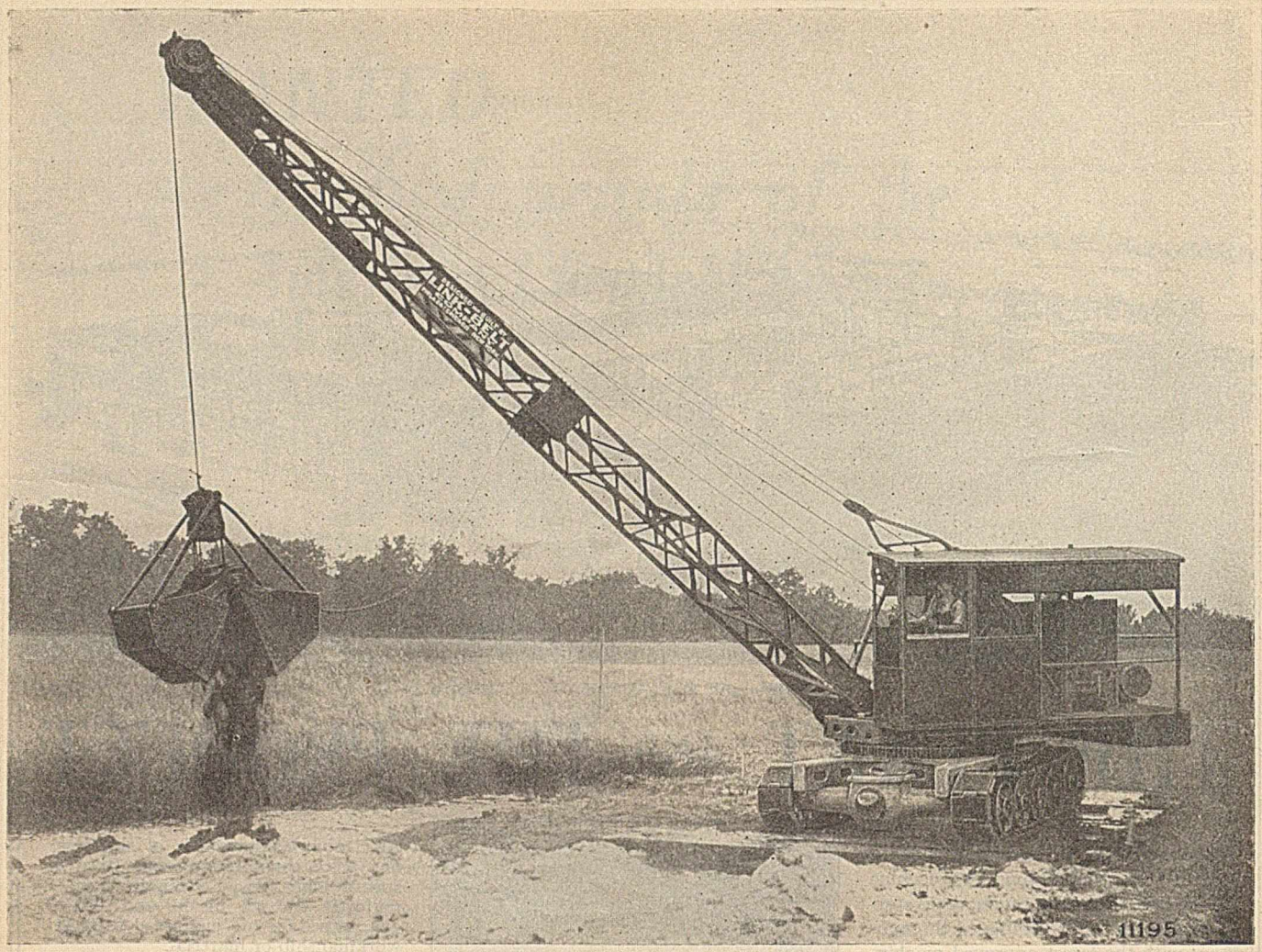

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Flight a true spiral—result of rolling process.	Flights irregular spiral, due to riveted offset joints.
Can run high speed with increased capacity, because perfect spiral.	High speed whips and throws over material.
Outer edge true cylinder—result of rolling process.	Outer edge irregular.
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Outer edge same thickness as corresponding sectional flight, but average thickness greater.	Flight same thickness throughout and no more than outer edge of corresponding Helicoid.
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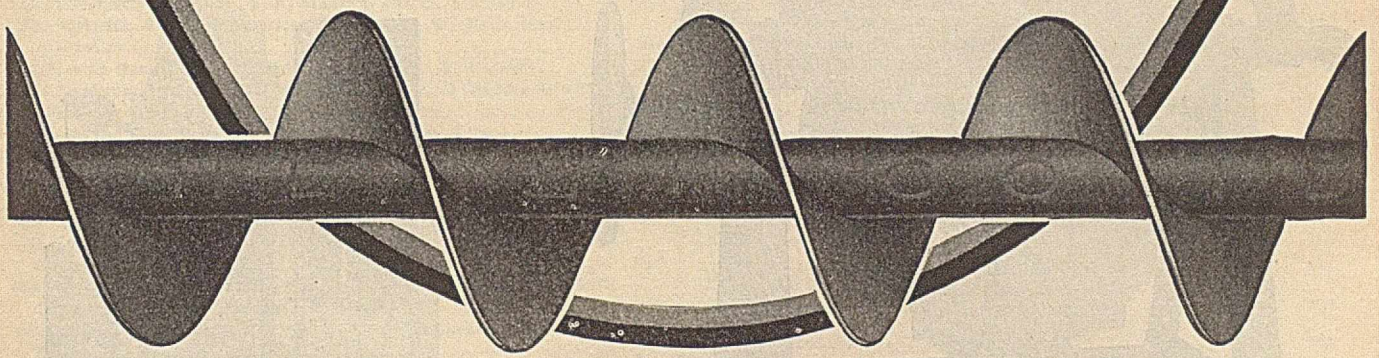

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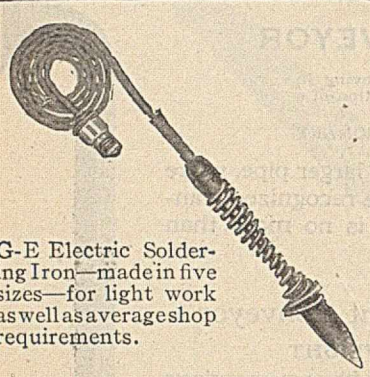

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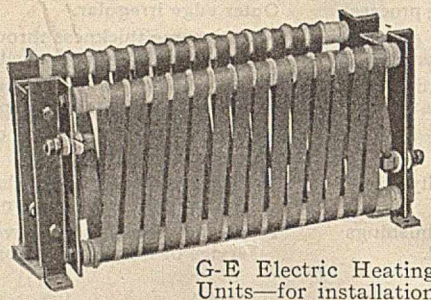

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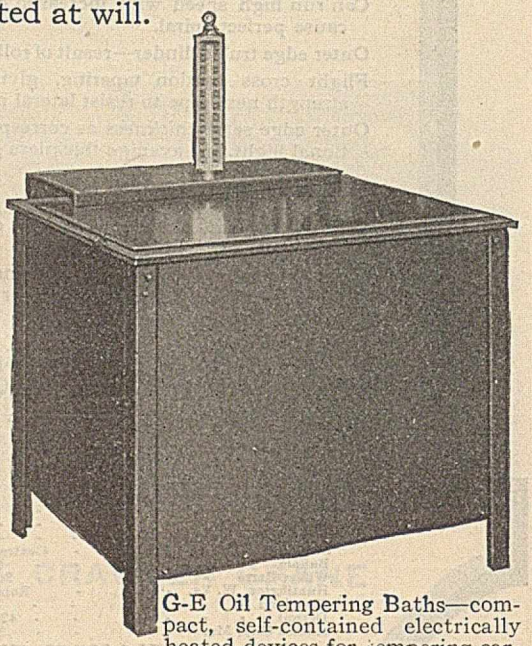

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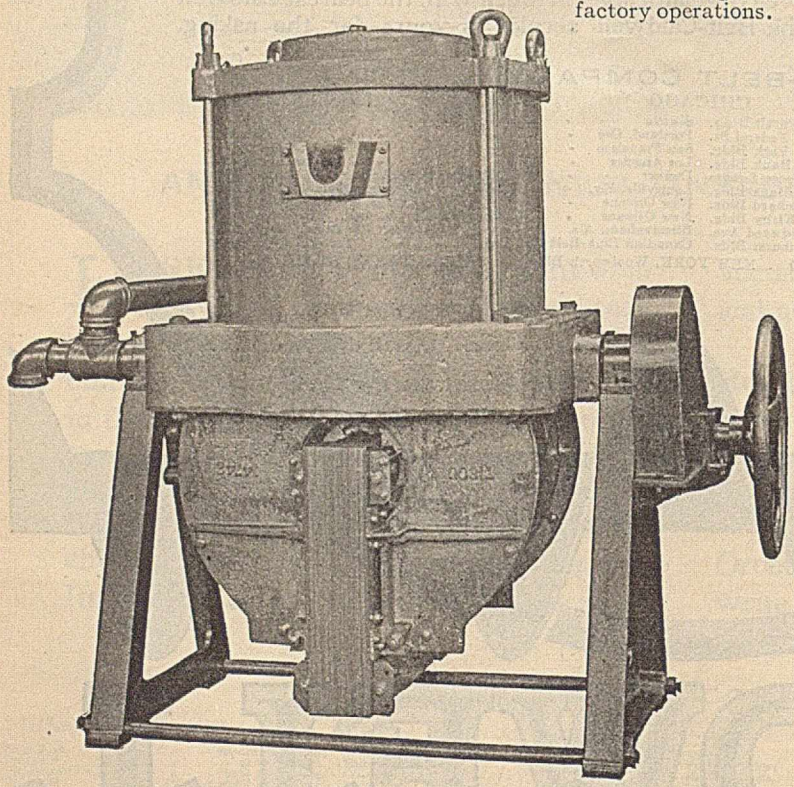

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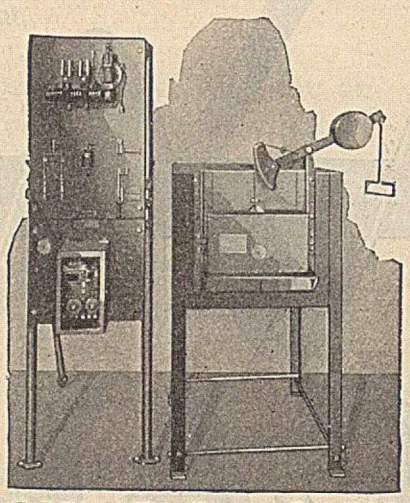

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