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EDITORIALS

Officers for 1923

The newly elected officers of the SOCIETY are:

President
E. C. FRANKLIN
Directors
W. D. BANCROFT
WM. HOSKINS
Councilors-at-Large (1923–1925)
ROGER ADAMS R. H. MCKEE
G. N. LEWIS WM. MCPHERSON

Congratulations!

Plans for 1923

THIS publication was established by the SOCIETY to supply a need, and its mission has always been one of service—service to the science, to research, to the industries, and to the profession. This could not be accomplished but for the whole-hearted coöperation of these very interests which we serve. The Rotary motto, "He profits most who serves best," may well be applied to this enterprise.

It is our aim continually to improve and increase our service. In 1923 we expect to make several giant strides. With this issue our name is shortened and, we think, improved. INDUSTRIAL AND ENGINEERING CHEMISTRY will no doubt continue to be known as the "Industrial Journal," but our new and shorter name will prove an advantage.

Two additional prominent chemists have accepted service on our Advisory Board. This active board takes a real part in shaping our policy and guiding the efforts toward improvement. We shall present several important series during 1923, among them one which will deal with patent law presented from an angle that we believe will be most informing to chemists, and another with various special topics in chemical engineering. Our foreign news is to be extended by letters from other countries. The arrangement of each issue will take into consideration the varied interests of our circulation.

An innovation will be the News Edition, issued on the 10th and 20th of each month. This will effect no material change in the regular or industrial edition, but will bring to our readers much news of passing interest, personal and industrial progress information, legal notes, and many of the activities of local sections and of chemists generally. In a sense the News Edition is to be a chemical newspaper in the publication of which our News Service is to play a leading part. A separate Advisory Board is being formed, correspondents secured in all sections, and arrangements made for a staff, differing from that responsible for the Industrial Edition, to prepare the News Edition.

The News Edition enables the SOCIETY to have at once a method of broadcasting employment information, as voted at the Pittsburgh meeting. A maximum of four pages in each news issue will be devoted to such announcements. Members in good standing are to be given the privilege of four insertions during the year, and local employment committees of sections and educational institutions, from which most of the employment information will come, are expected to perform the personal service which any successful plan for employment promotion demands.

We are to print 1320 pages in the Industrial Edition in 1923. Our ambition is steadily to raise the standard of papers so that authors will deem it more and more of an honor to see their work here. Again we ask the assistance of our readers in perfecting our service. We want to know what displeases as well as what pleases. You can help!

Pace Makers

WHILE each local section of the SOCIETY no doubt has some principal activity, a few examples worthy of emulation have been brought to our attention.

In the December, 1922, *Chemical Bulletin* an editorial states that for several years these sections which support the *Chemical Bulletin* have been of assistance to each other in arranging programs, and securing prominent speakers whose services are available to all coöperating sections. The Committee on Public Representation of the Chicago Section has even assumed entire financial responsibility for several speakers, prorating their expenses among the sections concerned. This same committee has prepared a list of speakers and chemical subjects, which is sent to local civic and social organizations with a letter inviting the recipient to make full use of the list, through the committee, which also assists in developing their programs.

This section is also directly interested, as is the Milwaukee Section, in making chemical information available to the city authorities. A member of the Chicago Section was called into consultation with the District Attorney on a matter of public welfare involving chemistry. He found this officer ignorant of the existence of the AMERICAN CHEMICAL SOCIETY, not to mention the Chicago Section, or the special Committee on Public Representation. The chemist utilized his opportunity and then and there laid the foundation for a close and cordial connection between the District Attorney's office and the Chicago Section.

The Indiana Section holds a weekly luncheon on Tuesday, and by a change in its by-laws has made these noon meetings regular business sessions. This greatly facilitates the transaction of business and leaves the scientific meetings free for discussion of topics presented by the speaker. As a result of the activities of the section, the local newspapers have come to seek the opinions of the section on matters of professional interest and public welfare, many of which are not strictly chemical. Activities in investigating promotion schemes of doubtful worth, efforts to keep in touch with legislation, and a variety of other special endeavors make the section a center of interest.

At Rochester a real advance has been made in handling employment information. The Chamber of Commerce has a chemical committee and arrangements have been perfected whereby the local industries call upon the employment department of the Chamber of Commerce when they desire chemically trained men. The applicants are first investigated by the local section and a decision reached as to whether they are qualified by training and experience for the positions sought. Then when a request for a chemist is received, the firm or individual desiring chemical assistance is given a carefully selected list of applicants from which to make a choice. This unique coöperation bids fair to solve the employment question in so far as the demands of local firms are concerned. The Chicago Section handles its employment problem in a similar manner.

In Cleveland, Pittsburgh, and some other large centers carefully planned and persistent campaigns for an increase in membership have been or are under way and with a result that is most gratifying. These efforts have brought the local sections into contact with many of those interested in chemistry who were not previously known to them, have revealed the attitude of local concerns toward chemistry, and have made it possible to develop constructive policies for the conduct of local chemical affairs.

Some time ago the secretary of the Western New York Section suggested that each section should compile its own history which might be abstracted for publication. Some of these accounts have appeared, the latest being in the *Syracuse Chemist*, which is the monthly publication of the Syracuse Section.

What special activity have other sections to offer?

Research among Trades

One function of Industrial and Engineering Chemistry and our A. C. S. News Service is to create interest in fundamental research and its adequate support. We believe that these activities of the American Chemical Society have had some part in furthering research supported by industry and especially by trade associations. The accomplishments of these associations are too little known, and to show our appreciation of their work and to give our readers even a partial list, we cite below a number of the trade associations engaged upon programs of research.

American Malleable Castings Association, Albany, N. Y.

American Gas Association, 128 E. 15th St., New York, N. Y.

American Institute of Baking, 1135 Fullerton Ave., Chicago, Ill.

American Petroleum Institute, 17 W. 44th St., New York, N. Y.

American Society of Heating and Ventilating Engineers, 29 W. 29th St., New York, N. Y.

Asphalt Association, 25 W. 43d St., New York, N. Y.

Associated Factory Mutual Fire Insurance Companies, 31 Milk St., Boston, Mass.

Associated Tile Manufacturers, Beaver Falls, Pa.

Association of Manufacturers of Chilled Car Wheels, Chicago, Ill.

Biscuit and Cracker Manufacturers' Association, 90 W. Broadway, New York, N. Y.

California Fruit Growers' Exchange, Box 518, Corona, Calif.

Clay Products Association, 113 W. Washington St., Chicago, Ill.

Container Club, 608 S. Dearborn St., Chicago, Ill.

Copper and Brass Research Association, 25 Broadway, New York, N. Y.

Crop Protection Institute, 1701 Massachusetts Ave., Washington, D. C.

Eastern Clay Products Association, 910 S. Penn Sq. Bldg., Philadelphia, Pa.

Glass Container Association of America, 3344 Michigan Ave., Chicago, Ill.

Hollow Building Tile Association, 111 W. Washington St., Chicago, Ill.

Institute of American Meat Packers, 509 S. Wabash Ave., Chicago, Ill.

Laundryowners' National Association, Drawer 502, La Salle, Ill.

Magnesia Association of America, 721 Bulletin Bldg., Philadelphia, Pa.

National Association of Corrugated and Fibre Box Manufacturers, 1821 Republic Bldg., Chicago, Ill.

National Association of Cotton Manufacturers, 45 Milk St., Boston, Mass.

National Association of Macaroni Manufacturers, Braidwood, Ill.

National Canners' Association, 1739 H St., N. W., Washington, D. C.

National Electric Light Association, 29 W. 39th St., New York, N. Y.

National Fertilizer Association, 1010 Arch St., Philadelphia, Pa.

National Lime Association, 918 G St., N. W., Washington, D. C.

National Lumber Manufacturers' Association, 750 McCormick Bldg., Chicago, Ill.

National Glass Container Association, care of C. L. Flaccus Glass Co., Pittsburgh, Pa.

National Gypsum Association, 7647 Greenview Ave., Chicago, Ill.

National Warm Air Heating and Ventilating Association, Columbus, Ohio.

National Varnish Manufacturers' Association, 1845 B St., N. W., Washington, D. C.

National Wood Chemical Association, 76 Main St., Bradford, Pa.

Paint Manufacturers' Association of U. S., 1845 B St., N. W., Washington, D. C.

Portland Cement Association, 111 W. Washington St., Chicago, Ill.

Refractories Manufacturers' Association, Oliver Building, Pittsburgh, Pa.

Silk Association of America, 354 Fourth Ave., New York, N. Y.

Southern Coal Appalachian Operators' Association, Box 687, Nashville, Tenn.

Southern Pine Association, care of J. B. Rhodes, New Orleans, La.

Tanners' Council of U. S. A., 130 N. Wells St., Chicago, Ill.

Underwriters Laboratories (National Board of Fire Underwriters), 207 E. Ohio St., Chicago, Ill.

Our Meeting Programs

A review of past programs clearly indicates that the American Chemical Society has reached the place where more thought must be given to division and section programs. Nothing is gained by having a long list of papers recorded and the time so fully occupied that there can be no discussion; neither is there any advantage in accepting a heterogeneous lot of papers. Often the titles are misleading and do not give a true idea of the real contents of the paper. Even abstracts may be no criterion. The following letter received from one of our members is pertinent:

> At the Pittsburgh meeting over four hundred scientific papers were presented in the various divisional meetings. It was obviously impossible for anyone to hear more than a small fraction of those read. I, therefore, made arrangements to secure a complete set of the authors' abstracts as mimeographed by our publicity service. I found *eighteen* that were of real use to me. It is perhaps not surprising that the number was so small, for each person is naturally interested in a rather special field. That which amazed me most, however, was the rather large percentage of abstracts which, scientifically, were absolutely worthless. If I had not known that these were authors' abstracts, I would have insisted that they must have been prepared by a rather unintelligent office boy or, at least, by someone who had no scientific training.
>
> To illustrate my point—the following hypothetical abstract is a good example of a number of papers, from the title of which I had hoped to gather some interesting information:
>
>> The Preparation of Phosgene by M. I. T. Chemist. The literature on the preparation of phosgene is reviewed. Important defects in the older methods of manufacture are pointed out. By the use of a new reaction and a radical modification of the conventional apparatus, the author has found it possible to prepare an exceedingly pure product at a very low cost.
>
> Perhaps this is a bit extreme, but at least it imparts as much *information* as do many of the authors' abstracts. I contend it is not an abstract; it is not scientific; and it is imposing on the intelligence of the members of the American Chemical Society and of the newspaper reporters to hand out such "statements" as "abstracts." If the author is afraid he will let a little information leak into the abstract, then he should refrain from reading his paper before our Society. If he does not know how to prepare an abstract, I would suggest that he study the next few issues of *Chemical Abstracts* rather intensively. I cannot understand how anyone who uses our abstract journal can fail to appreciate what an abstract should contain. The policy of our *Industrial Journal* of requiring an abstract to be placed at the head of the published paper is an excellent one if for no other reason than that it may assist to train authors to write abstracts. I venture the guess, however, judging from my recent experience, that the abstracts published by Industrial and Engineering Chemistry are not always "authors'" abstracts.

Let us make several New Year's resolutions:

Plan meeting programs a full year in advance. Decide on definite objectives and obtain papers accordingly. Invite authorities to prepare these papers and allocate the time so that there may be real discussion. Take steps to insure this discussion. Do not attempt to cover too much ground at any meeting, but provide for miscellaneous papers by having real analytical abstracts of them presented for discussion.

We decide the place of our meeting a year ahead. Let us likewise plan our programs.

News of Progress

As announced in the September, 1922, issue, we will publish from time to time notes of the progress of applied chemistry in many fields, and we offer several such summaries in this issue.

Interest in the reports published in September reached beyond chemical circles, reprints having been sent to many libraries of chambers of commerce and other centers.

A Central Library of Chemistry

NOTHING is of greater importance to the chemist than contact with the great mass of literature of his profession, yet at present there is no library fully equipped to give him this contact. Throughout the country local libraries attempt, more or less successfully, to serve various branches of industry. Universities and industrial plants maintain libraries that provide workers with the most obvious sources of information, and many public libraries at central points provide some of the best-known reference works. Yet there is not to be found in the United States a complete library of chemical literature.

Probably the nearest approach to a central chemical library is that of the Chemists' Club in New York, but on account of the limited funds available for its support even this falls far short of the ideal. No institution in the country is more accurately representative of the science and practice of chemistry than this club through its seventeen hundred members in all parts of the country, and no institution is better placed to carry out such a service as industry needs. The AMERICAN CHEMICAL SOCIETY has recognized this fact officially by making the club custodian of its library. Service to members of the recognized national societies is provided through translations, abstracts, bibliographies, and photographic reproductions of available material, at a nominal cost. In all other particulars the library is supported by the club itself without outside aid. On this account the funds available for expansion are necessarily limited, and it is with the idea of encouraging support for this worthy institution that a partial list of its needs in the way of periodical literature is published elsewhere in this issue. Will you contribute duplicates from your collection to help fill these gaps?

Licensing Laws

WITH a few exceptions, chemists and chemical engineers believe that the conditions which make it desirable to have architects and land surveyors licensed by law do not apply to chemists, and that opposition to the passage of such laws must be alert and vigorous. Your attention is called to the reiteration of opposition by the AmericanInstitute of Chemical Engineers, as given on page 95.

Some of the reasons why licensing is not favored by chemists are: Selection of an examining board is likely to be affected by politics. It is difficult to secure an examining board capable of passing on the credentials of the many kinds of engineers. Any licensing system is liable to confer, in the mind of the public, a seal of approval on an engineer whether he is competent or incompetent. Under ordinary conditions, without a licensing system, the incompetent engineer does not secure work. No satisfactory statement has yet been made of the benefits which will accrue, through a licensing system, either to engineers or to their clients.

Chemical engineers are not mentioned as such in the various state laws, but they would of course be included in such terms as "professional engineers" and "engineers."

The present status of licensing laws in the various states is shown by the following summary:

Florida, West Virginia, Oregon, Indiana, Minnesota, and Colorado have laws regulating "professional engineering."

Wyoming, Tennessee, New York, South Carolina, North Carolina, and Iowa have laws providing for registration or licensing of persons practicing "engineering" or "engineering and surveying."

Arizona has a law to regulate the practice of the professions of "architecture, assaying, engineering, and land surveying."

Connecticut, Montana, Delaware, New Mexico, Idaho, Illinois, Texas, Wisconsin, and Louisiana have laws regulating "architects, structural engineers, or civil engineers and land surveyors."

Oregon and Florida define professional engineers as "those who practice any branch of engineering other than military engineering."

Nebraska and New Jersey have submitted incomplete information.

Alabama, Georgia, Kansas, Mississippi, and Oklahoma have not been heard from.

Arkansas, North Dakota, Washington, South Dakota, Vermont, Rhode Island, Missouri, Nevada, and Utah have no licensing laws for engineers.

Kentucky, California, Maryland, Ohio, and Massachusetts do not require licensing of chemical engineers.

Michigan and Pennsylvania require the licensing of chemical engineers, but not of chemists.

Members of the AMERICAN CHEMICAL SOCIETY have been prominent in opposing licensing legislation as applied to chemistry and chemical engineers, and will continue to be alert.

Increased Support for Research and Publication

BY ACTION of its Board of Directors, the General Electric Company has set aside a fund of $400,000, to be known as the "Charles A. Coffin Foundation," the income from which, amounting to approximately $20,000 per year, will be available for encouraging and rewarding service in the electrical field by giving prizes to its employees, recognition to lighting, power, and railway companies for improvement in service to the public, fellowships to graduate students, and funds for research work at technical schools and colleges.

The Foundation will be controlled and administered by a Foundation Committee appointed by the Board of Directors. This committee, within the limits of the purposes for which the Foundation is created, will have power to determine the conditions applicable to the distribution of the fund and the amounts for each particular purpose.

We applaud any group which has the foresight to reward research, to encourage qualified men and women to embark upon research as a career, and to support this vital work without expectation of immediate financial return.

What is urgently needed is an endowment fund, the proceeds of which may be used for the prompt publication and wide distribution of the results of research. There is no better way to develop a science, to avoid duplication of effort, and to promote an interchange of ideas. Any one experienced in raising funds knows that money is often available for research but seldom for broadcasting its findings.

The AMERICAN CHEMICAL SOCIETY is admirably equipped to administer and expend such an income in publication.

Earning Power of Research

EVERY experienced chemist can cite many pieces of work which illustrate the earning power of research. We recently heard the following on the train:

When the manufacture of potassium chlorate in electrolytic cells was begun in this country, the yield was about 45 per cent, which was the efficiency generally obtained elsewhere. Research disclosed the fact that if a little calcium chloride were added to the bath the efficiency could be raised to 87 per cent. Such a difference meant a decided cost advantage which was enjoyed for a period of years before another piece of research, conducted in another country, indicated that the same results could be obtained with a trace of permanganate.

Research is often at the very foundation of forming a new enterprise, and an excellent example is that given on page 78.

Physical Chemistry in Industry

By R. S. Tour

University of Cincinnati, Cincinnati, Ohio

PHYSICAL CHEMISTRY, as the name implies, may be considered as that branch of science lying in the great borderland of physics and chemistry where the problems of each become so interconnected that they cannot be separately studied. Pure chemistry as a science has to do chiefly with the composition and constitution of substances and classifies matter in terms of its component elements. The chemist may use specific physical properties or definite energy relations to distinguish compositions or constitutions, yet these characteristics themselves are but the means to an end. Physics, on the other hand, is concerned especially with the properties or the energy relations of matter *per se*, and classifies matter in terms of its characteristic properties. Thus both physics and chemistry are concerned with properties of matter and energy, and for more complete correlation or greater generalization, the problems arising must be studied from both the physical and the chemical standpoint.

R. S. Tour

Towles

It is obvious that these two basic branches of natural science, physics and chemistry, must have a great common ground, and it is logical that this common ground should have first been known as physical chemistry. It is only here that really conclusive generalizations may be drawn, laws formulated and resultant theories propounded. Thus, most of our hypotheses and theories of chemistry and of chemical action have been developed in the realm of physical chemistry. This has been the case to such an extent that physical chemistry, principles of chemistry, and theoretical chemistry have become of recent years practically synonymous. To quote Arrhenius: "The theoretical side of physical chemistry is and will probably remain the dominant one; it is by this peculiarity that it has exerted such a great influence upon the neighboring sciences, pure and applied, and on this ground physical chemistry may be regarded as an excellent school of exact reasoning."

The Beginning of Physical Chemistry

It has been said that chemistry as a science began with Lavoisier in the latter part of the 18th century. It may further be said that Lavoisier was the first great exponent of physical chemistry. He insisted that the balance, an instrument for purely physical measurement, be used for chemical investigation and finally established the "law of conservation of mass." Previous to this time most of the experimentation and research was disorderly and uncoördinated, although Boyle had pointed out in his "Sceptical Chymist" (1662) the unsatisfactory results of the prevailing methods and the importance of the logical application of the principles of experiment and deduction. Yet, as late as 1775, Priestley, the discoverer of oxygen, writes: "More is owing to what we call chance—that is, philosophically speaking, to the observation of events arising from unknown causes—than to any proper design or preconceived theory in this business."

After Lavoisier, more orderly investigations were carried on and far-reaching discoveries in chemistry followed. Dalton attempted to summarize much of the work that had been done before him and in his "New System of Chemical Philosophy," published in 1811, he laid the foundation stones for our physical chemistry or theoretical chemistry. He brought forth an "Atomic Theory" wherein he assumed that matter was composed of "atoms," of fixed characteristic weight, which were simple in the true elements and complex in compounds. He further stated that elements combine in fixed proportions, and formulated what we now know as the "Law of Multiple Proportions."

Physical Chemistry of To-day

The present realm of physical chemistry, i. e., the theoretical chemistry of to-day, may be considered as a still more recent development than indicated above. It dates back perhaps no further than the last half of the 19th century, when the laws of thermodynamics were being established. It has been by the study of the relations of energy and matter that many of the great strides in physical chemistry have been accomplished and that many of our present theories have been developed. The present physical chemistry may be considered as based on three distinct developments: the application of thermodynamic reasoning to chemical problems; the generalized extension of Avogadro's hypothesis; and the rise of the theory of electrolytic dissociation. These three developments incidentally typify the fundamental requirements for a normally rapid growth of any science: exact reasoning, generalized hypotheses, and logical theory.

The requirements for the normal growth of a science, exact reasoning, careful generalization, and logical theory, are also prerequisites to the successful application of the results of any scientific investigation outside of its own sphere. Since physical chemistry demands and fulfils these prerequisites, it is in a large measure responsible for the application of chemistry in the world to-day; and the world benefits by scientific investigation only in so far as such investigation finds application. The individual investigator may, and generally does, derive his reward in a purely psychological medium of exchange, but the community upon which, in some way or other, he must depend for his necessities must be paid many times over for the outlay.

The present status of human knowledge, and that is present civilization, is an evolution of the study of cause and effect. When such study of related phenomena develops generalizations and laws from which in turn other phenomena may be prophesied or explained, civilization has been given a most valuable tool. This tool may or may not have an immediately apparent application to the needs of humanity, but if it gives the scientist a better understanding of his science, or if it aids in the advancement of that science as such, it will lead indirectly to applications which are of benefit to the community.

The Application of Physical Chemistry

The application of the sciences for the benefit of mankind is a true definition of engineering. The sciences are the tools of the engineer. The value of physical chemistry as an engineering tool is sometimes questioned. A few industrial executives still remain who complain that the "theoretical" man is not "practical." As this statement is generally interpreted, it may apply in individual cases. Yet this cannot condemn the value of theory for practical application. Who can deny the value of the phase rule developed by thermodynamic reasoning and mathematics, in the fields of metallurgy or in the industrial operations of distillation or crystallization? Who will question the applicability of the laws of equilibria in reversible chemical reactions? Who doubts the importance of the theory of solutions?

As any problem arises in an industry, it may be attacked in one of two ways, either empirically or scientifically. The former method is that sometimes known as "practical." But, in general, even the so-called or self-styled "practical" man attempts a scientific mode of attack on his problem. As a rule, he will proceed according to some hypothesis or theory that he has developed to fit the particular case in hand. How much better and how much more certain of success he would be if the hypothesis or theory were always based on exact reasoning and correct principles. The truly empirical method of attack, not based on theory or reason, depends for its success on chance. Success may come quickly but the probability of success is generally remote.

No one who has come into contact with the chemical industry will deny that there are to-day too many plants operating under conditions no less than archaic. In these plants will be found the hard-and-fast rule, "let well enough alone." However, such plants or branches of the industry are rapidly changing their methods and policies or are disappearing. Modern competition will not permit of their survival without change. Many executives are to-day searching for men of sound training in fundamentals and principles combined with the ability of applying such training to their respective plants with a view to improving efficiencies.

The Importance of Physical Chemistry

It may be said that industry is interested only in dollars and cents. That is as it should be. Money is merely a medium of exchange and the cost (unfortunately not always the selling price) of a commodity represents the expenditure of energy and labor by the community in return for the use of that commodity. If the cost may be reduced by improved methods or increased efficiencies, the community in the end must gain. The energy or labor saved can be put to other service.

In an attempt to harness natural forces to do man's bidding, it is patent that the best mental equipment is a knowledge and understanding of the laws governing the action of such forces. The chemical engineer, in the application of chemistry in industry, perhaps does not realize to what extent he depends on theoretical chemistry, or to what extent he makes use of the laws and theories that have been evolved in the realm of physical chemistry. He probably never even appreciates that every step he takes is based on fundamental laws, which may seem axiomatic to him but which are the result of laborious work and tireless study on the part of the physical chemist.

In closing one of his treatises, Lavoisier says:

> It is not indispensable, in order to deserve well of humanity and to pay his tribute to his country, that a man should be called to those public and pompous functions which coöperate in the organization and regeneration of empires. The physicist, in the quiet of his laboratory and of his study, can also exercise patriotic functions; he can hope to diminish by his labors the many ills which afflict the human species, and to increase human pleasures and prosperity. And if he should only contribute, by the new methods which he may have shown, to the lengthening of the mean age of man by a few years, or even by a few days, he also may aspire to the glorious title of benefactor of humanity.

Moving Picture Films

The General Electric Co., Schenectady, N. Y., maintains a lecture service to give reliable information on the progress of the electrical industry by means of illustrated lectures and also to provide moving picture films illustrating and describing the manufacture of electrical products and their use. These may be borrowed without charge for exhibition in the interest of commercial development, education, welfare or other purposes acceptable to the company, with the understanding that they are to be used with care and shipped according to instructions after exhibition.

The Pathéscope Co. of America, Inc., New York, N. Y., has recently issued a descriptive classified catalog of educational films for classroom use which may be purchased for $2.00. This book lists and describes a large number of films, including many relating to various phases of chemistry, physics, domestic science and arts, and industry. For greater usefulness, the films are indexed both by subjects and by alphabetical titles.

. . . . .

The following list of films is given as supplementary to those mentioned in our December issue, and further data concerning any of them may be obtained from the editorial office:

Book and Magazine Making

Chemical and Mechanical Experiments (Science at Home)

Electrical and Mechanical Experiments (Science at Home)

From Mud to Mug
Fuel

Gyro-Designer and Smoke Rings (Science at Home)

Improving America's Sheep and Cattle

Mahogany
Making a Fine Watch
Manufacture of Condensed Milk
Manufacture of Evaporated Milk
Motor Cars
Music Factories

Newsprint Paper

Paints, Varnishes, Colors
Power of Clouds

Quicksilver (Science at Home)

See-Saw
Shoes
Shredded Wheat
Silk Industry
Silk Industry in Japan
Silk Industry in Lyons
Snow and Ice
Sonny's Microscope; Microscopic Animalculae
Specific Gravity of Liquids
Spirit of the Corn
Steel
Story of Abrasives
Story of Asbestos
Story of Atmosphere
Story of a Box of Candy
Story of a Cake of Soap
Story of a Loaf of Bread
Story of Lucifer Match
Story of Magnet
Story of a Tire
Story of Coal
Story of Evaporated Milk
Story of Ham
Story of Linen-Making in France
Story of Natural Gas
Story of Oil
Story of Oxygen
Story of Petroleum
Story of Sound Waves
Story of Steel
Story of Sulfur
Story of Zinc
Sugar-cane Industry
Sugar Industry
Sugar Industry in the Hawaiian Island
Sugar Refining
Sweetest Story Ever Told

Tests of Building-Construction Material
Thermit Process
Through the Wonderland of Science
Time
Triplex Process of Making Steel at the South Works of the Illinois Steel Co.

Vacuum-Tube Experiments

War Methods
Water: Crystallization
Water Supply of a Great City
Wave Motion
Welch's Grape Juice
Welding
Why of a Volcano
Wireless Telegraph and Telephone
Wireless Telegraphy
Wonders of the Modern Oil Refinery
Wool
World's First Scientific Harness

X-Rays

Zinc Mining, Milling and Smelting

Recent Progress in the Chemistry of Sirups and Molasses

By F. W. Zerban

Research Laboratories, Penick & Ford, Ltd., Inc., New Orleans, La.

THE SUBJECT matter of this article is so closely interwoven with the chemistry of cane sugar and related carbohydrates that it is somewhat difficult to draw a line between the two. Although many advances in the sugar industry proper have a bearing on the sirup and molasses industry, we will consider here only those that are of direct application.


F. W. Zerban

New Sources of Sirups

The world's demand for food, and particularly for sweets, during the war greatly stimulated the sirup and molasses industry, as it did most others. Not only was the production of the well-established sirups from cane, corn, and sorghum about doubled, but new sources of food sirups were eagerly sought. It was natural that in both Europe and America great interest was aroused in the manufacture of an edible sirup from the cane's closest competitor, the sugar beet. The undesirable flavor of beet sirup, as produced in the sugar factory, had entirely prevented its direct use as a food, but under the circumstances it is not surprising that many attempts were made to prepare a palatable and pleasing product from the beet. A number of patents were taken out, and the importance of the subject at the time is best shown by the fact that a book of 146 pages was written on it by Block. Sherwood, as well as Ort and Withrow, found that those parts of the beet which contain the undesirable flavors in largest amount should be cut off, or that a preliminary extraction should be made before expressing the juice; the flavors that still remain should be removed by heating under pressure and releasing the pressure at intervals. The necessity of using high temperatures was also recognized in Europe, where, in addition, the use of acids for partial inversion was advocated to prevent crystallization and improve the flavor.

While beet sirup seems to have been produced on a large scale only in Europe, the sirup that seemed most promising in this country and really reached the manufacturing stage was maltose sirup, containing up to 76 per cent of maltose and but very little dextrin. It is made by treating starch, modified starch, or starchy materials with malt, and refining, probably with the aid of decolorizing carbon. Maltose sirup is free from malt flavor, sweeter than corn sirup, heavy bodied, and does not crystallize. There have appeared newspaper accounts of other sweet sirups made from corn, but no authentic information has been available.

A very interesting product, in whose preparation malt is also used, is the sweet potato sirup originated by the Bureau of Chemistry, principally with the idea of utilizing culls that are not marketable. This sirup is of pleasing appearance and color, and has a characteristic flavor similar to that of the raw material.

Willaman has proposed the utilization of the inulin of the Jerusalem artichoke, which can easily be grown commercially for the preparation of levulose sirup, the sweetest known sirup. Another interesting suggestion, recently made in Canada, is the hydrolysis of wood waste, and the use of the resulting molasses as cattle feed. A simple method for making invert sugar sirup from dates has been described by Patterson.

New Methods of Preparation or Purification

Unfortunately, the severe business depression of the last two years was unfavorable to a successful conclusion of the new developments just enumerated. Improvements in methods of manufacture of well-established products had a better chance of success under such conditions, particularly where the changes needed did not entail much expense for new equipment. The use of invertase in the manufacture of cane sirup, investigated and recommended by the Bureau of Chemistry, is gaining a foothold in the industry. At least one cane-sirup manufacturer in Louisiana made a large proportion of his output last season by the new method. The process is very simple, but its introduction had been somewhat retarded by the lack of an active invertase preparation at a reasonable price. This difficulty has in large measure been overcome, and a rapid spread of the new method may be expected. The sirup, instead of being boiled directly to full sirup density with about 71 per cent total solids, is first evaporated to only about 45 per cent solids, the invertase added at 55°, the mixture allowed to stand over night, and then boiled to around 78 per cent solids. This sirup, of 35 to 40 per cent purity, keeps without fermenting or crystallizing. The use of invertase is also advocated by Harding for the preparation of invert sugar sirup from cane sugar.

Another promising process, which is being studied in connection with scientific investigations on the colloid chemistry of sugar products, has been given attention by the Bureau of Chemistry and the Louisiana Sugar Experiment Station. This is the use of adsorbents, such as infusorial earth and decolorizing carbons. Tests made by the Bureau of Chemistry on a small factory scale have shown that a clean and bright sirup, of light color and pleasing flavor, can be produced by filtering the entire cane juice with infusorial earth and evaporating *in vacuo*, or in open pans if desired. The additional use of carbon resulted in a sirup which on account of its mildness and very light color "should win favor in those regions where sweetness rather than strongly marked flavors is the quality principally desired." Willaman reports that a sorghum sirup factory in the North is using Filter-Cel for filtering all of the juice, and has experimented with decolorizing carbon also. The flavor of the product is said to be very fine. Decolorizing carbon is now actually used instead of boneblack in at least one large corn-sirup factory, and others are experimenting with its use.

A number of articles and patents have been published on the purification of sugar products of all kinds by means of decolorizing carbons and other adsorbents. Some well-known old processes for the purification of beet molasses have lately been patented again, with a view of using the treated molasses for human food. One of them is the precipitation and removal of potash as acid tartrate, patented by Bonner, and the other the osmosis process, preceded by inversion and followed by boiling in the open, filtration and evaporation *in vacuo*, as patented by Cutler.

NATURE AND COMPOSITION OF SIRUPS AND MOLASSES

The old question of the nature of cane molasses has recently been studied again in Java. Since Prinsen-Geerligs' classical investigations on the subject, cane molasses has been considered as a saturated aqueous solution of chemical compounds between sugars and salts. Van der Linden was the first to reach the conclusion, on the basis of equilibria studies, that cane molasses is in fact a saturated solution of sucrose in nonsucrose; but the work of Kalshoven, done directly after that, called attention to a source of error, consisting of the presence of very fine sugar crystals in Java molasses. Kalshoven devised a method for determining this fine grain by refractometric measurements, and a repetition of Van der Linden's experiments by Helderman, with the necessary corrections, gave further strength to Van der Linden's views. Helderman has since then shown in other ways that Java molasses does not contain any chemical compounds between sugars and salts at ordinary temperature. Tiemann maintains that the chemical molasses theory still holds for beet molasses.

As in most technical fields, colloid chemistry has lately begun to play a more important part in the sugar branch. Much of this work, particularly that on juice clarification, belongs to both the sugar and the sirup industry, and is therefore mentioned here only in passing, such as the adsorption theory of clarification developed at the Louisiana Sugar Experiment Station, and similar work by Dedek, Harloff, Herzfeld, and others. The Bureau of Chemistry has also taken a leading part in this field by applying dialysis and ultrafiltration to the determination of colloids in sirups and molasses, as well as to the isolation of gum from beet molasses and from diseased sugar cane. This method has made possible a close chemical study of these gums. Helderman and Khainovsky in Java have found that the colloids in cane molasses, though small in quantity as determined with the ultramicroscope, have a decided effect on the viscosity. Treatment of the molasses with infusorial earth or decolorizing carbon reduces not only the color, but also the colloids and with them the viscosity. It was also shown that carbonation produces molasses of lower viscosity, lighter color and with a smaller number of colloid particles than does ordinary liming. Unfortunately, the ultramicroscope is not very reliable when dealing with emulsoids.

The coloring matter of sirups and molasses has also received a greater amount of attention since the advent of decolorizing carbons. Investigations made at the Louisiana Sugar Experiment Station have shown that the color of cane products made according to best practice is almost entirely due to the presence of polyphenol compounds and their iron combinations. These polyphenols are derived from constituents of the cane itself, belonging partly to the true tannins, whereas others originate in the anthocyanins of the rind and the saccharetin of the cane fiber. Only in overlimed products is a large part of the color due to the effect of lime on reducing sugars in the presence of amino acids, and in overheated products to condensation products of the sugars. The color of commercial cane sirups and molasses, even those produced on the same plantation, often varies considerably, but average analyses of large numbers of individual samples have shown that there is a distinct tendency toward a mathematical relationship between color and purity.

A very unexpected and surprising result has lately been announced by Sale and Skinner. They conclude from carefully conducted tests that, contrary to generally accepted belief, invert sugar sirup is about 11 per cent less sweet than the cane-sugar sirup from which it is derived.

The precipitate that is always found when clarified cane juice is evaporated to sirup has been studied by Brewster and Raines, who have found that its composition varies considerably; however, its total quantity increases with the amount of soil adhering to the cane when it is milled, and the precipitate is probably largely derived from that source. Vinson and Catlin have shown that the ash in sorghum sirup from dry lands is not any higher than in that from regions of greater rainfall.

Browne has made the interesting observation that molasses and similar sugar products separate into layers, on standing, the lower ones showing a higher proportion of ash and organic nonsugars. This proves the importance of thorough mixing of samples to be analyzed.

ANALYSIS

The determination of total solids in sirups and molasses is still in an unsatisfactory state, because there is no absolute method. Considerable progress has been made, however, toward greater relative accuracy and toward speed. A rapid and easy method of actual drying in a specially constructed electric oven has been devised by Spencer. Proper conditions for the drying of beet products on sand have been worked out by Aikin. Newkirk has designed a pycnometer by which the specific gravity of molasses can be determined quite accurately. The use of the refractometer for determining apparent solids is increasing. At least one sirup and molasses company uses this instrument exclusively in its factory control; tests recently made by a corn-sirup concern have shown that the solids determined by refractometer agree more closely with solids by drying than those determined by the common hydrometer method. The refractometer has also been found to be well suited for the analysis of maple products. Atkinson recommends a wider use of the instrument on account of accuracy, convenience, and speed, and a committee has been appointed by the Sugar Division of the SOCIETY to revise the tables of refractive indexes of solutions of various sugars. The refractometer is also used in the determination of fine grain in molasses by Kalshoven's method. The latter has been critically studied by Dedek, Kraisy, von Lippmann, and Schoorl, and there is still difference of opinion about the correct procedure to be followed. Unfortunately, the Baumé scale is still widely used in the sirup and molasses trade, usually without specifying whether the "old," the "new," or the latest Bureau of Standards scale is meant.

The error in sucrose determinations in cane molasses due to excessive dilution on account of dark color, and to well-known other causes, has been overcome by Walker (revised by Brodie), who uses Horne's dry subacetate of lead and removes the excess of lead with free phosphoric acid in small enough quantity not to cause measurable inversion. Kalshoven and Sijlmans get light-colored filtrates by the use of basic lead nitrate, followed with aluminium sulfate. Saillard, who has lately again brought forward arguments in favor of his "neutral" double polarization method for beet molasses, reports that differences between direct polarization and Clerget value in these products are caused principally by optically active nitrogenous substances, and change from year to year with the nature and quantity of the latter.

Bakker has successfully applied the inactivation method of reducing sugars by means of alkali to the determination of sucrose in honey. Methods based on the titration of dextrose with iodine are coming into more extended use. More concordant results have been obtained in this way in the analysis of potato-starch sirup than by the use of Fehling's solution, and the method has also been applied successfully to the analysis of honey. A complete scheme for the analysis of technical invert sugar sirups has been published by Bruhns.

A method for the determination of raffinose in beet molasses by the enzyme method has been described by Paine and Reynolds, and the acid method has been revised by Jackson. Schecker states that the most reliable results are obtained by first concentrating the raffinose through repeated precipitation with barium hydroxide, treating with carbon dioxide, and then determination by the Herzfeld method.

Viscosity determinations on molasses have been made with the Fischer viscometer, as compared with the Engler instrument, and with a modification of the Arndt viscometer. The dialysis method of the Bureau of Chemistry for determination of colloids, and of gums in particular, has already been mentioned. The hydrogen-ion method of measuring acidity superseded titration in the corn-sirup industry, and the work of Brewster and Raines has paved the way for its introduction in the cane-sirup industry also.

It has lately been found that the commonly and officially accepted correction factor in the determination of sulfated ash in cane sirups and molasses is erroneous; the factor is not constant, and is nearer 20 per cent than 10 per cent. There is no need of using the sulfated ash method at all, as the direct ash method is in most cases just as rapid and convenient and requires no empirical correction factor. Adkins and Withrow have shown that, if the sulfated ash method is employed, it should be carried out with dilute instead of concentrated acid.

Since the introduction of decolorizing carbons the determination of color in sirups and molasses has become of great importance. The Bureau of Standards has therefore inaugurated a fundamental study of the light transmission of sugar products, and has already worked out a reliable method for color determination. The ordinary color matching instruments have been found to be of no value for the purpose, and some sort of spectrophotometer must be employed.

According to Kauffman, caramel determinations in sirups and molasses are meaningless, and the only method that has any value for comparative purposes is that of Ehrlich. Determination of electrical conductivity by Snell has found an important application in the detection of adulteration of maple sirups. The question of detecting the presence of technical invert sirup in honey has not been definitely settled; a new simple test, using resorcinol and β-naphthol, has been described by Litterscheid.

UTILIZATION

The Steffen method of extracting sugar from beet molasses is now universally used in this country. Potvliet has shown, however, that the baryta process (used in Canada) and the strontia process have certain advantages over the Steffen method. The lead saccharate process, experimented with two years ago in Michigan, has evidently been abandoned again. Other, old and new, methods of sugar extraction from molasses are at intervals suggested and patented, but none of them seems to have found favor of late.

The profitable disposal of the large quantities of final waste molasses from both cane and beet is quite properly receiving more and more attention. The two main reasons for this activity are the threatened danger of a scarcity of gasoline in the not distant future, and the low price of molasses since the close of the war period. In certain tropical countries gasoline is already so expensive that the use of automobile fuels containing material percentages of alcohol has become an actuality. The alcohol produced from molasses is very simply and easily converted into a practical motor fuel by the admixture of ether which is made from part of the alcohol produced. Pyridine, kerosene oil, and ammonia are the common denaturants. Wherever the new fuel has been carefully manufactured, it has proved a complete success. In the United States conditions have not yet advanced to the point where alcohol motor fuels can successfully compete, but interest in the matter is constantly increasing, as is well demonstrated by the large number of patents, and technical as well as popular articles on the subject.

In Europe a number of chemical products are now being manufactured from beet molasses and in this country some work has been done along the same lines. Special fermentation processes, or dry distillation, followed by chemical treatment, are being used or have been proposed for the production of acetone, glycerol, methanol and higher alcohols, fatty acids, ammonia and the methyl amines, methyl chloride, cyanides and other salts of soda and potash, and similar chemicals. Some of these, such as glycerol, butyric acid, nitrogenous compounds, and potash salts can also be made from the distillery slops. The production of potash from the latter was a thriving industry during the war, but has come to a complete standstill again. Whitaker advocates the use of silicon fluoride or hydrofluosilicic acid as a bactericidal agent in fermentation, and also for precipitating the potash from the molasses itself, instead of making it from the slops.

While the manufacture of fuel alcohol from molasses represents the largest potential market of the future, molasses may be profitably utilized in other ways. Arnstein suggests a larger use of molasses for the manufacture of yeast. The foodstuff market absorbs considerable quantities of molasses, whenever it can compete with grain. As a direct fuel, molasses has in most cases been disappointing, but von Stietz has recently designed a special furnace which will burn the molasses properly. Molasses is used as a fertilizer with good results in Mauritius, whereas in other places it has been found of little or no value. Mixtures of molasses with other residual products have lately been tried out in Java, likewise with very poor results.

This account would not be complete without mentioning the "Reading List on Molasses," compiled by C. J. West, comprising a complete bibliography on the subject up to 1920.

Further progress in the sirup industry, particularly cane and sorghum, will probably be in the direction of standardization, and of the manufacture of products that have an appearance and flavor acceptable to the consumer outside of the restricted area where these sirups now enjoy their greatest popularity. The use of molasses will gradually increase as time goes on and as gasoline becomes scarcer, and it is not beyond the range of possibility that the molasses, now a drug on the market, may yet rival coal tar in value as the source of a variety of important chemicals.

Royal Society Medal Awards

Among the awards made by the President and Council of the Royal Society (England) are: The Copley medal to Sir Ernest Rutherford, for his researches in radioactivity and atomic structure; the Rumford medal to Prof. P. Zeeman, for his researches in optics; the Davy medal to Prof. J. F. Thorpe, for his researches in synthetic organic chemistry; the Buchanan medal to Sir David Bruce, for his researches and discoveries in tropical medicine; and the Hughes medal to Dr. F. W. Aston, for his discovery of the isotopes of a large number of the elements by the method of positive rays. The Royal medals have been awarded to Mr. C. T. R. Wilson, for his researches on condensation nuclei and atmospheric electricity; and to Mr. J. Barcroft, for his researches in physiology, and especially for his work on respiration.

Chemical Progress in Cane-Sugar Manufacture

By Guilford L. Spencer

The Cuban-American Sugar Co., New York, N. Y.

IT MIGHT appear at first glance that chemistry has played a small part in the development of the cane-sugar industry. This is true as far as its applications in processes are concerned, but the chemist, in his control at all stages from the materials of equipment to products and by-products, has done much to advance the manufacture.

Lime is still the only chemical used in making raw sugar, as was true twelve centuries ago in Egypt. Lime and sulfurous acid, or lime, sulfurous and carbonic acids are used in making plantation-white and near-white sugars. These three reagents are the only ones that enter directly into the current processes. Sodium carbonate is occasionally, but not usually, used to assist in the elimination of the lime. Caustic soda and hydrochloric acid are employed in cleaning the heating and evaporating surfaces. Vegetable carbons are used to a limited and probably increasing extent, in the direct manufacture of white sugar. Animal charcoal is now used only in decolorizing refinery liquids. It is probable that more than 90 per cent of the world's cane sugar is made with lime as the only chemical entering the process.

The limited use of chemicals is not due to the lack of suitable reagents, but to the small possible margin of profit in changing existing methods. Unless some revolutionary process is developed that will eliminate much of the effort in the present juice treatment, evaporation, and purging of the sugar, present methods may be expected to persist. The French have long looked to alcohol to revolutionize the manufacture. More than sixty years ago they purified sorghum-cane juice with it, removing the gums by precipitation; and over thirty years ago the U. S. Department of Agriculture used it similarly in treating sorghum sirup. The French later carried the process further, and, after a preliminary alcoholic precipitation of the gums, continued the addition of alcohol for the nearly complete precipitation of the sugar. Thus, a method was developed that eliminated several of the present operations and directly produced crystallized sugar. This is an example of a perfectly feasible process that so far has proved too expensive for its application, or is hedged in by too strict governmental restrictions.

Other precipitation processes are possible, such as the calcium, strontium, barium, and lead saccharate methods, but none has yet been applied in regular manufacture. These processes are practicable from the commercial view only in their application to the molasses residue obtained in the present process. This residue is approximately $3^1/_2$ per cent of the cane worked. The calcium saccharate process of Steffen is used by many of the American beet factories, but has only been tried experimentally with cane molasses. The molasses from the beet usually contains no reducing sugars or but traces of these, whereas that from the cane may contain as much as 25 per cent, or even more, dextrose and levulose. In a direct treatment of cane molasses, the reducing sugars would be largely precipitated with the sucrose and with no manufacturing advantage. Reducing sugars in solution made alkaline with lime may be destroyed by heating. After this treatment, the sucrose may be precipitated as a saccharate, and, after removing the metallic base by carbonation, be recovered by crystallization. The market value of molasses has been large enough to deter the use of precipitation processes, but recently the price has been so small that large quantities of the by-product have been run to waste, and these processes may be considered. A precipitation process was developed and patented by Batelle,[1] in which the reducing sugars are destroyed in the juice instead of the molasses.

It seems like wilful waste to destroy the fermentable reducing sugars in order to recover the sucrose, which at most is about 35 per cent of the material. Possibly some selective fermentation method may be found to utilize the reducing sugars and make the sucrose available. Alcohol and ether are now produced at low cost in the tropics, and are used as motor spirit. Tropical countries can utilize very large quantities of alcohol and ether in the motors of tractors for plowing and general haulage. The conversion of the molasses into alcohol and ether would therefore apparently provide a profitable means of disposing of the by-product, and leave little opportunity for precipitation processes.

The ash resulting from burning the bagasse for fuel is rich in potash, but in a combination that is insoluble in water and of little value as a fertilizer. A low-cost method of rendering the potash salt soluble would be valuable. No doubt considerable quantities of potash could be recovered from the flue gases by electrical precipitation.

Von Lippmann,[2] in 1909, published a list of 622 proposed processes for sugar manufacture. Several processes have since been reported, and he doubtless omitted many, but of this long list few have persisted, as is indicated at the opening of this article. Possibly the reason for failure in many cases is the small margin of profit, even if nearly all the sugar were recovered. The value as sugar of all the sucrose left in average molasses, at present market price, is about 85 cents per ton of cane. The present market price is probably higher than may be expected when Europe again produces fully. It is easily conceivable that a fall in the price of sugar and a rise in that of molasses would leave little encouragement for a larger recovery of sugar, if a new process were involved.

There has been considerable progress in the mechanical equipment of the cane factory, especially in the development of mills, the handling of cane, and the settling of juices. The experiments in diffusion nearly forty years ago under Dr. H. W. Wiley in Washington, Kansas, and Louisiana, spurred mill builders to better design and resulted in demonstrating the economic superiority of mills. These developments could hardly have been possible without the chemists' control, from the foundry mixtures of mill rolls and other elements of the machinery to the bagasse from the last mill of the train. Boiling-house methods have progressed along such lines that laboratory control is imperative. The modern cane factory is chemically controlled at every stage of the manufacture, and an increasing number of factories require the superintendent and his principal assistants to have a good chemical training.

Summarizing, there has been little chemical progress in the treatment of the juice of the cane, no chemicals are used at other stages of the manufacture, but the reasons for present usages are much better understood. There has been great progress, however, in mechanical equipment at all stages of the manufacture, and often with the assistance of the chemist. The construction of the mills, the grooving of their rolls, the delivery and feeding of the cane to the mills, the

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[1] Special Report, Hawaiian Sugar Planters' Assoc., **1913**.

[2] *Deut. Zuckerind.*, **34** (1909), 9.

settling devices for juices and parts of the evaporation have markedly improved in the past ten years. A grinding capacity of 2500 tons of cane per 24 hours per train of mills was thought to be near the maximum with high efficiency, in 1912. There are now single trains of mills that will grind 3600 tons of cane with even higher efficiency. There has been great progress in factory output. In 1912 there was but one factory with an annual capacity of 85,000 tons of sugar; in the present year, several factories have largely exceeded this output and one has produced 170,000 tons of raw sugar. These increases are largely due to progress in mill design and construction.

The Manufacture of Sulfuric Acid

By L. A. Pratt

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Chamber Process

During the last ten years there has been a determined effort to intensify the production of acid by the chamber process, and to this end numerous improvements have been made in the methods of chemical control and in the design of "sets" and their accessories. During the war the production of chamber plants was greatly enlarged by increasing the proportion of nitrogen oxides to sulfur dioxide in circulation. This leads to higher niter losses and larger repair charges, and is therefore not applicable to these times. As a result, chemical engineers are devoting their efforts to changes in design which will afford a better mixing of the gases and a more efficient removal of the heat of reaction, with a view to minimum unit cost of investment, operation, and maintenance.

The Falding[1,*] high chambers are built to utilize the mixing of gases by convection currents caused by the heat of the chamber reactions. The saving in cost of lead and ground space is, however, offset by the extra cost of construction of the high chambers. There is no adequate provision made for the condensation of the acid mist.

Gaillard[2] uses, in place of the usual chambers, lead towers built in a slightly conical form, truncated, and having the larger diameter at the top. A hollow shaft extending inside the tower through the closed top serves for the introduction of a small stream of cold, dilute sulfuric acid which falls onto a revolving channeled disk located on the lower end of the shaft. The cool acid is projected against the upper part of tower, down which it flows in a cooling and protective film. The speed of the disk is sufficiently great to cause some of the acid to rebound and fall in a fine, heavy rain to the bottom. It is claimed that this rain serves to thoroughly mix the gases and to condense the acid formed in the tower. It is further claimed that the temperature throughout the tower is readily controlled, thus increasing the efficiency as well as the life of the apparatus.

The Mills-Packard[3] system, which was developed in England, has as its object the water cooling of the lead surface of the reaction chambers. The chambers are built in the form of truncated cones down the outside of which runs a continuous stream of cooling water. Plants of this design have been erected by 23 companies, in England, France, Italy, and New Zealand. The first two chambers were erected in 1914 and the number has increased to 112 at the present time. The results of actual operation have shown that a set of this type can be successfully operated on 3.66 cu. ft. of chamber space per pound of sulfur burned per 24 hrs., with a niter consumption of 3.62 per cent. The cost of construction is materially lower than in old style sets, and the life of the lead should be longer because of the efficient water cooling. None of these chambers has been built in this country as yet, so far as the writer knows. According to the published results, this system is one of the important developments in chamber acid manufacture. There is no special provision for thorough mixing of the gas in this design, but it is reported that modifications are being considered which may further increase the efficiency of this system.

Several types of "intermediate" or "reaction" towers have been brought forth, the purpose of which is to both cool and mix the reacting gases. These are inserted between the chambers and offer a large amount of contact surface. One of the most successful types is designed by the Chemical Construction Company and consists of a lead-lined tower packed with spiral rings. Results of careful tests in a set where the tower space is equal to 7 per cent of the total chamber space, have shown that 33.5 per cent of the "make" of the plant was produced in the intermediate towers. The efficiency of the chambers alone was 10.7 cu. ft. per lb. of sulfur, and of the chambers plus the tower capacity was 7.6 cu. ft. per lb. sulfur. Larger intermediate towers are now being designed with a view of cutting down the chamber space proportionately.

A patent was recently taken out by C. H. MacDowell[4] which covers the spraying of a large amount of dilute sulfuric acid (in place of water) into a chamber set for cooling purposes. The necessary amount of sulfuric acid is continuously drawn from the chamber pans, diluted, cooled, and re-sprayed into the chambers. It is reported that the capacity of the plant where this process was tested over a period of 6 mo. was increased 40 per cent, making it possible to operate the set on $6^1/_2$ cu. ft. of chamber space per pound of sulfur burned with a 3 per cent niter consumption.

A radical departure from the use of large reaction chambers is embodied in a process patented by Opl[5] in 1908, and in two processes which have recently been patented and are now being tested in this country. The Opl process is carried out in a series of six towers. In the first three towers the sulfur dioxide gas comes in contact with a descending stream of nitrosylsulfuric acid dissolved in concentrated sulfuric acid. Denitration of the acid takes place just as in the ordinary Glover tower and simultaneously the sulfur dioxide is oxidized. The last three towers are for the absorption of the oxides of nitrogen evolved in Towers 1, 2, and 3. By this arrangement it is claimed that 1 lb. of sulfur may be burned per 2.1 cu. ft. of tower space per 24 hrs. About 30 of these systems are in operation in Europe.

A recent British patent by P. Parrish[6] and The South Metropolitan Gas Company claims to double the efficiency of the Opl process by passing the reacting gases through a 4-in. layer of nitrosylsulfuric acid.

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[*] The numbers in the text refer to patent references at end of the article.

The tower process developed by E. L. Larison[7] of the Anaconda Copper Mining Company is known as the "packed cell" process. The gases from the Glover tower are passed through a set of towers constructed of acid-proof brick and filled with a checkerwork of the same material. Cold acid of 48° to 50° Bé., in which neither sulfur dioxide nor oxides of nitrogen will dissolve, is run down the checkerwork, thus effectively controlling the temperature at the points of reaction. The thorough mixing and cooling, together with the extremely high niter circulation (equivalent to 70 pts. sodium nitrate per 100 pts. sulfur), causes very rapid reaction. A large Gay-Lussac space is necessary for recovery of the oxides of nitrogen. It is claimed that the cost of construction of the packed cell plant is only 50 to 60 per cent of a well-constructed chamber plant. It is doubtful whether there would be so great a saving in construction in most localities. The cost of maintenance and the efficiency of niter recovery are points in question.

The other procedure referred to above is the "tube" system patented by Kaltenbach.[8] In this development, the chambers are replaced by series of lead pipes, the pipes in each unit being connected in parallel. They are approximately 31 in. in diameter and may be packed with Raschig rings. The gases pass up around the rings while a regulated stream of cold dilute acid flows downward. The advantages claimed are:

1—Ease of temperature control.
2—Rapid dissipation of heat in close proximity to place of its generation.
3—Intimate contact between the reacting gases and liquids.
4—Elimination of water atomizers.
5—Flexibility—any tube may be cut out to change the capacity or to effect repairs.

Results of operation of a commercial unit are not available at the present time.

Several other processes have recently been patented. T. Schmiedel and H. Klencke[9] have covered the spraying and mechanical mixing of nitrosylsulfuric acid into sulfur dioxide gases.

R. E. Dior[10] has protected a design consisting of a series of chambers each resembling an inverted funnel, the sides of the upper portion being more nearly vertical than those of the lower section. The gases are said to move through each chamber in a spiral fashion.

C. J. Reed[11] heats a mixture of air, sulfur dioxide, and oxides of nitrogen, absorbs the gaseous reaction products in concentrated sulfuric acid, subsequently removes the oxides of nitrogen from solution and recovers concentrated sulfuric acid.

G. Mirat and P. Pipereaut[12] have designed a set with a series of small lead chambers and with several special features.

METHODS OF INTRODUCING NITROGEN OXIDES—There are four methods in use for supplying nitrogen oxides in the ordinary chamber process: (1) potting niter; (2) adding nitric acid in the Glover tower; (3) spraying sodium nitrate solution into the first chamber; (4) catalytic oxidation of ammonia.

In the potting of niter, there has been a decided tendency toward the installation of the pots outside the flues, thus necessitating the use of fuel to fire them. This change has come about largely because of the accumulation of niter cake in the flues by the older process. In the opinion of the author there is little trouble from this source if the niter pots are properly designed.

The use of nitric acid in the Glover tower is excellent for companies having a supply of weak nitric acid at their disposal. Care should be taken to obtain a constant flow of the nitric acid and a uniform distribution over the tower.

The spraying of sodium nitrate solution into the first chamber has been used successfully by certain concerns, notably fertilizer manufacturers, where the contamination of the sulfuric acid with sodium sulfate is not objectionable. The sodium nitrate solution must be carefully strained and the spray nozzles kept in good working order so that liquid nitric acid will not be formed in the pan of the chamber.

Oxidized ammonia gas is being used in certain countries where the price differential of nitrogen is sufficiently in favor of ammonia. This process has been adopted in England and the details have been carefully worked out. It is doubtful whether it will gain much headway in the United States, in the near future. Two of the large companies in this country have, however, installed the process in one or two of their plants for the purpose of collecting data. The argument has been used that it affords a saving in labor, but this is certainly not true in cases where only one man per shift is employed in operating a chamber set which includes potting the niter as well as running the sulfur burner and controlling the process. In isolated cases, where the niter cake formed in the niter pot process is a waste product, it is possible that the ammonia oxidation process may find favor.

RAW MATERIALS FOR SULFUR DIOXIDE—For nearly 20 years prior to 1914, pyrites was the great raw material for the production of sulfur dioxide. During the war it was impossible to obtain anything like the required amounts of Spanish pyrites, and American manufacturers were forced to return to the use of brimstone. New sulfur fields have been opened up ensuring a sufficient supply of excellent brimstone, and there seems to be very little desire on the part of manufacturers in this country to return to the use of pyrites. The higher purity of acid produced from brimstone, coupled with the simplicity of operation and lower labor requirements, are factors in favor of the continued use of sulfur.

Large amounts of sulfuric acid are manufactured from the gases produced in the roasting of copper and zinc sulfide ores. One of the notable developments for utilization of waste gases from copper blast furnaces is the large plant of the Tennessee Copper Co., at Copperhill, Tenn.

IMPROVEMENTS IN DESIGN OF SULFUR BURNERS, DUST PRECIPITATORS, TOWERS, AND ACCESSORIES—Since sulfur so largely displaced pyrites in this country, the design of a burner suitable for the combustion of the brimstone became important. The Tromblee and Paul burner, better known perhaps as the "Glen Falls" burner, has found great favor and is highly satisfactory.

In many plants employing roaster gases or pyrites as a source of sulfur dioxide, the Cottrell electrical precipitator has been installed for removing the dust. This process has been modified and improved to a high state of efficiency. It has also found valuable use in the precipitation of fume from the stacks of sulfuric acid concentrators.

The development of the acid-proof masonry Glover and Gay-Lussac towers without the use of lead curtains is worthy of special mention. The use of towers of this design will be watched with considerable interest during the next few years.

Water has very largely displaced steam for furnishing the necessary moisture in the chambers and several very satisfactory spray nozzles have been developed for atomizing the water into the chambers.

In the concentration of sulfuric acid, some very important steps have been made in the direction of higher efficiencies and greater stability of apparatus. Special mention may be made of the Gaillard, the Mantius, and the Gilchrist concentrators. The latter has had a very rapid development in this country, particularly for the concentration of acid from the sludge acid produced in the refining of petroleum. It is well designed, embodying several new principles, and has shown excellent thermal efficiencies over long periods of operation.

Contact Process

There are four contact processes in successful operation: the Badische, Mannheim, Grillo-Schroeder, and Tentelew systems. Very few improvements of recent date have been recorded in the manufacture of contact acid. H. F. Merriam[13] has patented a process which consists of drying the air used for combustion of brimstone. This procedure permits the passage of the hot burner gases to the converter after being slightly cooled to the proper temperature. The advantages claimed are: (1) conservation of heat; (2) simplicity and stability of apparatus; (3) longer life of contact mass because of the elimination of sulfuric acid mist.

F. Slama and H. Wolf[14] have patented a catalyst consisting of vanadium oxide deposited on pumice or kieselguhr. A 96 per cent conversion of sulfur dioxide to sulfur trioxide is claimed with this catalyst.

W. A. Patrick[15] proposes a process for the conversion of sulfur dioxide to sulfur trioxide catalytically by passing the gases through silica-gel previously treated with certain metallic salts. The process has not been tried out on a commercial scale as yet but experimental work has been in progress for some time.

Patent References

1—U. S. Patent 932, 771 (1909).
2—Fr. Patent 528, 080.
3—U. S. Patents 1, 112, 546 (1914); 1,312,741 (1919); 1,312,742 (1919).
4—U. S. Patent 1, 402, 941 (1922).
5—U. S. Patent 1, 012, 421 (1911).
6—Brit. Patent 156, 328 (1921).
7—U. S. Patents 1, 334, 384 (1920); 1, 342, 024 (1920).
8—Brit. Patent 159, 156 (1920).
9—Brit. Patent 149, 648 (1920).
10—Brit. Patent 164, 572 (1920).
11—U. S. Patent 1, 363, 918 (1920).
12—Brit. Patent 163, 030 (1921).
13—U. S. Patent 1, 384, 566 (1921).
14—U. S. Patent 1, 371, 004 (1921).
15—Brit. Patent 159, 508 (1921).

Stabilizing the Sulfur Market for Chemical Industry

By Harold S. Davis

Arthur D. Little, Inc., Cambridge, Mass.

THE STABILITY of any industry is greatly influenced by the degree of accuracy with which the prices of the raw materials it needs can be predicted. Sulfur, owing mainly to the ever-increasing usefulness of sulfuric acid, has become one of the basic elements for chemical industry. Let the reader consider for a moment whether, if the price of sulfuric acid were to double in the next few years, the particular organization with which he is affiliated would not be adversely affected by the rising price of some necessary raw material. It is therefore a great satisfaction to be able to predict a stable sulfur market in America for at least the next ten years, with almost complete independence of production and consumption in foreign countries.


Harold S. Davis

The Past

Up to the present century, only negligible quantities of sulfur were mined in the United States and practically the world's supply came from Sicily. The deposits in this island contained originally about 65 million tons of sulfur available for mining.[1] More than half of this has now been mined. The total sulfur recovered up to 1885 was estimated at 10 million tons and 13.6 million long tons were exported from 1885–1919.[2] About one-quarter of the sulfur mined has been lost in processing, a factor which must be considered in estimating the value of the supplies that remain.

In the past the methods of mining were very crude, manual labor being employed for the most part in transporting the ore from the pits to the surface. Even to-day, thousands of children still work in the Sicilian mines.[3] The methods used for separating the sulfur from the ore were also very wasteful.

It is true that scientific methods of production and conservation have been to some extent introduced into the Sicilian sulfur industry, but the cost of mining the deposits is of necessity rather heavy. The ore, containing only 10 to 20 per cent of sulfur, must all be transported to the surface before the sulfur can be recovered. The resulting product contains 2 to 11 per cent of impurities, and for most purposes must be further refined by distillation. To-day this sulfur must compete with the American product which, by one process, is brought to the surface nearly 100 per cent pure and which is handled at the mines, transported to the seaboard and loaded on ships entirely by mechanical means.

The plain fact seems to be that no large quantity of Italian sulfur can be mined and sold to-day in free competition with the American product, even in Europe, except at a loss.

The Present

America now dominates the world's sulfur industry. She owes the position primarily to the daring genius of Hermann Frasch, who originated and developed the method of mining which made available the vast supplies of sulfur existing in the so-called "salt domes" of the Gulf coastal plain. In the Frasch process, the sulfur which exists in great beds about 800 to 1000 ft. below the surface is melted *in situ* by means of superheated water and then raised to the surface in a molten condition by means of an air lift.[4]

The basic Frasch patents expired in 1908 and to-day three large and well-financed companies are utilizing his methods for mining. One company is in Louisiana and two are in Texas. In addition a new company apparently well financed has recently entered the field. All the essential features of the process as it is still used were worked out by Frasch. However, some of the companies have employed the highest

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[1] *J. Soc. Chem. Ind.*, **7** (1888), 140.

[2] *Mineral Ind.*, **1** (1892); **9** (1900); **13** (1904); **21** (1912); **38** (1919); Thorpe's "Dictionary of Applied Chemistry," **5** (1913), 287.

[3] *Eng. Mining J.*, **112** (1921), 138.

[4] This Journal, **4** (1912), 134; Bacon and Davis, *Chem. Met. Eng.*, **24** (1921), 65.

technical skill in the control of their operations and have effected unexpected economies in the consumption of fuel which constitutes the main operation cost. The Texas Gulf Sulfur Company maintains a large-sized model of its deposit in which all the mining operations are carefully checked so that its engineers are able constantly to visualize what is taking place underground.

Those who uphold the principle of the conservation of natural resources may feel assured that little of the sulfur in these vast deposits will be lost to industry.

It was mentioned above that crude Sicilian sulfur contains a large percentage of impurities. The American sulfur mined by the Frasch process has a degree of purity that is extraordinary. Think of sulfur being pumped out of the ground over 99 per cent pure at the rate of over 500 tons a day from one well. Furthermore, average well samples taken over considerable periods have, when freed from moisture, analyzed over 99.9 per cent pure.

The sulfur, however, almost invariably contains traces of petroleum oil, and this gives rise to effects which occasionally lead the consumer to believe that the sulfur is fairly impure. This oil is dissolved in the sulfur to form a true solution and is not easily removed. Even minute traces have an adverse effect upon the burning properties of the sulfur in an open dish because of the asphaltic film that forms on the surface. However, special methods have been devised which completely overcome any difficulties encountered in burning.

THE FUTURE

Estimates vary as to the amount of sulfur in the domes which are now being mined, but it is reported that in some cases reliable drill tests have shown over 10 million tons in a single deposit which may be raised by present equipment. It seems likely that more sulfur-bearing domes will yet be discovered.

There exist in addition great surface deposits of sulfur in the United States and in other parts of the world. In some localities transportation costs provide a margin on which these can be successfully worked for a local market even to-day. In 1920, however, 1,255,000 long tons of sulfur were mined in the United States and of this quantity 99.5 per cent was produced in Texas and Louisiana.[5]

It would require a rather substantial rise in the price of fuel to put the margin of profit again in favor of the exploitation of surface deposits, so that it seems likely that the supply of sulfur for America, if not for the world, will be drawn from the Gulf Coast domes for the next ten years and probably longer.

NEW USES FOR SULFUR

Unquestionably, the use of sulfur for purposes old and new will steadily increase. Those properties which suggest certain possible uses for sulfur in large quantities are its exceptional insulating qualities, its resistance to being wetted by water, and its inertness toward most acids, all combined with a fair degree of physical strength.

Engineers are naturally and properly conservative about the introduction of new materials into construction work. Still, sulfur is about as easily handled as asphalt, so that when concrete and other materials fail, they will do well to keep in mind this old familiar substance which is now so readily available.

[5] *Chem. Age* (*N. Y.*), 30 (1922), 231.

Problems in the Determination of Physical Properties

In preparing for publication the data on physical properties of chemical substances, the editorial staff of International Critical Tables, 1701 Massachusetts Ave., N. W., Washington, D. C., will find from time to time that important physical properties of substances of technical and scientific importance are missing from the literature. As fast as they become aware of missing data of this character, it is their policy to formulate research problems covering such missing data and to endeavor to interest chemists and physicists in undertaking the necessary investigations to supply the required data.

Most of the research problems formulated in this way will be suitable for bachelors' or masters' theses and in a few instances topics sufficiently broad to be suitable for doctors' theses will also be available. Many of them will be suitable for experimental problems in the ordinary laboratory courses in physical chemistry and physics. Thus, for example, the laboratory experiment covering the determination of solubility might to advantage deal with substances whose solubility is needed but is unknown. The average of the determinations made by a class of students, while not as accurate and reliable as the determinations made by a skilled investigator, will nevertheless be very valuable when they constitute the only data available on the subject. Moreover, the average student will be more interested in laboratory experiment, the results of which are of actual value and worthy of publication, than he would be in repeating for the nth time the measurement of a property of some system which has been measured many times before.

International Critical Tables will be glad to submit to interested instructors in universities and colleges lists of problems of this character and to advise as far as it can concerning suitable apparatus and methods of measurement. It may be possible also in some instances to secure moderate financial assistance to aid in the purchase of materials and apparatus for investigators interested in carrying out work of this character. The results of such work may be published by the investigator in any appropriate publication medium, and they should also be reported in duplicate to the office of International Critical Tables on completion of the work.

A number of problems on the following subjects are available at the present date:

Heats of combination: solid oxides, iron compounds.
Specific heats: brass, solid oxides, steels, oils and fats, petroleum products, metals, salts, iron compounds, asphalts.
Latent heats of fusion: brass, metals.
Heat conductivity: steels.
Latent heats of vaporization: petroleum products.
Viscosities: industrial materials, solutions.
Kinetics: rates of drying, hydrolysis of industrial materials, catalysis, transpiration of moisture, biochemical.
Strength: industrial materials.
Thermal expansion: steels, iron compounds.
Freezing-point-solubility diagrams: salts, acids, metals in water, soaps.
Boiling points: solutions.
Solubility of gases: in molten metals, in water.
Chemical equilibrium: dissociation pressures at 1600° C.
Electrical conductivity: metals, refractories.
Properties of colloidal systems: industrial materials.
Vapor pressures: metals, solutions.
Specific rotary power: gliadin.
Index of refraction: solids.
Density: certain organic compounds, solutions.
Flash points.
Surface tensions: solutions.

The Electrochemistry of Organic Compounds[1]

By Alexander Lowy

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THE APPLICATION of electricity to organic chemistry is not new but comparatively undeveloped. Experimental work dates back to the beginning of the 19th century. As early as 1807, Grotthus electrolyzed an alkaline solution of indigo-white and obtained the characteristic blue precipitate on the surface of the anode. Although many papers have been published on the electrochemistry of organic compounds, up to date very few commercial processes have been worked out. Patent literature reveals the fact that up to 1910 approximately 100 patents were granted in this field, 89 of which were taken out in Germany. Only a limited amount of research work has been done in this particular line, especially in the United States. Within the last few years the Swiss, German, and Japanese journals have contained many articles on this subject.


Alexander Lowy

In comparison with inorganic chemistry, this phase of organic chemistry is practically undeveloped. Provided the same impetus is followed in the electro-organic field as in the electro-inorganic field, within the next decade we will undoubtedly see new methods for the preparation of organic compounds, perhaps new industries will be developed and thereby substitute electrical energy for more expensive chemical reagents to effect certain organic reactions.

In conducting experiments for the preparation of organic compounds by the electrolytic process, the organic compound can act as an electrolyte, as in the case of organic acids, salts of these acids, etc., but in most cases, the organic compound is a nonelectrolyte. If the organic compound is a nonelectrolyte or one of very low conductivity, an electrolyte must be added in order to produce electrolytic effect. In order to accomplish this, inorganic acids, bases or salts are generally utilized. Upon electrolyzing the mixture, the ions migrate to their respective electrodes and are discharged. At the moment of their discharge to the atomic or molecular state, a reaction takes place and the carbon compound is acted upon by the primary or secondary products of the electrolysis. The carbon compound acted upon by this means is called a "depolarizer." If the organic compound is added to the catholyte it is known as a "cathodic depolarizer;" if to the anolyte, as an "anodic depolarizer." Depolarizers may be dissolved or suspended in the electrolyte. In the electrolytic oxidation of anthracene to anthraquinone, sulfuric acid is the electrolyte and anthracene is the anodic depolarizer. In the electrolytic preparation of *p*-chloroaniline, hydrochloric acid is the electrolyte and nitrobenzene is the cathodic depolarizer. For the preparation of organic compounds direct current is generally used. The utilization of alternating current has hardly been touched upon.

Many organic compounds can be prepared electrolytically by the following type reactions: oxidation, reduction, halogenation, synthesis, etc. Since at the anode, oxygen or halogens may be evolved, by using certain inorganic electrolytes, oxidation or halogenation can be effected; while at the cathode, hydrogen is evolved, thereby effecting reduction. Since oxidation, reduction, halogenation, substitution, etc., reactions are used extensively in organic chemistry, oxygen, hydrogen, and halogens generated electrolytically could be used to produce the same reactions during the course of the electrolysis in place of more expensive chemical compounds.

Reduction of organic compounds by means of electrolysis has been more thoroughly investigated than oxidation and substitution reactions. Reduction of an organic compound generally takes place at certain reducible groups in the molecule without further destroying the latter. On the other hand, oxidation of organic compounds is far less selective and takes place by degrees. Possibilities exist between a slight attack of oxygen and the complete destruction of a compound. Therefore, in conducting experimental work for the preparation of an organic compound, it is absolutely necessary to note all possible details of the variable factors affecting the course of the reaction.

The following are the important variable factors which affect the course of reactions, yields and the selective depolarizations of organic compounds: current density; concentration and conductivity of electrolytes; concentration of the depolarizer (organic compound); temperature of bath; diaphragm; dimension of electrodes; composition of electrodes (overvoltage effect); e. m. f. of cell; structure and shape of

Nitrobenzene in the Cathode Compartment

Cathode Compartment	Anode Compartment	Electrodes	Current Density in Amperes	Voltage	Temperature	Time in Ampere Hours	Product
Alcohol + twice its weight of 25% H_2SO_4	25 per cent H_2SO_4	Lead	4–5	3.7–4	65°–80°	35	Aniline
Concentrated H_2SO_4	Concentrated H_2SO_4	Platinum	6–8	7–8	30°		*p*-Aminophenol
3 per cent sodium hydroxide	15 per cent sodium sulfate with very little H_2SO_4	Anode, lead Cathode, nickel	5–6	6–8		22	Azoxybenzene
70 per cent ethyl alcohol with sodium acetate	Cold saturated sodium carbonate solution in porous cell	Anode, platinum Cathode, nickel	6–8	8–9		30	Azobenzene
70 per cent ethyl alcohol with sodium acetate	Cold saturated sodium carbonate solution in porous cell	Anode, platinum Cathode, nickel	First 6–8 then 2–3	8–9		35	Hydrazobenzene
Concentrated hydrochloric acid	20 per cent H_2SO_4	Platinum	1.5–2	5–6.5		50	*o*- and *p*-chloroanilines

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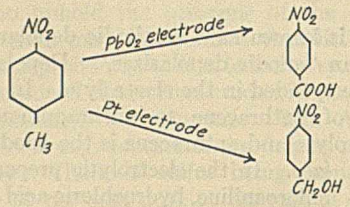
[1] Extracts from lectures presented before the Cincinnati, Cleveland, and Pittsburgh Sections of the American Chemical Society, 1921–22.

electrodes; relative position of electrodes; rate of addition of organic compounds; time of electrolysis; overvoltage effect; use of catalysts, and stirring.

A few examples given below show the effects of the abovementioned variable factors in producing certain organic compounds under specific conditions.

Effect of Electrodes



Effect of Electrodes $CH_3OH \xrightarrow{\text{Bright Pt. anode}}$ 80 Per cent yield of HCHO
$\xrightarrow{\text{Platinized Pt.}}$ Less HCHO – More CO_2
$\xrightarrow{PbO_2}$ All to CO_2

Effect of Alkalinity and Acidity of Bath $C_2H_2 \xrightarrow{\text{in alkali}} HCOOH$
$\xrightarrow{\text{in acid}} CH_3CHO \rightarrow CH_3COOH$

Effect of Concentration of Electrolyte $CH_3OH \xrightarrow{\text{in N. } H_2SO_4}$ 80 Per cent yield of HCHO
$\xrightarrow{\text{in 3N. } H_2SO_4}$ No HCHO

Effect of Voltage $C_2H_5OH \xrightarrow{\text{1.33 volts}}$ Only CH_3CHO
$\xrightarrow{\text{1.66 volts}}$ Only CH_3COOH

Effect of Catalyst Anthracene $\xrightarrow{\text{without catalyst}}$ Small yield of Anthraquinone
$\xrightarrow{\text{with } Ce_2(SO_4)_3}$ 100 Per cent yield of Anthraquinone

Effect of Current Density Iodoform $\xrightarrow{\text{1 Amp/dcm.}}$ Current efficiency = 95 to 97 Per cent
$\xrightarrow{\text{2 Amp./dcm.}}$ Current efficiency = 80 to 93 Per cent
$\xrightarrow{\text{3 Amp/dcm.}}$ Current efficiency = 73 to 79 Per cent

Effect of Electrode Camphor $\xrightarrow{\text{Hg cathode}}$ Borneol
$\xrightarrow{\text{Pb cathode}}$ No reduction

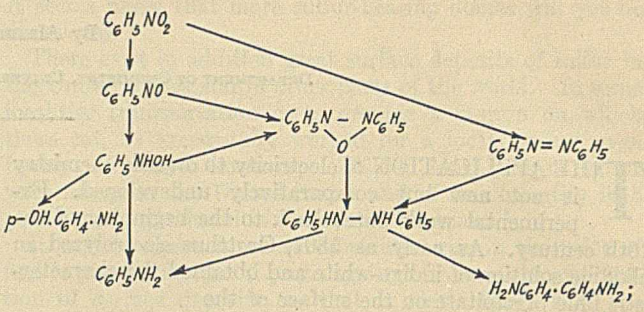
The study of these variable effects, although complex to a certain extent, shows them to be within range of experimental manipulation, and foreshadows great possibilities for the utilization of electricity for the preparation of certain organic compounds.

The following are some of the aliphatic compounds that have been prepared by electrolysis: formaldehyde from methanol with an 80 per cent yield; chloral; propionic acid from *n*-propyl alcohol with a 90 per cent yield; aldehydes from primary alcohols; ketones from secondary alcohols; halogenated acetone; isopropyl alcohol from acetone; chloroform, bromoform, and iodoform (industrial process); hydrocarbons; esters, etc.

In the aromatic series there is a more fruitful field for research for the preparation of intermediates, dyes, drugs, developers, etc. Among the aromatic products prepared by electrolysis, the following are listed:

o-Toluidine from *o*-nitrotoluene; benzaldehyde from toluene; *o*-nitrobenzyl alcohol from *o*-nitrotoluene; anthraquinone from anthracene; vanillin from isoeugenol; benzoquinone from benzene; *o*-amidophenol from *o*-nitrophenol; malachite green color base from its leuco base; eosin from fluorescein; saccharin from *o*-toluenesulfonamide; terephthalic acid from *p*-toluic acid; piperidine from pyridine; *p*-amidophenol from nitrobenzene, etc.

The reduction of nitro compounds gives the following types:



It has been reported that a number of these compounds have been made in Germany on a commercial scale by means of electrolytic methods. During the war several tons of *p*-amidophenol were made in this country by the electrolytic reduction of nitrobenzene.

As to future possibilities, the field for the utilization of electricity for the preparation of certain organic compounds is unlimited. A few of the topics listed below will be investigated in the near future at the University of Pittsburgh.

1—The oxidation of toluene to produce a good yield of benzaldehyde.
2—The oxidation of nitrotoluenes to nitrobenzaldehydes.
3—The oxidation of *o*-cresol to salicylic aldehyde and acid.
4—Oxidation of leuco bases of dyestuffs to their color bases and dyes.
5—Oxidation of hydrocarbons to aldehydes and acids.
6—Halogenation of aromatic hydrocarbons.
7—Use of catalysts in electro-oxidation processes.
8—Nitration and sulfonation with dilute nitric and sulfuric acids, respectively. During the electrolysis of dilute solutions of these acids concentrated acids are produced on the surface of the anode; therefore nitration or sulfonation of the organic compound can take place.
9—Utilization of both the anode and cathode compartments of an electrolytic cell for simultaneous oxidation and reduction reactions.
10—Use of alternating current.

The following advantages may be given in connection with the utilization of electricity for the preparation of organic compounds:

1—Electric current produces changes in place of expensive oxidizing and reducing agents, such as PbO_2, CrO_3, $SnCl_2$, etc.
2—Only electrical energy is used.
3—No by-products of inorganic chemicals to remove.
4—It is easy to manipulate, provided conditions have been worked out.
5—The use of both the anode and cathode compartments simultaneously in order to obtain full current efficiency.

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Recent Developments in the Organic Chemistry of Arsenic

By W. Lee Lewis

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ARSENIC-CARBON compounds have gained a peculiar place in man's troubles, war and disease. This, together with the fact that arsenic in an organic compound does not interfere with many typical organic reactions, has maintained a considerable volume of research in this field the past two years.

Much of this material is obviously an extension or an elaboration of certain war-time studies on organic arsenic compounds used or proposed as military weapons. Thus, Morgan and Vining[1,]* have further studied the preparation of the cyanoarsines, obtaining a 90 per cent yield from $(Ph_2As)_2$ and $Hg(CN)_2$ at 250° C. McKenzie and Wood[2] used $(Ph_2As)_2O$ with HCN and prepared the same diphenylcyanoarsine in 90 per cent yield. Pope and Turner[3] similarly report improvements in the preparation of triphenylarsine from arsenic chloride, phenylchloride, and sodium, and in the conversion of the resulting tertiary arsine into the primary and secondary chloroarsines. Matsumiya[4] has studied this method of preparing the tertiary arsine, comparing it with the action of the Barbier-Grignard reagent on arsenic chloride. By the latter method he obtained 70 per cent yields as against 20 per cent yields by the sodium method. Contardi[5] has made a thorough report of the large-scale manufacture of the war "gas" known as "D. M."—namely, 6-chlorophenarsazine—making it from the primary materials arsenic oxide, hydrochloric acid, and aniline. Wieland[6] has made a long series of derivatives of this compound, preparing the oxide, the methyl ether, acetate, the tertiary amine, the *N*-methyl and various nitro and amino derivatives. The analogous 6-chlorophenoxarsine, from arsenic trichloride and diphenyl ether, was first made by Pope in the hope that it might possess properties similar to "D. M." Its various derivatives, as the oxide, sulfocyanate, arsinic acid, etc., as well as the related 7-chloro-7,12-dihydro-γ-benzophenarsazine and its derivatives, have been studied by Lewis[7] and his students.

The very interesting β-chlorovinyl arsines prepared by the action of acetylene upon arsenic chloride in the presence of aluminium chloride have been reviewed by Green and Price.[8] The marked vesicant action of the β-chlorovinyl dichloroarsine and the gradual loss of this effect in the secondary and tertiary members, apparently paralleling the presence and amount of chlorine on the arsenic, are noteworthy in view of the theory of the action upon tissue of vesicants of the type of mustard gas and the chloroarsines. This theory postulates the absorption of the lipoid-soluble compound with subsequent hydrolysis and liberation of hydrochloric acid in the aqueous phase of the cell. It is interesting that in the β-chlorovinyl arsines the halogen attached to doubly bound carbon is apparently not hydrolyzable, as is to be expected from the usual chemical inactivity of such halogen.

Steinkopf[9] has found the thiocyanates of secondary chloroarsines, prepared, for example, from dimethylchloroarsine and sodium thiocyanate, quite stable, but the corresponding derivative of methyldichloroarsine and other primary chloroarsines could not be prepared.

Job[10] has employed the instability of the As-CN linkage in a patent for the preparation of arsenated acids and amides. Thus, the intermediate cacodyl nitrile with dilute sulfuric acid yields dimethylarsino formic acid.

Arsphenamine Research

Early Investigations—By far the larger portion of recent research in the arsenicals has had in view the preparation of new pharmaceuticals designed to overcome the imperfections of arsphenamine and its variants. Arsenic in inorganic form was employed in the treatment of syphilis as early as the 16th century. Cacodylic acid, discovered by Bunsen in 1842, was the first form in which organically bound arsenic demonstrated its lesser toxicity with continued activity of the element. Murphy[11] first used the sodium salt in America in certain forms of syphilis with promising results, and despite subsequent proof that its American popularity was unwarranted, it is still in minor use. Variations of this product are "arrhenal," in which a methyl group of sodium cacodylate is replaced by the NaO group, and the more recent "mon-arsone" in which the methyl group of "arrhenal" is replaced by an ethyl group.

Bechamp in 1860 prepared arsanilic acid, whose sodium salt, "atoxyl," and acetylated derivative, "arsacetin," each had a limited vogue in medicine. Ehrlich and Bertheim's studies on "atoxyl" in 1907, leading to the correct formula of this substance as an analog of sulfanilic acid, was the beginning of that remarkable series of syntheses which produced "spiraysl," No. 418, the sodium salt of arsenophenyl-*p*-glycine; arsphenamine, No. 606 (1910), the dihydrochloride of 3,3′-diamino-4,4′-dihydroxy-arsenobenzene; "neoarsphenamine," No. 914, the sodium formaldehyde sulfoxylate of arsphenamine; and "sodium arsphenamine," No. 1206, the disodium derivative of arsphenamine.

Present State of Research—Despite the vast amount of work, chemical and pharmacological, since carried out on the arsenicals, it is remarkable that we still do not possess adequate methods of analysis, that we are not sure of the structure of many leading compounds, such as neoarsphenamine itself, and that we cannot distinguish primary toxic properties, those inherent in the compound, from secondary, those resulting from variations in the preparation or administration of the drug. Toxic samples cannot be distinguished by chemical tests from nontoxic. The nature of the impurities in the preparations, the production of a uniform substance, and the best method of administration, are still unsolved problems. We have neither expanded nor confirmed Ehrlich's dicta as to the relation of structure to physiological effect—i. e., the toxophoric character of trivalent arsenic and the haptophoric nature of an amino group ortho to hydroxyl. Of the many new organic compounds of arsenic for which antisyphilitic claims are made, it is significant that but five are officially licensed by the Treasury Department of the United States—i. e., arsphenamine, neoarsphenamine, sodium arsphenamine, an arsphenamine derivative containing phosphorus (4,4′-dihydroxy-arsenobenzene-3,3′-phosphamic acid, No. 1116 of Mouneyrat's series) and called phospharsenamine or "galyl," and finally silver arsphenamine. Multiplicity of trade names does not indicate a corresponding fertility in the scientific field, for arsphenamine appears in the United States under the trade names of "salvarsan," "arsenobenzol," "diarsenol" and "arsaminol;" sodium arsphenamine as "sodium diarsenol," and "salvarsan sodium;" neoarsphenamine as "neosalvarsan," "neodiarsenol" and "neoarsaminol;" silver arsphenamine as "silver salvarsan" and "silver diarsenol;" and phospharsenamine as "galyl."

The extensive researches on arsphenamine and the quest for a substitute are well justified by the inadequacy, not

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* The numbers in the text refer to the bibliography at the end of the article.

generally appreciated, of this drug. Roth[12] concludes a splendid contribution to this subject with the observation that "arsphenamine is potentially a dangerous therapeutic agent after all precautions are taken," a view which is confirmed in varying degrees by Foulerton,[13] Hymen,[14] Todd,[15] Lurz,[16] and others.

Studies on Synthesis—It is reassuring that the current synthetic work designed to overcome the shortcomings of the accepted drugs is being conducted in close coöperation with pharmacologists, a coöperation which finds significant support in the pathetic lag that has too often separated the discovery and application of benign medicinals.

One of the most outstanding and comprehensive series of syntheses has been carried out by Heidelberger and Jacobs.[17] Taking as their starting materials the two pentavalent compounds, arsanilic acid and *p*-hydroxyphenylarsonic acid, and using the reactive amino and hydroxyl groups, the following types of derivatives were developed: diazoamino compound AN:NNRR′ (A = arylarsonic acid radical, R and R′ = H, alkyl, aryl, or substituted aryl groups); azo dyes, AN:NR; *N*-substituted amides of *N*-phenylglycine-*p*-arsonic acid, $\mathrm{ANHCH_2CONRR'}$; substituted ureides of *N*-phenylglycine-*p*-arsonic acid, $\mathrm{ANHCH_2CONHCOHNR}$; substituted *o*-phenylglycolyl derivatives of arsanilic acid, $\mathrm{ANHCOCH_2OR}$, and substituted amides of *o*-phenylglycolic-*p*-arsonic acid, $\mathrm{AOCH_2CONHR}$.

The ureide of *N*-phenylglycine-*p*-arsonic acid ("tryparsamide") of the foregoing series is reported upon favorably in pharmacological studies by Pearce and Brown.[18]

Hoffman,[19] in connection with the relationships of structure and effect, makes some remarks of significance to the many aspirants for Ehrlich's mantle. He believes the connection between chemical structure and physiological action has been exaggerated. Under his direction some 600 pharmaceuticals are synthesized yearly, and "when three of these (about 0.5 per cent) prove of any value, the effort is considered well spent."

Toxicity—The vested position of arsphenamine in therapy has led to a vast amount of scholarly effort to explain and correct its somewhat temperamental qualities. Most of such researches belong more properly to a review of the present pharmacological aspects of arsenic, but the outstanding works of Christiansen, Hunt, and Raiziss are worthy of mention in the present connection. Christiansen[20] states that relatively toxic or nontoxic products may be obtained from either of the three commercially feasible processes of manufacture of arsphenamine. The addition of so much as 5 per cent of such probable impurities as $\mathrm{4,3,5\text{-}HO(O_2N)_2\text{-}C_6H_2AsO_3H_2}$, or a mixture of 2,5- and $\mathrm{2,3\text{-}HO(O_2N)C_6H_3AsO_3H_2}$ before reduction, caused but a slight variation in the toxicity of arsphenamine. Methods of forming the dihydrochloride from the base were not responsible for the variations, which Christiansen finally considers as dependent upon the conditions of reducing the parent $\mathrm{4,3\text{-}HO(O_2N)\text{-}C_6H_4AsO_3H_2}$. He obtained products of low toxicity using hypophosphorous acid as a reducing agent. In subsequent articles Christiansen[21] concludes that there is no direct relation between the total sulfur and the toxicity, and searchingly discusses toxic types in general. Hunt[22] cites three distinct toxic types: (*a*) preparations the toxicity of which was due to the presence of *m*-amino-*p*-hydroxyphenylarsenous oxide (arsenoxide); (*b*) preparations the toxicity of which seemed to be due to the presence in the manufactured product of toxic substances other than arsenoxide; (*c*) those toxic on account of the presence of easily destroyable toxic principles.

Type (*a*) were not encountered commercially but were demonstrable in the laboratory. No toxic substance of type (*b*) was isolated but their occurrence is probable. Warming and in some cases standing at room temperature reduced the toxicity of type (*c*). Unique and unexplainable toxic types were also encountered.

Raiziss,[23,24] Schamberg, and their associates have prepared and studied the toxicity of probable impurities in arsphenamine, and have compared its action on animals with that of sodium arsphenamine, developed to avoid the objections met in preparing the other arsenobenzenes. Thus Raiziss[24] concludes from a study of commercial samples that neoarsphenamine is a mixture of the mono- and disulfoxylated bases, containing uncombined sodium formaldehydesulfoxylate, sodium sulfate and chloride, and methanol or water as impurities. The As: N ratio is a fair index of purity.

Voegtlin and Smith[25] explain the toxicity of the arseno compounds on the basis of their change to one type—namely, the trivalent oxide R As: O—and submit data on the conditions of oxidation in aqueous solutions. Thus, neoarsphenamine shows a rapid oxidation on exposure to air and light amounting to 50 per cent in the first ten minutes. Roth[26] shows that shaking alkalinized solutions of arsphenamine and neoarsphenamine renders them highly toxic. This they attribute to the formation of the "arsenoxide." Shaking in the absence of air had no effect. DeMyttenaere[27] gives an elaborate report on arsenobenzenes, their composition and toxicity, and states that in general toxicity was found to parallel the loosely bound arsenic.

Constitution—As to the constitution of arsphenamine, Fargher and Pyman[28] state that arsphenamine contains two molecules of water and is free from methanol. The correct formula is $\mathrm{C_{12}H_{12}O_2N_2As_2.2HCl.2H_2O}$. British and German products contain 1 to 3 per cent of sulfur, probably as a sulfaminic acid. The reduction of nitro compounds with sodium hydrosulfite in alkaline solutions leads, sometimes in part and sometimes wholly, to the formation of $\mathrm{RHNSO_3H}$. This assumption is further supported by a lack of equivalence between the chlorine content of commercial samples of arsphenamine and the alkali needed for neutralization. Arsenic sulfide and physically associated sulfur are also possibilities. Precipitated from methanol by acetone, arsphenamine contains one molecule of acetone, not removable in vacuum at ordinary temperatures. These findings are supplemented by the painstaking work of King.[29]

Kober[30] maintains that Ehrlich's arsphenamine contains as much as 7 per cent of methanol, probably one molecule free or combined, which probably increases its toxicity. He also emphasizes the increase in the tolerated dose from the German 60 mg. per kg. (white rats) to the American 100-mg. article, and has himself prepared methanol-free arsphenamine above the 100-mg. standard.

Macallum[31] comments upon the greater variation in the European arsenic drugs in comparison with the American products, with respect to lack of uniformity and agreement with the maker's claims as to constitution.

Voegtlin[32] comments favorably upon the newer sulfarsphenamine, an organic arsenical prepared from arsphenamine, formaldehyde, and sodium bisulfite, and differing from neoarsphenamine by an extra oxygen in the solubilizing group. It is thus an ester of sulfurous acid instead of a sulfoxylate. The author is of the opinion, based upon extensive animal experiments together with the greater stability of the compound, that this drug will play an important part in the treatment of syphilis.

OTHER INVESTIGATIONS ON ARSENIC COMPOUNDS

Among recent investigations which have made fundamental contributions to the pure chemistry of organic arsenic compounds, are those of Adams and Palmer,[33] who have compared the action of arsine and the substituted arsines with the corresponding nitrogen compounds. They were able to condense phenylarsine, the analog of aniline, with aldehydes. Primary aromatic arsines react with aldehydes in three ways according to the conditions—i. e., $\mathrm{R\,AsH_2 + R\,CHO \longrightarrow R\,As\,(CHOHR)_2}$; "$\mathrm{R\,AsH_2 + 4\,R\,CHO \longrightarrow (R\,CHO\,As\,R)_2 + 2\,R\,CH_2OH}$ (Adams regards this product as a phenyl substituted heterocyclic ring of arsenic, carbon and oxygen); $\mathrm{R\,AsH_2 + 2R\,CHO \longrightarrow R-As = As - R + R\,CH_2OH}$.

Quick and Adams[34] have also exhaustively studied the preparation of aliphatic arsonic and arsinic acids, and aliphatic aromatic arsinic acids. These authors have improved upon Meyer's method of arsenating aliphatic compounds using alkyl bromides and chlorides instead of the iodides and employing water as a solvent. Thus, the reducing effect of the liberated hydriodic acid on the arsonic acid is avoided on the one hand, and the formation of ether greatly lessened on the other. The arsinic acids are prepared from the arsonic acids by reduction with sulfur dioxide, in hydrochloric acid solution, to the alkyldiochloroarsines, which are then treated with sodium hydroxide and the alkyl halide.

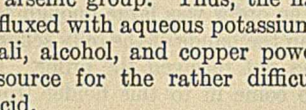
Burrows[35] has confirmed previous findings that arsenic is peculiar in not functioning as a center of optical activity. By treating γ-phenyl-*N*-propylmethylchloroarsine with aluminium chloride, he was able to close the ring and obtain an As-methyltetrahydroarsinoline. He was, however, unable to resolve this and similar compounds which from analogy with nitrogen should give optically active products.

Rosenmund[36] offers a new method of arsenation as a substitute for Bart's reaction replacing halogen in the ring directly by the arsenic group. Thus, the halogenated benzoic acids are refluxed with aqueous potassium arsenite in the presence of alkali, alcohol, and copper powder. This may offer an easy source for the rather difficultly obtainable *m*-benzarsonic acid.

One of the most useful methods of arsenating ring compounds is that of Bart.[37] Despite the widespread use of this method among arsenic workers, the reaction had never been thoroughly studied as a laboratory process prior to the recent excellent contribution of H. Schmidt.[38] In this reaction a diazo solution is treated with a neutral or slightly alkaline solution of potassium arsenate. The arsonic acid forms, accompanied by the evolution of nitrogen, according to the following typical equation:

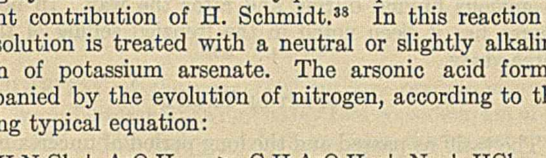
$$\mathrm{C_6H_5N_2Cl + AsO_3H_3 \longrightarrow C_6H_5AsO_3H_2 + N_2 + HCl}$$

The reaction is completed with warming in the presence of finely divided copper. The reaction is thus one of a group in which salts of arsenious, antimonious, sulfurous, and nitrous acids, or the free acids, similarly react, the final products holding the arsenic, antimony, sulfur, and nitrogen in the higher valence. This latter effect is usually explained by assuming an equilibrium in the several cases, of the type:



$$\mathrm{As(OH)_3 \rightleftarrows As(H)(=O)(OH)_2}$$

the reaction taking place to give a pentavalent arsenic derivative. Schmidt states that oxidation by the diazo compound is equally probable, forming an unstable compound which loses nitrogen and goes over into the arsonic acid.



$$\mathrm{C_6H_5N_2OH + As(OH)_3 \longrightarrow (C_6H_5N_2)(HO)As(OH)_3}$$

$$\mathrm{(C_6H_5N_2)(HO)As(OH)_3 \longrightarrow C_6H_5As(OH)_2(=O) + N_2 + H_2O}$$

The favorable effect of weak alkaline solutions on this reaction is considered by the author as supporting Hantzsch's theory that the syndiazo form favors diazo splitting.

The condition of formation of by-products such as benzene, azo- and hydrazobenzene, aniline, and the arsenated dimolecular compounds of the type of phenylphenylenearsonic acid are thoroughly studied.

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New Resistant Enamel

An intensely white enamel, which exhaustive tests show is resistant to acids in a degree hitherto unknown, has been developed by the Paint Department of the du Pont Company. The new enamel has been the subject of study for more than a year on the part of experts, and its development is expected to meet the need for protection of surfaces subjected to gas or fumes such as are found in hospitals, chemical laboratories, bakeries, rubber factories, canning plants, or for the interior of any factory or building where fumes are present.

Repeated practical tests show that the new enamel has a hard drying finish which approximates porcelain, can be easily washed, and will not discolor with age or the action of acid or alkali fumes. Recently in one of these tests, the material was placed in actual contact with dilute sulfuric acid, and after twenty-four hours the film showed no disintegration, discoloration, or other change. This test was a more severe one than would be encountered on a finished wall or article in any of the factories or institutions for which an enamel of this kind is intended. Other experiments showed that even under accentuated conditions its color stability is excellent.

The company reports that the material keeps in good condition in the container and stays in suspension well. Another advantage is that an expert is not required to apply it and it is adapted for either spray or brush.

Heavy Chemicals in Commerce in 1922

By D. H. Killeffer

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FINANCIAL conditions at home and abroad and the continued uncertainty of the tariff situation were ruling factors in the market for heavy chemicals during the past year. Beginning in May, 1920, the general movement toward the liquidation of stocks by all concerned continued with growing impetus well on into 1921 and more slowly into 1922. At the time of the presidential election in 1920 and again immediately preceding the inauguration of President Harding, there was developed a passing feeling of hopefulness that there would be a sudden change in the situation. As subsequent developments showed, fundamental unsoundness prevented such an occurrence.

By January, 1922, the greater proportion of stored stocks had been passed into consuming channels and had ceased to form quite so depressing an influence in commercial affairs. However, their place had been taken by continuous heavy imports of low-priced foreign material, and sellers in all lines were facing an almost identical situation. Prices had been forced to levels which made profits either inconsiderable or negative by this influx of foreign goods below American costs. Promised action on measures of protection was delayed time and again. Importers thrived on the low value of German exchange. Not only were chemical raw materials imported, but to an even greater degree the finished products of other industries into which these enter. Everyone connected with the industry, whether as a producer or consumer of its products, suffered acutely during the first half of the year.

Electrolytic Alkali Industry

In the midst of this anomalous situation surprising inconsistencies developed, not the least remarkable of which was in the electrolytic alkali industry. Demand for caustic soda in all world markets was quite surprisingly active and makers had difficulty in keeping up with it on the limited scale on which they were operating. American caustic soda was even sold in quantity to German consumers through the Berlin and Hamburg markets in competition with the German product. In sharp contrast to this activity was that of bleaching powder and other chlorine products which are necessary by-products of the industry. German bleaching powder was sold in the New York market at as much as 25 to 30 per cent below the minimum prices named by makers here. Accumulations of chlorine, hydrochloric acid, and bleaching powder caused grave concern in this country, especially in view of the continued heavy imports. This situation, in part at least, has led to extensive work on new uses for these products, and has resulted in their use to some extent in the petroleum industry. The first commercial plant for refining petroleum distillates by means of bleaching powder has very recently been put into operation.

Financially, the industry has been strengthened through its long period of liquidation by the gradual elimination of most of those "fly-by-night" firms which were formed suddenly during and after the war to take advantage of the easy profits of the bull market then existing. This has not in any sense been through the freezing out of small firms by large ones, but has been essentially the elimination of a purely speculative element after the reason for its existence ceased to exist. Although the financial status of even the strongest firms was not as secure as might have been desired through the stress period, yet the industry as a whole has been unquestionably strengthened by the removal of these highly disturbing influences. Consumers, who had been forced by the prevailing organization of business to trade through middle men who added nothing to the value of the goods handled, are now able to place their business directly with producers and thus avoid an unnecessary profit to sellers and cost to themselves. Inflation of demand beyond its actual proportions by the appearance of a single order to buy in the hands of many middle men and inflation of stocks by the similar multiple appearance of orders to sell had been largely done away with before the beginning of 1922.

The extreme uncertainty of the market under the influence of this re-selling element may well be illustrated by a case in point. At one time during 1921 an order came into the New York market from one of the large soap makers in the Middle West for a carload of caustic potash and potassium carbonate. This particular order was sent by the buyer to eight firms who had previously supplied him with these products but none of whom were primary producers. It so happened that the order was large enough to virtually wipe out stocks then in the hands of the only seller who could supply but who had not received the order. Immediately inquiries began to come in to this holder from all sides, and his natural reaction was to raise his price. When this was done the buyer refused to place the order and what had been an apparently active market collapsed in an hour. Such inflation was evident in the market throughout the period of anxious buying during and after the war. In no less a degree has it been noted in the frenzied selling of the past three years.

Effect of Tariff

The tariff as passed and the long period of uncertainty preceding its passage have operated as depressing influences, but have not been as generally potent in the situation as other factors. In contrast to the organic industry, the inorganic group, generally designated as "heavy chemicals," lends itself readily to quantity production, at which America naturally excels, and for this reason it is not illogical that the tariff should occupy a position of somewhat secondary importance in the influences controlling the heavy chemical market. Marked exceptions to this general rule are to be noted in those cases where Germany, in particular, is able to provide her own raw materials, as in the manufacture of compounds of potash and barium. In potash the lack of duty, especially on the crude salts, is operating as a very serious obstacle to expansion and even to continued operation of existing plants. Barium salts received protection to some extent, but it is believed by many makers of these compounds that even the advanced rate of duty as compared to the Underwood rate will not be sufficient to insure continued operation in the face of many other disturbing elements.

The depressing effect of the uncertainty of the tariff was well illustrated by the general upward movement of prices after the final passage of the bill. No other upward movement has assumed such broad proportions since that which followed the war and the rapidly increasing foreign trade which that brought about. This movement was so sudden and sellers were so poorly prepared to cope with the demand which caused it, that conditions became immediately congested and forced even further advances than the actual demand justified. However, this feature is being cleared away and the trend toward normal business is developing rapidly.

Case of Arsenic Trioxide

One of the most interesting features of the heavy chemical market during the past year has been the behavior of arsenic trioxide. Production in this country has been always closely dependent on the output of copper from which it is a by-product, and on this account it has been necessary to import large quantities to eke out domestic supplies for use in insecticides. Recently, experiments have been completed under the supervision of the Department of Agriculture which have led to the recommendation of calcium arsenate as a means of destroying the cotton boll weevil. This opened an entirely new field for the consumption of arsenicals, which bids fair to eclipse all others and has caused widespread speculation in this product during the previous buying season—i. e., the winter of 1921–1922. Unfortunately, the financial condition of the farmers generally prevented the realization of the hopes of the speculators, and it is only now that prices are reacting normally to this influence.

Cyanides

One of the most interesting recent commercial developments was in the field of cyanides. The manufacture of a low-grade cyanide from cyanamide of sufficient purity for most metallurgical operations has been put on a commercial scale, and has resulted in quite a saving to operators of cyaniding plants in the West.

Present Outlook Hopeful

In general, however, the year has been notable for the actual accomplishment of the long-expected turn in prices from a general decline to an average advance. Improvement in the financial condition of industry as a whole has been closely reflected in improvement in the chemical market. Buyers may be considered to have actually acquired the confidence so long lacking and so necessary to improved business. This confidence certainly is not as great as may be expected to grow from the present beginning, but nevertheless it is sufficiently well developed to lead to a decidedly more comfortable feeling throughout the trade. As yet few buyers are anticipating their wants for years ahead, but certainly they are anticipating for months now where they were formerly content to cover requirements in terms of weeks or even days. Certainly, there can be no room now for the widespread pessimism that characterized the situation of a year ago.

Commercial Developments in the Organic Chemical Industry, 1922

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The Tariff

A REVIEW of the year 1922 by any organic chemical manufacturer leads inevitably to a consideration of the tariff and its making, which has been the largest single controlling factor, and will undoubtedly continue to be so for a considerable time to come. As everyone knows, the tariff was certainly a very long time in the making, but after a number of years of uncertainty as to what its final form would be, a tariff bill was at last passed, and whether it be good or bad, it will nevertheless mark a point from which will be noted either progress or the lack of it in the organic chemical industry in America. 1922 will, therefore, be remembered as a milestone for the dyestuff, and, in fact, the entire synthetic organic chemical industry in America.

As everyone who is at all conversant with the subject knows, the first milestone of the industry was the situation created by the war. Supplies of dyes and medicines formerly imported were absolute essentials if our progress was to continue. New plants for the production of these materials came into being all over the country, and the cost of their erection was a decidedly secondary consideration. The materials they were to produce could easily be sold at a high enough price to offset for the time being the disadvantages of improper and uneconomical installations. Then the war ended. With it also ended that phase of the situation that made almost anything possible. It was realized that we must produce as good products as any country in the world and at reasonable prices. This naturally meant that the feverish development that had gone on before in an attempt to keep pace with the demand must cease immediately, and that in the future only such processes could be adopted and those installations made which after careful study and consideration showed at least a reasonable chance of being economically sound.

With this changed condition some of the earlier manufacturers, who had entered the field simply because of the attractive profits available at the time, realized that they could scarcely continue unless by an entire reorganization of their plants, and so they quietly dropped out of the picture. Others tried to continue, only to lose everything they had previously made, and more besides.

Those manufacturers who had gone into the thing more seriously in the first place, gave very serious thought as to the "how" of remaining in business and continuing to occupy a place in American industrial life. While making every effort to increase their efficiencies within their organizations, it was at once realized that some governmental protection also was needed if they were to stay in business long enough to reach a place where they could be really competitive with an industry so long established and so highly coördinated and organized as that of the Germans and the Swiss. As a result, much time and thought were spent in trying to devise some form of tariff protection which would foster the organic chemical industry, but which at the same time would not be an onerous burden on other and more important industries which the newer one served.

With this thought in mind, it was naturally very difficult

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[1] Vice President.

to devise any scheme that would be absolutely perfect. It was thought by the dye manufacturers that an embargo on products made here, while permitting other products to be readily imported at nominal rates of duty, would be the fairest way of handling an admittedly difficult situation. The opponents of this proposal, while not so great in number, were very loud in their denunciation of this plan, and were also not without considerable influence, so that we have to-day a tariff which has abandoned the embargo plan entirely and has substituted tariff rates as the means of protection, and the manufacturers, of course, assume that this tariff is much more to the liking of the opponents of the embargo plan. No one can say at this early date what its effect will be on the American industry which it was designed to protect and encourage. The impression is very general, however, that, while it apparently over-protects some of the cheaper products, it is woefully inadequate on the higher-class and higher-priced commodities.

Uncertainty as to the future always retards progress in any industry. Consequently, while there has been some development during the years when it was not known what form or how much protection would be decided upon, nevertheless the uncertainty as to the outcome of the tariff legislation put everyone in a very cautious and fearful frame of mind, and the general tendency has been for all manufacturers to refrain from extensive developments which would entail any great capital expenditures.

NEW PRODUCTS

In a sense this cessation of active new development has been beneficial, because considerable time and effort have been devoted toward the improvement of products already on the market. Improvement, such as referred to, is not necessarily confined to quality. It is more often improvement in yields obtained or in manufacturing methods, the tendency in both cases being to reduce manufacturing costs. New development has also been along much more conservative lines than it might otherwise have been. While the new products introduced were fewer in number, those that were brought out have been such as were actually needed to complete lines of high-grade fast colors, which will eventually make us more and more independent of foreign sources of supply. Illustrative of this sort of development was the introduction of Naphthol A. S. and its attendant products, Direct Fast Scarlets, Diazotized Fast Scarlets, Fast Light Yellow, Alizarine Cyanine Green, and Direct Fast Blue like the old Solamine Blue F F or Diamine Fast Blue F F B, which were the fastest-to-light Direct Blues known. All these, it will be noted, are very high-grade dyes—that is to say, they are such as will answer the very insistent and ever-increasing demand for fast colors.

A survey of the entire American production of dyes is very gratifying in that it reveals that we are almost self-sustaining in this respect. Outside of a few vat dyes, a few more fast-to-light direct colors, a few developed colors, principally Blues, and some specialties, such as those used for printing, this country could, if it were shut off from all foreign supply, still produce shades of all kinds for all kinds of fabrics on which dyes are used, with practically any degree of fastness that might be desired.

Unquestionably, future development will be along the same lines, and in connection with the statement before made, that lines now manufactured in this country are fairly complete, we look with confidence to the development of entirely new products, which will represent not only an advance as far as the American industry is concerned, but which will be a new and original scientific chemical advance in the industry no matter where located.

ECONOMIC FACTORS

Progress in this, as in every other industry, depends on the ability of the manufacturer to convince the banker or the investing public as to the soundness of their investment, and the factor that is never overlooked by the investor is the possibility of profit on his investment. The thought so often expressed in the abstract, that we should have, and in fact must have, a self-contained American organic chemical industry, is all very well, but when a man comes to make an investment, he wants to see at least a possibility of a fair return on that investment. If, therefore, the tariff law, as we have it to-day, does not provide sufficient protection for the products on which further progress should be expected, then we can hardly expect that money will be invested freely so as to make such progress and development possible. The thought expressed before to the effect that the present tariff is woefully inadequate in its protection of the high-grade and high-priced commodities appears then to be particularly unfortunate, because it is in this line of products that we would naturally look for future development, and if there is insufficient protection, then very naturally this hope for development will not be realized.

Far from having a monopoly, the American organic chemical industry has been highly competitive during the year, with the result that there has been a consistent decline in prices, which has not been confined to any particular group of products, but has been very general. The decline in price of many commodities has been so great that present price levels are actually less than the cost of reproduction of the same merchandise. There is every reason to believe, therefore, that there will be an upward trend of prices on a great many of these commodities so as to again establish them on a profitable basis. Another price-depressing influence was the continuing during 1922 of the liquidation of excess stocks which was begun in 1921. This process of liquidation has undoubtedly been completed by now, so that the whole trend of prices must in the future be based on current production.

We have a good start in this industry. We could have been further ahead of our present position if we had profited by the years of experience of German leaders, particularly along the lines of coördination and coöperation. The great value of coördinated and coöperative effort is certainly appreciated to the full by the Germans—as witness the present I. G.

If our American industry needs any one thing more than anything else, this is the one thing it needs. Naturally, the antitrust laws prevent any combination like or similar to the German I. G., but nevertheless any efforts that have as their goal greater coöperation between manufacturers should be of great benefit. If, instead of all the duplicated effort in research and manufacturing, each producer had worked along some particular and predetermined line, then we might have to-day not so many duplications, but a much greater variety of products. Our total investment would certainly be no greater and might have been much less than it is.

New Journal in London

The *Journal of the Society of Chemical Industry* is to undergo a radical change at the end of the current year. The Review section, which was initiated in 1917, will disappear, and in its place there will be issued a weekly journal to be called *Chemistry and Industry*. This journal will be the official organ of the Society of Chemical Industry and of the Federal Council for Pure and Applied Chemistry. With the disappearance of the Review, its editor, Dr. E. H. Tripp, is severing his official connection with the Society, and Dr. Stephen Miall will edit the new venture. Dr. Miall is chairman of the Brimsdown Lead Co., and a solicitor by profession.

Medicinal Chemicals in 1922

A Review of Prices, Tariff Legislation, General Conditions, and Progress during the Past Year

By J. F. Queeny[1]

Monsanto Chemical Works, St. Louis, Mo.

THE DEMORALIZATION of prices which had prevailed in the field of fine and medicinal chemicals for twelve to fifteen months still affected the market at the beginning of 1922. No explanation or search for reasons is necessary, because it was essentially a continuation of the period of liquidation. There was a change in some of the factors which may be discussed, but prices were low and stationary, largely because conditions were stationary or uncertain. The level showed no particular inclination to change until midsummer, when prices stiffened perceptibly.

A factor contributing to this result was the exhaustion of "distress" stocks and of reserve supplies both in the manufacturers' and consumers' hands. Inventories had been carried at as low a margin as possible for months, until, with the unemployment situation greatly relieved and a consumers' demand created, it was necessary to begin manufacturing operations on a more nearly normal scale. Prices for such goods were, of course, set primarily on the cost of production, rather than the former fictitious one of realizing sales or of abnormal demand. This change in the market aspect was a welcome one. It was reflected in increased activity throughout the industry.

A movement of prices sideways was characteristic of the market, until the opening of the final quarter approached. Then a number of factors bearing on the situation resulted in substantial gains over practically the entire list.

In midsummer, the striking miners in many cases were farming on a small scale or working in other industries; the railway shopmen's strike resulted in many cases merely in the exchanging of positions with fellow craftsmen in other cities, but the situation created a demand for workers in those lines which was never completely satisfied as far as some of the roads were concerned. These factors, together with the activity in the building trades, made unemployment a rare thing by fall. With its disappearance a great restraining influence was eliminated; a feeling of some certainty and confidence regarding the immediate future was a natural sequence. The final passage of the administration tariff bill at least let the manufacturer know what to expect in the way of protection from, and of competition with, foreign producers.

It must be remembered that the American chemical industry is now a part of productive business. It is therefore in line to suffer or profit with the rest of the business world, as long as it is not singled out for especial attack.

It may be fairly stated that the influence which caused the increase in the prices of other commodities was the power behind the recent upheaval in the chemical industry. Stress has been put on the effect of our several months of extravagant indulgence in nation-wide strikes. This and the later rise in the cost of ordinary labor have been important factors, but repetition of the details adds no emphasis to the generally agreed wastefulness of strikes, except as it points to a particular susceptibility of our industry to such influences.

Chemical plants, like most others, probably entered the period of the coal strike last spring with a three months' fuel supply on hand. There were indeed few who did not deem this ample and to spare. But by midsummer it became necessary to purchase spot coal, often of poor quality, at the seller's price. When this price exceeded that of crude oil, many plants switched to the latter, because of the more dependable deliveries and quality. The cost of making the necessary changes in the boiler room, installing pipe lines and storage tanks, and ultimately of dismantling all this equipment and changing back to coal as a fuel, was an additional burden.

The heroic efforts of the railroad to offset the effect of the shopmen's strike could not prevent delays in transit. Duplication of freight shipments of finished goods which were not received within a reasonable time by express shipments, and the frequent necessary delivery of bulky crude materials by express were further items of unusual expense.

In a merely casual consideration of prices, the effect of the new tariff is likely to be given too much weight. Concerning this we shall comment presently, but the more important factors at present are the economic conditions at home and abroad and the indecisive ending of the recent labor-capital conflicts such as in the coal industry. In this case the stage was left all set for repetition of the performance by the respective groups. This may only be prevented by a constructive report of the recently appointed Coal Fact Finding Commission, followed quickly by control legislation which must provide power of enforcement.

Confidence breeds confidence. The substantial gains and the hardening of prices beginning with the last quarter were followed almost immediately by the closing of an increased number of contracts, first for products, then for the crude material. These contracts, running from three to twelve months, are a definite indication that the present general level will carry over well into the new year. Further predictions as to the trend are as yet speculative but promising.

TARIFF

Broadly speaking, the Tariff Act of 1922, as it relates to medicinal chemicals, represents a great improvement over the so-called Underwood Act. Nearly all rates were increased, this being necessary due chiefly to depreciation of the German mark and the fact that costs in Germany of labor, materials, etc., did not advance in sympathy with the fall in the value of German currency. However, there are many individual items of great importance, the manufacture of which should be continued in this country and which apparently did not receive appropriate rates. This is particularly the case with several of the non-coal-tar synthetics, such as chloral hydrate, barbital, etc.

The tariff-making bodies of Congress rejected a plea for a 25 per cent ad valorem rate on synthetic camphor, a rate which would have assured American independence on this important product as against our present complete dependence on a Japanese monopoly. As this requested rate was not to apply until production reached at least 2,000,000 pounds per year, it is hard to understand why so reasonable a proposal was rejected, when it is remembered that practically all the simple synthetics, as well as the inorganic medicinals, were given at least a 25 per cent ad valorem rate.

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[1] Chairman of the Board.

The rates for the high-priced coal-tar synthetics may prove inadequate as the specific of 7 cents per pound, as named in paragraphs 27 and 28, is of small value in protecting such of those items selling for more than $1.00 per pound.

Credit must be given for the insertion of paragraphs 315, 316, and 317 in the Tariff Act of 1922, as under their provisions the President is given unusual latitude (with certain limitations in the case of coal-tar chemicals) to review schedules, to change the basis of valuation, and to combat effectively cases of discrimination against American-made goods as compared with those of other nations. Such drastic measures are only necessary to render the probability of their use negligible.

Perhaps the greatest virtue to be claimed for the whole tariff law is recognition of the value and the provision for broadening the activities of the Tariff Commission. The power vested in the President is, after all, only nominal, since he cannot act on any proposed change in the tariff bill as passed, except after investigation by and (by implication, at least) in accord with the report of the Tariff Commission. This general provision is a plain admission by Congress that the proper regulation of tariff matters involves the consideration in detail of too much technical information to be left to any but a group of impartial experts in the particular field concerned. The Tariff Commission when completely organized will have such experts in its employ as are necessary to handle properly the cases referred to it for investigation. This is not only an important advance in the administration of what we feel is otherwise quite a mediocre measure, but the future may show that its greatest value lies in the existence of a well-organized and authoritative body for assisting in the framing of succeeding tariff bills intelligently.

It is the hope of the present commission, as expressed by Vice Chairman Culbertson, that tariff making in the future may cease to be the periodic cause of economic upheaval and uncertainty; that the appeals of proponent and opponent, instead of being made to respective individuals or groups of legislators known to lean toward the cause of one or the other, will be presented, so to speak, in open court before the impartial Tariff Commission. The latter having facilities for independent investigation may proceed to gather any additional data which may be necessary and quickly render a decision based on and supported by the indisputable facts. Such procedure is fair, it is direct, it is economical, and as applied to our industry—we must add the important qualification—it is scientific.

NEW PRODUCTS

Under the circumstances which have prevailed during the past two years, it is natural that the American manufacturers, as well as those abroad, have confined their principal efforts to the perfection of processes and more economical production of the materials for which a demand existed. That research of an active, thorough and forward-looking type has not been entirely suspended by our manufacturers, has been shown directly, however. Perhaps the best example is the recent formal introduction by the Abbott Laboratories of a new synthetic local anesthetic. This product is the result of several years of pioneer work, during which Dr. Roger Adams and coworkers collaborated with the Abbott staff. That other innovations of a similar character will be brought forward from time to time is to be expected of this type of applied science.

CONCLUSION

The medicinal and fine chemical industry has carried its full share of the burden of uncertainty. The current improvement in business conditions is most welcome and it is believed that the low prices of the reconstruction period are back of us, as far as the medicinal chemicals are concerned. The great changes which have occurred throughout the world within the past few years and the leadership assumed by America necessitate our chemical independence, and it is hoped that lack of friendly coöperation of our government agencies will not militate against the heroic efforts and substantial accomplishments already made by commercial institutions in this field.

To Commemorate Benjamin Silliman

On April 4, 1804, Benjamin Silliman delivered the first lecture on chemistry ever given in Yale College. On April 4, 1923, Yale University will dedicate the new $2,000,000 Sterling Chemical Laboratory, with the AMERICAN CHEMICAL SOCIETY as a guest. This date was chosen in order to commemorate the beginning of chemical instruction in Yale.

Benjamin Silliman graduated from Yale College in 1796 at the age of seventeen. Two years later he returned to New Haven as a student of law, and in 1799 was appointed a tutor in the college, at the same time continuing his study of law. At about this time the Yale Corporation voted to establish a professorship in chemistry and natural history. President Dwight felt that it would be better to select a young man of proved ability and high character and give him time and assistance in order that he might prepare himself for the work, rather than to risk the appointment of even a distinguished man who would be a stranger and probably a foreigner. In the fall of 1802, Benjamin Silliman was formally elected to this position. He immediately went to Philadelphia and began his studies of chemistry under Dr. James Woodhouse, of the Medical School of Philadelphia. Associated with Silliman as a fellow student and intimate friend was Robert Hare, the inventor of the oxyhydrogen blowpipe. During his stay in Philadelphia, Silliman also had the opportunity of meeting Dr. Joseph Priestley. In March 1804, Silliman returned to New Haven to take up his professorial duties. His own account of his first lecture is given in his published reminiscences.

> MY FIRST LECTURE—April 4, 1804. In a public room, hired for college purposes, in Mr. Tuttle's building on Chapel Street, nearly opposite to the South College, I met the Senior class, and read to them an introductory lecture on the history and progress, nature and objects, of chemistry. I continued to lecture until the Senior class retired in July, preparatory to their Commencement in September. My first efforts were received with favor, and the class which I then addressed contained men who were afterwards distinguished in life.

At the close of the session of 1805, Silliman set sail for England on a mission from the college to buy books and apparatus, and at the same time to spend another year in study. There he met William Henry, whose treatise on chemistry he afterwards revised and edited, Dalton, Sir Humphrey Davy, and other distinguished scientists of the day. While in Edinburgh, Silliman became very much interested in geology, and in his subsequent career he devoted as much time and effort to geology as to chemistry.

Returning to America, Silliman took up again his teaching duties, continuing as a professor until 1855. During that time he not only taught the chemistry and geology in Yale College, but delivered a large number of popular lectures all over the United States, gave much of his time to public activities and development of new industries, particularly the petroleum industry, and founded and through his lifetime edited the *American Journal of Science*. Professor Silliman was a gifted writer and brilliant public lecturer, a great teacher, and a broad-minded and public-spirited citizen, enjoying the confidence and friendship of the leaders of his day, among whom were Daniel Webster, President Adams, President Jackson, and Lafayette.

It is indeed fitting that Yale University and the AMERICAN CHEMICAL SOCIETY should honor the memory of one of the pioneers in the teaching of chemistry in America by dedicating a great research and teaching laboratory on the anniversary of the first lecture delivered by Benjamin Silliman in Yale.

Die Castings

By Sam Tour

Doehler Die Casting Co., Brooklyn, N. Y.

DIE CASTINGS, as referred to in this article, are castings made by forcing molten metal, under pressure, into a metallic mold or die. The casting of metal into metallic or permanent molds was practiced many centuries ago, but the application of force or pressure to this process is somewhat in the nature of a recent development, although machines for doing this were developed almost fifty years ago. The history and evolution of the process,[1] as well as the various types of casting machines,[2] and the various types of alloys that are commercially die cast and their general properties, have all been ably described by Mr. Charles Pack.[3]

Alloys Cast

Die casting, as it was first developed, was limited to tin and lead base alloys having melting points not exceeding 350° C. A short time later, zinc base alloys having melting points up to approximately 450° C. were introduced. This was the status up until about 1914, when the die casting of aluminium base alloys, with melting points up to 650° C., was developed on a commercial scale. In other words, the tendency has been to go to alloys of higher and higher melting points. The proposed steps after aluminium alloys are the brasses, and then the bronzes, and so on to cast iron and then to steel. In this progression, not only do the melting points increase, but also the total heat to be absorbed by the die increases. In Table I the figures have been largely taken from "Metallurgical Calculations" by Richards. To the left are the metals considered. With the exception of brass and cast iron, the elements have been chosen as they illustrate the point sufficiently, and also because there do not exist in technical literature many data of this nature concerning alloys.

It will be noticed that each step forward in types of alloys has been in the direction of higher temperature and greater heat to be absorbed by the die per casting made. It is this increase in temperature and heat that has for the last decade retarded the development of the art and industry of die casting.

Die-casting machines and die-casting dies are complicated and expensive, and unless a considerable number of castings can be made from such equipment before it becomes unserviceable the whole process must fail.

Life of Dies

For tin and lead alloys having casting temperatures approximately 332° and 427° C. and heat-absorption values of 192 and 178 cal. per cc., respectively, dies made of plain carbon machinery steel without heat treatment will last almost indefinitely, so far as heat effect is concerned. For zinc alloys having casting temperatures up to 519° C. and heat absorption values of approximately 450 cal. average-sized dies made of plain carbon machinery steel not heat-treated will develop heat cracks or thermal-fatigue cracks after having made from 20,000 to 30,000 castings. These same dies properly heat-treated will make 50,000 to 75,000 castings before developing these cracks. By using a high-grade alloy steel a life of 40,000 to 50,000 castings can be obtained in the non-heat-treated state, and by proper heat-treatment of this steel dies can be made having a life of over 100,000 castings. For aluminium alloys having casting temperatures up to 757° C. and heat-absorption values approximately 562 cal., the life of a die is very much less. The type of steel at present used for dies for die-casting aluminium alloys will, if not heat-treated, develop heat cracks before 1000 castings are made. This same steel properly heat-treated will give the die a life of from 10,000 to 15,000 castings. For brasses having casting temperatures around 1000° C. and heat-absorption values approximating 753 cal. no material has as yet been found that, even when heat-treated, will result in a die with a life of over 1000 castings.

Thermal Fatigue of Dies

The heat cracks referred to above are very clearly shown in Figs. 1 to 4, inclusive. Fig. 1 shows the initial casting made from the die in question; Fig. 2 shows the sixteen-thousandth casting from a duplicate die. Fig. 3 shows the die block itself after the making of about 20,000 castings; and Fig. 4 shows an enlarged view of a portion of Fig. 3. As this was a casting much larger than the average, the die began to heat-check after only 5000 or 6000 castings were made. It is, of course, seldom necessary to discard a die when it first develops heat cracks. As well illustrated in the photographs, the heat cracks in the die result in a network of fins on the casting. The die can be used until these fins develop to the point where they cannot be economically removed, or until they interfere with the operation of the die.

The mechanism of the action which results in heat cracks in a die is very similar to that described by Tchernoff.[4] While the die is filled with the molten alloy suddenly forced in under

Table I

	Melting Point °C.	Specific Heat 0° to M.P.	Heat in Solid at M.P. Cal./G.	Latent Heat of Fusion	Heat in Liquid at M.P. Cal./G.	Specific Heat of Liquid	Casting Temp. °C.	Superheat °C.	Heat in Liquid at T_c Cal./G.	Temp. of Removal °C.	Heat Removed per Unit Weight Cal./G.	Specific Gravity	Heat Removed per Unit Volume Cal./Cc.
Symbol	M. P.	S_m	Q_s	L. H.	Q_l	S_l	t_c	t_s	Q_c	t_r	Q_{wr}	d	Q_{vr}
Formula	....	....	M. P. × S_m	....	Q_s + L. H.	....	....	T_c − M. P.	$Q_l + t_sS_l$	....	$Q_c - t_rS_m$	....	dQ_{wr}
Tin	232	0.058	14.34	13.82	26.16	0.060	332	100	32.16	100	26.36	7.29	192.1
Lead	327	0.036	11.60	6.00	17.60	0.040	427	100	21.62	150	16.22	11.00	178.4
Zinc	419	0.112	45.20	22.60	67.80	0.179	519	100	85.70	200	63.30	7.10	449.5
Aluminium	657	0.273	167.40	90.90	258.30	0.308	757	100	289.10	300	208.20	2.70	562
Brass	900	0.100	.....	....	.....	....	(1000)	...	130.00	400	90.00	8.40	753
Copper	1083	0.125	118.70	43.30	162.00	0.156	1233	150	185.40	500	122.90	8.30	1020
Cast Iron	1200	0.150	.....	....	.....	....	...	...	245.00	600	155.00	7.50	1162
Iron	1535	0.150	256.00	66.00	322.00	0.200	1735	200	362.00	750	236.40	7.70	1820

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[1] *Proc. Engineers' Society of Western Pennsylvania*, **33** (1918).

[2] "Die Castings and Their Application to the War Program," *Am. Inst. Mining Met. Eng. Bull.*, **146**.

[3] Paper presented at the spring meeting of the American Society of Mechanical Engineers, in 1920.

[4] "On the Erosion of Steel Guns by Powder Gases," *Rev. mètal*, **1915**.

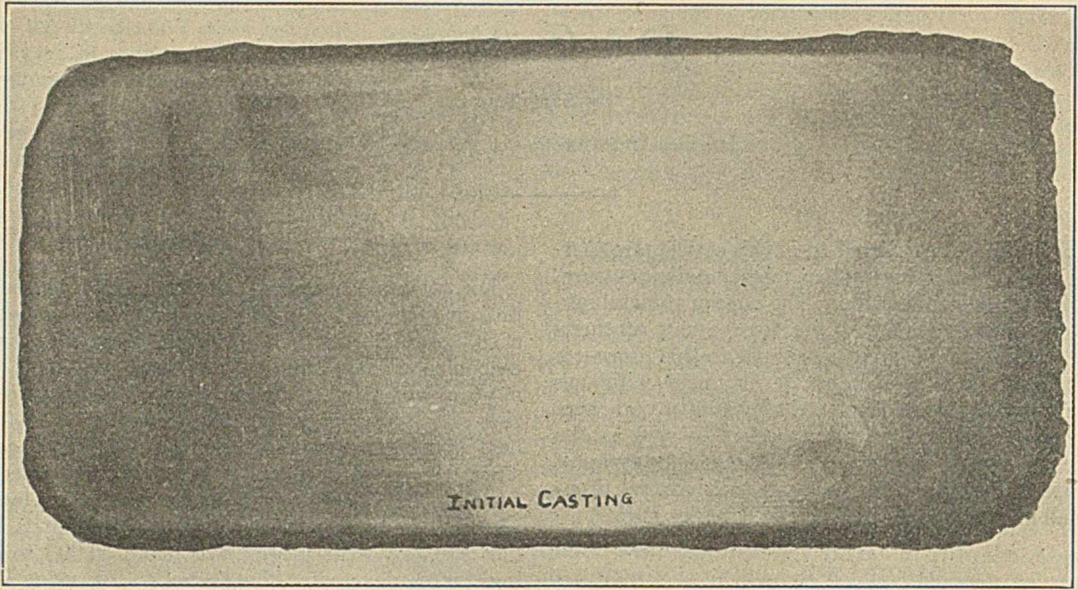

Fig. 1

pressure, the extreme surface of the die is considerably heated but very quickly cooled by the conduction of the heat back into the underlying metal. If an elementary prism of metal (*bfccfb*, Fig. 5) free of surroundings is heated in the described manner, on the end surface, *cc*, it would expand to a shape *bfeefb*. If, however, it were held in sidewise constraint, as it would be in a die, the shape assumed during the transient heating would be *bddb*. It is apparent that if the heating has been high enough the surface layers will be overstrained in compression and the metal at the surface will be plastically deformed. During cooling, therefore, the surface *dd* will contract more than enough to relieve the induced compressive stress, and a state of tension will exist in the cold surface now slightly higher than the original *cc*. If the range of temperature in the cycle is sufficiently high and wide, the stresses set up may develop cracks in only one cycle. Messrs. Guillet, Galibourg and Beuret[5] found it possible to develop heat cracks at will by pouring a little molten copper on a flat hardened surface and then immediately drenching with a strong jet of water. If the range in temperature is not sufficiently high and wide to develop cracks in only one cycle but is sufficient to cause a slight amount of permanent deformation of the surface, then for each cycle the surface is alternately stressed in compression and tension. Under these conditions cracks will develop after a certain number of cycles. If the range in temperature is not sufficiently high and wide to develop permanent deformation, then the stresses in elements parallel to the surface will alternate between compression and zero and the stresses in elements perpendicular to the surface will alternate between tension and zero. As found by H. F. Moore, of the University of Illinois, if this alternation of stresses is above the "endurance limit" of the material, it will cause fatigue failure (thermal-fatigue, heat-checking, heat cracks) after a certain definite number of cycles. The distance these stresses go beyond the "endurance limit" will determine the number of castings which can be made in a die before it develops heat cracks.

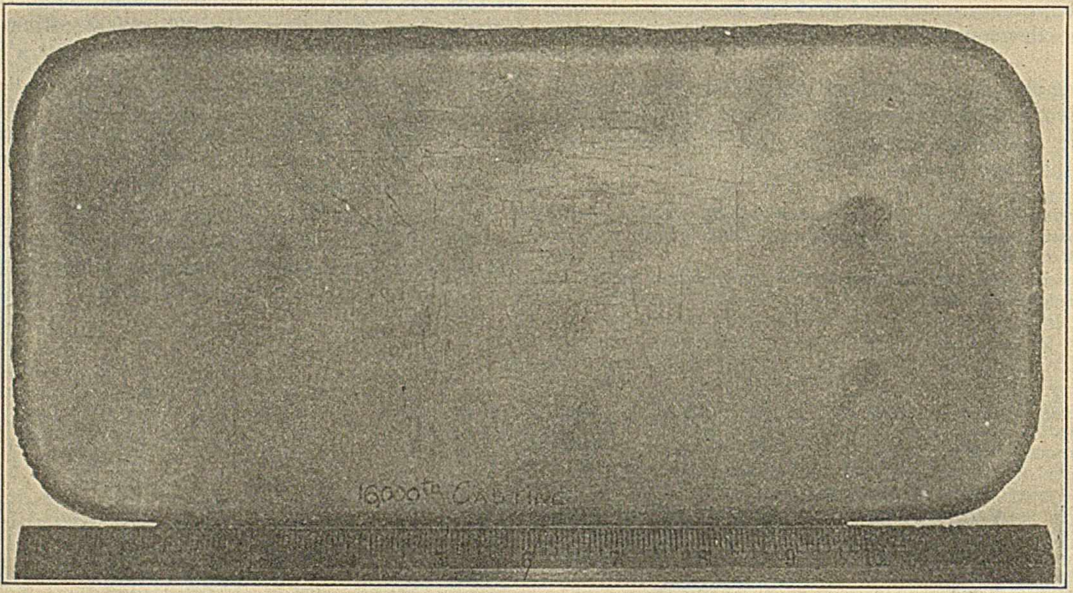

Fig. 2

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[5] *Rev. metal.*, **1921**.

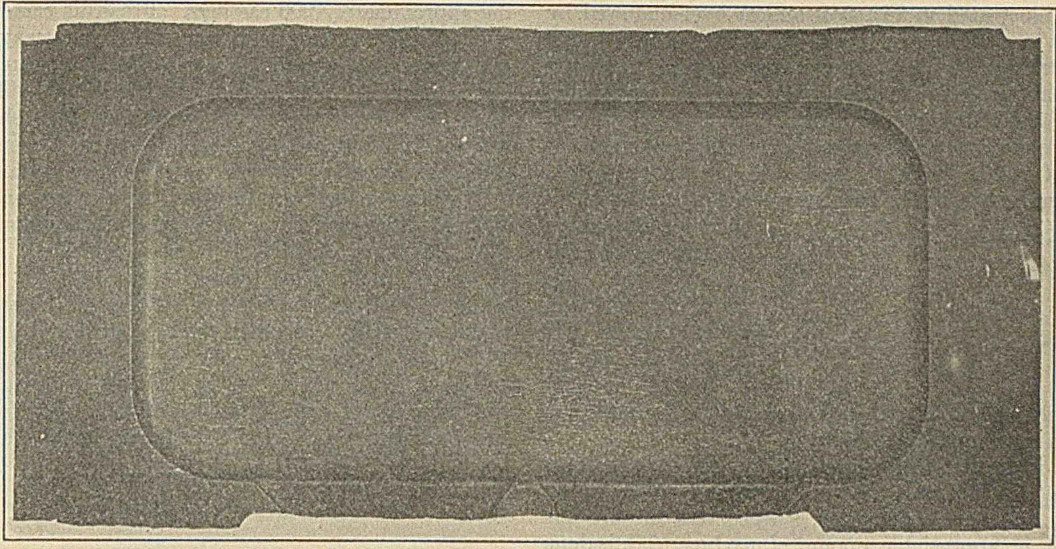

FIG. 3

The normal net result of the cycle described above and illustrated in Fig. 5 is shown in Fig. 6. But in die casting the cycle is not allowed to take this normal course. Just as soon as a crack appears, molten metal is forced into it at the start of the next cycle of operations and stays there while that cycle is completed. This metal in the crack acts like a wedge and spreads the crack wider and drives it deeper. In Fig. 4 it will be noticed that some of the heat cracks are white while others are black. The white ones are those in which the wedge of aluminium completely fills the crack, while the black ones are those from which the fins on the casting shown in Fig. 2 were derived. Even the cracks which appear black are not free from aluminium. An investigation under the microscope of a properly polished and etched specimen shows aluminium in the bottom of every crack.

ALUMINIUM DIE CASTING

That this situation in regard to thermal-fatigue of dies is the most important hindrance to the development of the die-casting industry is clearly shown by the curves in Fig. 7. In these curves casting temperatures are shown as abscissas and thousands of casting until the appearance of heat cracks are shown as ordinates. The improvements made during the last few years in type of alloy steel used for dies and in methods of heat treatment have resulted in Curve 4 and have made possible the expansion of the aluminium die-casting industry to its present status. Upon further improvements along this line depends further expansion. With each few thousand average increased life of die the less expensive aluminium die castings will become and the more uses will be found for them. Die-casting concerns throughout the country are continually experimenting. Hundreds of steels and other ferrous alloys and many nonferrous alloys are being tried under actual service conditions. It is possible that a better steel or material or type of treatment for aluminium die-casting dies is in its final development stage at this moment. That such a development can be made and not become known for some time is quite possible, owing to the attitude of secrecy adopted by practically all the die-casting concerns in regard to these matters.

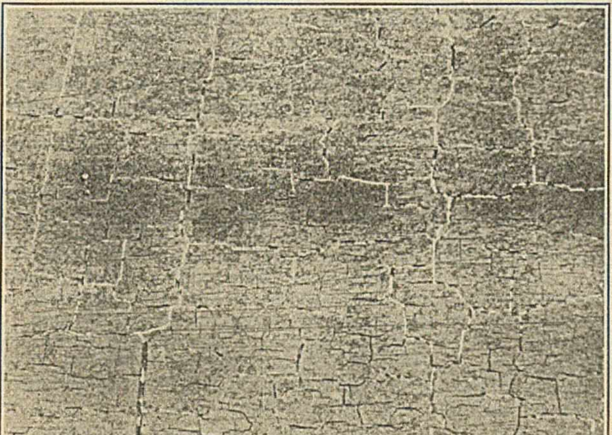

FIG. 4

Efforts in the direction of developing a new material are being made along the following lines: (*a*) steels which have greater normal strength; (*b*) steels which retain their strength at high temperatures; (*c*) steels which retain their hardness at higher tempering temperatures; (*d*) steels which have the property of red hardness; (*e*) materials with lower thermal coefficients of expansion than steel; (*f*) materials which will give service equal to that now given by heat-treated alloy steels but which will not give the usual trouble in hardening; and (*g*) machinable materials not requiring heat treatment.

BRASS DIE CASTING

In considering brass die castings another difficulty is encountered. Heat-treated alloy steel dies have been found best for aluminium die casting at 750° C., but brass must be cast at 1000° C. The extreme surface of the die does not reach the same temperature as the molten alloy forced into it, but reaches a temperature variously estimated for aluminium die casting of 550° to 650° C., and for brass die casting at from 800° to 900° C. Between these two temperatures lies the transformation range for most steels. For brass die casting the simple thermal expansion and

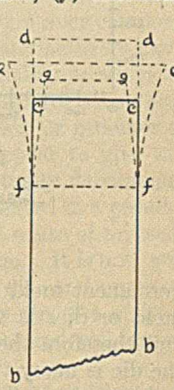

FIG. 5

contraction illustrated in Fig. 5 is almost overshadowed by the changes in volume resulting from changes of state and by the neutralizing effects of these changes of state upon any previous heat treatment. This is all further complicated by the decrease in strength and hardness of the steel when at elevated temperatures and further by the alloying or solvent properties of molten brass on steel. Just as improvements have been made during the last few years in the alloy steels used for aluminium die casting, it can be expected that the next few years will bring further improvements, but it is indeed doubtful if any simple alloy steel will be found that will make brass die casting a commercial possibility.

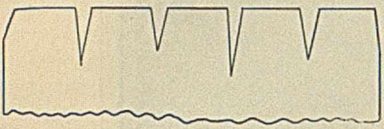

Fig. 6

The steel industry has for many years used cast iron for ingot molds, but this is a case of permanent mold casting and not die casting. Dimensions, surface, and life are not so important, no appreciable amount of machine work is done on the molds, the metal is not forced in under pressure nor instantaneously, the molds are not rapidly cooled, and the weight of the mold is small compared to the weight of steel cast. In die casting, the force and pressure behind the molten alloy cause it to come into much closer contact with the mold or die, and much more suddenly, so that the heating conditions are many times more severe than in permanent mold casting. In die casting, the mass of the mold or dies is very great compared to the casting itself, and therefore the rate of cooling of the extreme surface of the die is many times greater than is the case in permanent mold casting. The foregoing explains why a piece of cast iron, such as regularly used for steel ingots molds, when used in a die for brass die casting developed excessive heat cracks before fifty castings were made. Under similar conditions heat-treated alloy steel such as has proved best for aluminium die casting developed heat cracks after making approximately 200 castings. Brass die casting is further complicated by the shrinkage and high strength of brass and the resultant gripping of cores before they can be removed. Cores must be hard enough so that they will not score, must be strong and tough enough so that sharp corners will not be eliminated, and must be strong enough to withstand the force necessary to extract them from the casting.

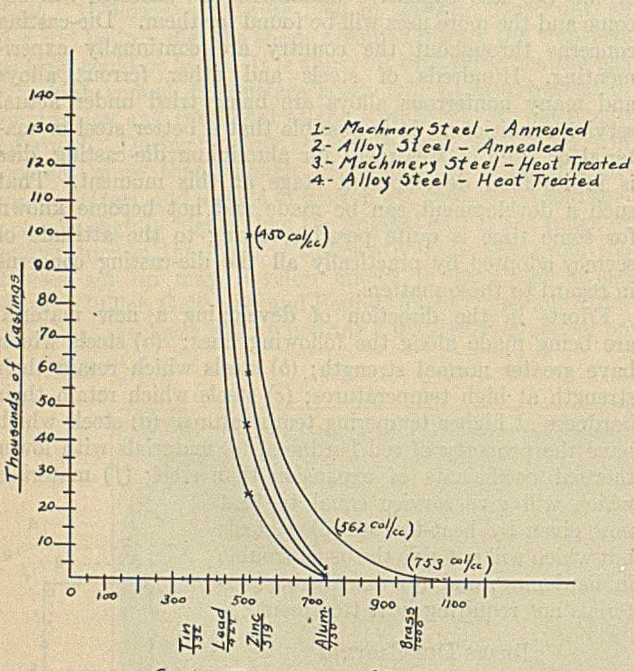

Fig. 7

The development of a lubricant or coating material which will not gasify and cause blowholes in the metal, but which will act as a protective film between the die and the hot metal and at the same time as a lubricant for cores, is certainly to be looked forward to. Such a lubricant or coating would materially cut down the rate of heat transmission to the die, and in doing so would not only cut down the maximum temperature to which the die surface is heated but also will lower the pressure it is necessary to apply to the molten metal in order to make it fill the cavity in the die.

A Good Beginning!

In an editorial in our November, 1922, issue, we called attention to the need of supplying chemical facts to those who have the making of our country's laws, with the suggestion that Local Sections undertake the task of furnishing their congressmen with information which they should have in order to best serve the interests of the chemical industry. The following letter, sent to an Indiana representative, is the first response of which we are aware. May there be others!

Hon. A. J. Hickey, November 23, 1922
Laporte, Ind.

Dear Sir:

You may not be aware that in this (South Bend) district, which includes the counties of Elkhart, St. Joseph, Starke, Marshall, and Laporte, there is a Local Section of the American Chemical Society.

Naturally there is little need to remind you of this organization in which all reputable chemists and chemical engineers are enrolled, but it might be worth while to tell you of the objects of the Society. The objects are the advancement of chemistry and the promotion of chemical research. This, you can see, has nothing to do with selfish motives, or organization for profit.

With such an aim in view, every American chemist desires the beneficial promotion of chemistry in America. The record of this branch of industry in the war will tell you its importance. As to your personal interest we are unaware, so we are writing to tell you we are quite ready to assist you should you wish to acquire information on any branch of chemistry that may not be clear to you, or on some particular phase on which you would like to be more thoroughly informed. Also, we wish to add that with the concentrated competition of foreign products, it does not seem right that our own chemical industries should suffer extinction.

We are enclosing a small digest, or "syllabus," which will be worth while looking over, as it will give you an idea of the field of chemistry in America to-day. Please consider that twenty years ago there were hardly twenty chemists in the state of Indiana.

We have nothing to ask except confidence and nothing to sell except service; therefore, please accept our coöperation and counsel to the common end of a more unified and complete country.

Our Section has expressed a desire to have you with us at one of our regular monthly meetings when convenient for you. It is anxious to hear some of the chemical problems which confront our congressmen. We should, indeed, appreciate an opportunity of having you talk to us on this subject, perhaps to the better understanding of us both.

Very truly yours,
Secretary

The *South African Journal of Industries* announced that the cover of the November, 1922, issue is of South African manufacture, having been made by the Premier Paper Mills, Klip River, Transvaal. This is the first occasion on which any South African journal has been issued with a cover of locally made paper.

White Metals

By Wm. A. Cowan

National Lead Co., New York, N. Y.

IN THE CLASSIFICATION of alloys, as established by ordinary usage, the term "white metals" is understood to designate alloys of lead, tin, and antimony. In some cases copper also is one of the lesser constituents, and alloys containing zinc may be included, but aluminium alloys are classified separately. Fusible alloys containing bismuth and cadmium are included as white metals. The nomenclature of most alloys of this class is based on the purpose for which they are used, the principal ones being bearing metals, solder, type metals, and casting metals. The names of the first three describe specifically the purposes for which they are used. They consist essentially of white metals, although the term "bearing metals" also covers bearing brasses or plastic bronzes. Casting metals, composed of white metals, are used for toys, plated articles, storage battery grids, bullets, etc., as well as in the manufacture of what are commonly termed "die castings." The development of standardized metal parts by die-casting to accurate size has resulted in large-quantity production by this process, bearing linings of white metal being frequently so made and in some cases die-cast directly on a brass back. The development of the die-casting industry has been very rapid, and a great deal of work has been done on the investigation of the alloys most suitable for the various purposes for which die castings are now manufactured. Rapid advances have been made in the art, and the alloys utilized have covered a wide range of composition, aluminium and zinc base alloys being used to a large extent. Since the subject covers a broader field than white metals as defined above, alloys for die castings will not be considered here.[1]

There are two additional kinds of white metals, the names of which are not derived from their fields of service. These are pewter and Britannia metal, the former being now very little used, while the latter is employed to some extent for silver-plated ware. Since they are of comparatively small commercial importance, and no noteworthy developments have been brought out in connection with them, these alloys will not be discussed.

BEARING METALS

The use of white metal alloys as lining metal for bearings has developed greatly since the introduction by Isaac Babbitt of a tin base alloy now commonly called "Genuine Babbitt." There is need of a comparatively soft metal as a lining for bearings to provide a bearing surface that is softer than the metal of the shaft, and that is sufficiently plastic to conform to any irregularities in alignment or running. Such a metal prevents wear of the shaft, and provides for the economical replacing of the lining when it is itself excessively worn. Metals of homogeneous structure such as possessed by pure metallic elements might have the requisite qualities of softness and plasticity, and yet they have been found unsuitable for bearings. Metals which have proved satisfactory are alloys of heterogeneous structure having hard components imbedded in a softer ground mass. When properly cast so that the hard components are more or less uniformly distributed and interlaced throughout the softer matrix, a structure is provided which is sufficiently resistant to pressure and yet has requisite plasticity. In actual service, such an alloy has strength to withstand the load and sufficient hardness of the rubbing surface, while the softer plastic matrix imparts to the metal the property of flowing under pressure, thus enabling it to conform to any irregularities in the running of the shaft. These requirements in the structure of alloys have long been established as constituting satisfactory bearing metals. It has more recently been recognized that under the ideal condition of running, which requires an unbroken film of lubricating oil, the question of friction and wear on the bearing linings is of very little moment, and it is only when the film is broken that the peculiar properties of the bearing metal come into play. An important requirement, therefore, in the design of bearings is to insure as far as possible the maintenance of a perfect oil film. It is now believed that in the characteristic structure of alloys previously found best for bearings, where the interlaced crystals of the hard component are brought out by wear and the softer metal of the ground mass is depressed, the resulting formation of grooves and hollows, although almost infinitesimal in size, tends to retain the oil film, somewhat as by capillary action.

For many years the practical development of bearing metals simply followed rule-of-thumb methods, alloys being made up to certain formulas according to hearsay or because of customary practice, without real study of the relation of actual requirements to the structure of the alloys employed. As careful investigations have been made of the properties of alloys required to render them serviceable for bearings, it has been found that many long-established ideas were based simply on prejudice or lack of full knowledge, and that a change in grade of metal should be made in order to give best and most economical service. This has resulted in finding many cases where drastic changes have been desirable, such as substitution of a tin base alloy for a lead base alloy, or vice versa, and also where slighter changes in composition could be made to produce greater uniformity. However, this situation has frequently been taken advantage of by unscrupulous dealers to persuade the nontechnical consumer that there was some peculiar quality in the particular brand of alloy of his manufacture, whereas the demonstrated difference has in fact been due only to change in grade or composition of the alloy. Following this, many manufacturers have made extravagant claims of exceptional quality in alloys of their make based on secret processes, addition of substances said to be impossible to be found by analysis, or presence of small amounts of elements, which may appear to give improvement in one direction but may be actually detrimental on the whole. These claims are often presented in a pseudoscientific manner, and have been a frequent cause of misleading the user having little technical knowledge. It is now well established that such methods are both unwise and unnecessary, since the best alloys can be made by the use of good practice in the art based on skilful experience and well-known metallurgical principles.

Alloys of wide variations in composition have been suggested and put into practical service as bearing metals. In many cases these have varied from each other by only small percentages of the constituent elements, so that the difference in actual properties has been slight. It is now the tendency to concentrate on a fewer number of formulas, selected as

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[1] See Tour, "Die Castings," p. 25 of this issue.

giving the best characteristics in each grade, as based on the properties conferred on the alloy by its structural components. This has been recommended by committees of the War Service Association of Manufacturers of Solder and Bearing Metals and of the American Society for Testing Materials. The grades specified can be classed very roughly as lead base, tin base, and intermediate grades. The latter, containing considerable amounts of both lead and tin, have as a structural component the eutectic mixture of these two elements. This has a low melting point, while the other components have a higher one, thus giving a wide range of temperature through which the metal continues to freeze in cooling. Partly on account of this and the presence of the eutectic mixture, these alloys have certain undesirable characteristics as bearing metals and are being largely eliminated in favor of either tin base or lead base alloys. They are, however, suitable for a special purpose, where very thin linings are desired, requiring a high degree of fluidity in pouring and the quality of adhering well to the metal in connection with which they are used as a lining.

A new alloy has been introduced as a bearing metal which has given excellent results in service. It is known as Frary metal and consists of an alloy of lead with only small amounts of barium and calcium. Although it contains approximately 98 per cent of lead, the added elements impart to it a hardness similar to that of other bearing metals, and also similar structural characteristics. It is used in the same way as other white metals for bearing linings, and has besides been found to give extraordinary service when cast in form of the entire journal for bearings of railway cars, particularly on interurban electric railways.

The study of the application of alloys to the needs of their service as bearings is based on the proportions and methods of distribution of their several structural components—namely, solid solution, eutectic mixture, chemical compound, or pure metal. Difference in hardness of the separate crystals of microscopic size comprising these components can now be investigated by means of an apparatus called the "Microcharacter," recently developed by a subcommittee of the American Society of Mechanical Engineers, C. H. Bierbaum, Chairman. This apparatus is to be applied to the general study of alloys by the Subcommittee on Microhardness of the American Society for Testing Materials.

There is more attention now being given to the question of proper pouring temperatures and rate of cooling in casting, as determining the distribution of structural components without undesirable segregation in bearings when put into service. The properties of each separate casting of an alloy as influenced in this way depend upon its particular treatment since last remelting.

The need is now recognized of giving consideration to changes in properties of the alloys which take place at temperatures attained by bearings while running in actual service. Some work has been done on determining the properties of certain bearing metals at elevated temperatures.

SOLDER

There has been little change in the composition of alloys used for solder. For ordinary soft solder, lead tin alloys have been consistently used. They have the following qualities requisite for the purpose: low melting point, high degree of fluidity at temperature only little above the melting point, and property of adhering well to surfaces of most other metals. Although the alloy having the composition of the eutectic mixture—63 per cent tin and 37 per cent lead—is actually best in these respects, there is seldom need of using it, since the 50/50 alloy is about as serviceable. The latter contains some excess of lead, which, however, does not solidify at a temperature sufficiently above the melting point of the eutectic to affect the practical working qualities. The advance which has been made in the practice of soldering has been in adapting the composition of the alloy to requirement of the work in hand as determined by the proportions of eutectic and excess lead.

The alloys of this series within a short range of composition contain such proportions of these two components that they acquire the property which is of value in making a so-called wiping solder. The metal becomes plastic on cooling when passing through a comparatively long range of temperature wherein it is partly fluid and partly solid. This property is valuable in wiping pipe joints, the solder being applied in this plastic condition and held in place until entirely solidified. It was formerly a frequent practice to allow the individual workman to use his personal skill in mixing wiping solder to the proper composition by the addition of tin or lead. With better knowledge of the properties of the alloys, the workman is now usually provided with solder ingots of the correct composition and not allowed to make any change.

During the war, when there was a scarcity of tin, an alloy made by replacing some of the tin with a less amount of cadmium was suggested for solder. The composition recommended, and on which much work was done by the U. S. Bureau of Standards, was 80 per cent lead, 10 per cent tin, and 10 per cent cadmium. However, since the war this cadmium solder has not been commercially used. The addition of a small amount of phosphor tin to solder has also been frequently suggested for the purpose of replacing to some extent the full amount of tin otherwise required in certain grades. Such an alloy, however, has not been found fully satisfactory.

In the manufacture of electric lamps with tungsten filaments, which attain a higher temperature than the old incandescent lights, a high melting-point solder is required, for which purpose an alloy containing a comparatively low amount of tin is used.

Progress has been made in applying solder by means of automatic machinery and by dipping in connection with large production of standard parts or finished articles. An improvement in commercial practice of selling solder by brands was long ago made by many manufacturers in doing away with an old custom of misbranding. It was formerly the universal custom to sell most grades of solder as "half and half," whether or not they were actually 50/50. Some qualification was made by branding the different grades as "warranted," "strictly" or "commercial half and half," but the latter grade contained as little as 37 per cent of tin. Such misbranding has now been stopped, as the result of a United States Supreme Court decision.

TYPE METALS

The introduction of type-setting machines in the printing industry has brought about necessary variations in the percentage composition of type metals. Change has resulted also on account of the general practice of using the type form first set simply as a die in preparing papier-mâché matrices for casting the plates which are actually used for printing. The latter are called "stereotype plates," and this method of printing is carried out in general where a great many impressions are to be made, as in newspaper, magazine, and book work. The harder alloys formerly required for small type are now less needed, and for some kinds of type metal, as linotype, alloys consisting of eutectoid mixtures of lead, tin, and antimony are most suitable. In this case sufficient strength is assured by the fact that the face of the type is cast as a continuous slug of metal the length of one line of type. For the various kinds of type-setting machines alloys are required having in general the following properties: low melting point, with solidification taking place in cooling either at one sharp point or else within a very narrow range of temperature; perfect fluidity above this point; slight amount of shrinkage; and property of taking sharp impressions when cast. Some differences in characteristics are required, however, in the particular alloys most suitable for stereotype and for the separate kinds of type-setting machines, according to whether the latter cast single letters, or a whole line. It has been possible to adapt the alloys to these different requirements from a thorough knowledge of the metallography of the ternary series, lead, tin, and antimony. This has been gained from the complete investigations of the thermal equilibrium of the series by Campbell,[2] Loebe,[3] and from the work of Heyn and Bauer.[4]

In the use of stereotype many separate plates cast in the same matrix may be needed to complete an edition, and for the very large issues of weekly magazines, etc., improvement has been made in the number of impressions possible to be taken from each plate by nickel plating the type face.

Other Research on Alloys

Valuable articles have lately appeared on the general subject of alloys by W. Guertler; on white metals by Mundy, Bissett, and Cartland, published as a preprint for the September 1922 meeting of the British Institute of Metals; and on bearing metals by J. Czochralski and others.[5]

Interest in the study of white metals has greatly increased through the work which is being done in connection with nonferrous metals by the U. S. Bureau of Standards and Bureau of Mines, committees of the American Society for Testing Materials, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, and other organizations.

General problems that are being investigated relate to the subject of corrosion, the effect of impurities on physical properties, standardization of methods of physical testing, and effect of shrinkage on the density and form of solid castings—this having to do both with the contraction taking place from the instant of complete solidification down to room temperature, and also with the change in volume accompanying the difference in density between the liquid and solid phases of the metal.

[2] "Lead-Tin-Antimony and Tin-Antimony-Copper Alloys," *Proc. Am. Soc. Testing Materials*, **13** (1915), 630.

[3] "The Constitution of the Ternary Alloy of Lead, Tin, and Antimony," *Metallurgie*, **8**, 7, 35.

[4] Investigation of Bearing Metals, Antimony-Lead-Tin Alloys, conducted by K. Materialprüfung Berlin—Lichterfelde.

[5] Czochralski, *Z. Metallkunde*, **12** (1920), 371; Guertler, *Ibid.*, **13** (1921), 257; Czochralski-Welter, "Bearing Metals and Their Technical Value," Springer, Berlin, **1920**.

The Wrought Nonferrous Alloys in 1922

By W. H. Bassett

The American Brass Co., Waterbury, Conn.

THE PAST YEAR has brought to attention nothing novel in the way of alloys or the treatment of alloys in the wrought nonferrous industry.

Copper Alloys

The outstanding feature has been a wider use of copper and copper alloys following the post-war depression. This has been brought about through a better understanding of the properties of the materials and their adaptation to industrial requirements. Much more attention is being given to the study of the properties of the metals and alloys and to methods of treatment than ever before.

The advent of the chemist and metallurgist in the industry dates back hardly more than twenty years, and up to the beginning of the World War only the larger and more progressive manufacturers maintained laboratories or attempted metallurgical control. The engineering specifications from the military establishments forced manufacturers who had been delinquent to establish testing laboratories at least.

Within the industry itself notable improvements of the present time are laboratory control of the quality of the raw materials used, of the composition of the alloys, and of the physical and electrical properties of the products, metallographic control of heat treatment and hardness, electric melting, and the better understanding of the properties of metals and alloys.

The statement is frequently made that the quality of copper is not as good as it was twenty or thirty years ago. Such statements are indicative of ignorance of the real facts, for at no time in the history of the industry has the quality of copper in the form of wire bars, cakes, and ingots been equal to that of the present delivery. The purity minimum of 99.900 per cent is now maintained by the important American producers. In wire bars and cakes the conductivity is regularly held at 100 per cent of the "Annealed Copper Standard." All this has been gained through systematic control testing on the part of both producers and consumers.

Improvements in Quality

Standard specifications for copper, zinc, and nickel have been prepared by the American Society for Testing Materials. Considerable progress has been made by the same society on similar standards for lead and aluminium. Such specifications have marked the progress made in improving the quality of raw materials and rendered the production of alloys of the highest grade a much more exact and simple matter.

The analytical laboratory is as essential a part in the production of nonferrous alloys as it has become in the steel works. In every modern metal works the composition and quality of the alloys is strictly a matter of laboratory control. While this condition is not a sudden development, it cannot be said to have become general until within the last few years. It certainly marks a notable feature in the progress of the industry.

The metallographic study of nonferrous metals and alloys has gradually grown in importance as a means of control and investigation, and 1922 has seen the publication by a national society[1] of the first specification in which grain size has been used as a definite measure of the physical properties of the material.

The study of the structure of the nonferrous metals at magnifications of 500 and 1000 diameters in the works laboratories, where nothing much beyond 75 to 100 diameters has heretofore been attempted, is another feature marking progress in applied metallography.

[1] American Society for Testing Materials.

Electric Melting of Alloys

The most important change in practice in the preparation of alloys which has occurred in the last few years is electric melting. This evolution, or more properly revolution, in casting practice is now in progress. The most popular and probably most efficient melting device is the induction furnace. In several of the more important establishments the greater part of the melting is being done in induction furnaces. Some of the mills and foundries have apparently made successful application of arc type furnaces. The most recent developments seem to indicate that each type has a distinct field in which it will find its most economic and efficient application.

Exaggerated claims have been made as to the superior quality of electrically melted brass. The truth of the matter is that electric melting has proved more economical than melting with coal or coke. The electric furnace removes any possibility of the absorption of gases from fuel combustion by the metal and allows a somewhat closer heat regulation. It is much easier for the workmen to operate than the crucible furnace. Electric melting reduces the zinc losses incident to crucible melting, but it has by no means overcome all the troubles that may occur in casting alloys, and the same careful practice and supervision must still be exercised to achieve success.

Corrosion

The question of the corrosion of metals and alloys is one of the most important which affect their industrial application and use. The National Research Council is now actively organizing and coördinating the research facilities of the country for comprehensive work in this direction.

Much effort has been put into the study of corrosion, with comparatively little definite or practical result. There is still considerable difference of opinion as to the choice to be made among metals or alloys for certain commercial purposes, and failures which now and then occur result in bringing the misapplied material into disrepute. Modern conditions have intensified the corrosive action to which metals are exposed in everyday service through increased pollution of the atmosphere and water supplies. Industrial uses are generally becoming more intense, and the proper choice of metals to meet the conditions of service is essential. This means that a more thorough understanding of corrosive action and its effect on various materials is necessary.

The persistence and insistence of Alfred D. Flinn in demanding that the reason for the spontaneous failure of certain alloys used by the New York Board of Water Supply be found and understood is still giving results. Means have been found for preventing the spontaneous cracking of rods and bars when exposed to corrosion, and there is no further danger of the failure of properly finished wrought bronzes and brasses from internal stresses when such material is exposed to corrosive action.

Other Lines of Progress

The cracking of tubes, both for condensers and water-supply pipes, has been eliminated, so there is now no danger from split piping in the water supply of buildings, if brass is used.

Considerable progress has been made with the study of the effect of fatigue on steels or ferrous alloys, but practically nothing has been done in the nonferrous field. The subject is important and researches are promised in this direction.

The use of the white alloys of copper, nickel, and zinc is becoming more prominent, particularly in the field occupied by plated material. Such alloys are resistant to corrosion, durable and pleasing in appearance, and at the same time have good physical properties. This type of alloy has been known for years under the general name of "German silver." It has always been an attractive field for "inventors" who, through want of knowledge of the nickel alloy, have made fanciful claims as to their remarkable properties. Just at present there seems to be a new epidemic of "invention" of "Super German Silver" with most wonderful properties, some of which are said to be obtained through the use of secret fluxes which leave no trace behind.

The growing use of electrical equipment, both in industry and for the household, has stimulated the use of copper in all forms and also that of many of the copper alloys.

Cadmium is now one of the commercial metals. It has, when used in small quantities, the effect of increasing the strength of copper without seriously decreasing its conductivity. Cadmium or cadmium and tin together are being used for producing stronger conductor and trolley wires.

Magnesium and magnesium alloys are receiving considerable attention, but have not yet become industrially important. The progress being made with aluminium and the light alloys has so recently been outlined by Gillett[2] that there is nothing further to be said at this time.

In general, 1922 has brought a revival in the wrought nonferrous industry, with continued study of the application of the metals and alloys to engineering and domestic needs. The educational campaign being carried out by several of the important factors in the production of metals and alloys will undoubtedly result in a more intelligent use of these products and an increased consumption. There is still much to be gained by such researches as have been mentioned, and more benefit will be derived from the systematic study of the properties of the materials already familiar than is likely to result in attempts to find new combinations.

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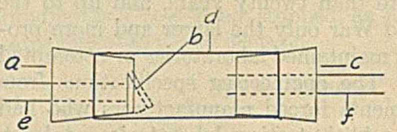
[2] This Journal, 14 (1922), 865.

A Simple Check Valve[1]

By J. F. Brewster

Louisiana Sugar Experiment Station, New Orleans, La.

The accompanying sketch is intended to represent a check valve made from materials to be found in the chemical laboratory. It was devised for use with the water vacuum pump to prevent flooding of apparatus when a "suck back" occurs in case of variation in water pressure.



A solid rubber stopper, shown at *a* in the sketch, is cut about three-quarters through at the small end so that a thin flap of rubber, *b*, is left to serve as the valve leaf. The stopper is then bored, leaving the flap intact, to receive the short length of glass tubing, *e*, which should be pushed to within a few millimeters of the valve seat.

A short length of glass tubing, of such diameter as to allow free play of the leaf and at the same time fit the stoppers tightly, is closed at one end by the valve stopper and at the other by the one-hole stopper *c*, carrying glass tubing *f*. By means of rubber tubing, *f* is connected with the pump, and *e* with the system to be evacuated. Any convenient sizes of stoppers and tubing may be used.

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[1] Exhibited before the Division of Sugar Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

The Pumping of Liquids in Chemical Plants[1,2]

By Clark S. Robinson

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

The problem of transporting liquids in chemical plants is one of the most frequent with which the chemical engineer has to deal. Often the liquids to be handled are of the most corrosive character and the wear and tear on pumping equipment cause serious concern to the management. The improvements in equipment for this work by manufacturers in recent years have, however, made it possible to handle difficult liquids economically in nearly all cases. It is the purpose of this article to indicate in so far as space is available the several types of pumping apparatus on the market and the uses for which they are most suitable. The following is a classification of pumping apparatus:

- *A—Mechanical pumps*
  - *I—Reciprocating pumps*
  - *II—Centrifugal pumps*
    - *(a) Volute pumps*
    - *(b) Turbine pumps*
  - *III—Rotary or gear pumps*
- *B—Pumps using compressed air*
  - *I—Eggs or elevators*
  - *II—Air lifts*
- *C—Siphons*

RECIPROCATING pumps were the first to be used for pumping purposes, and for that reason have been developed and refined to the point of standardization by nearly all manufacturers. In fact, the most important refinements in recent years have been in the direction of convenience in repairs and in the selection of the best materials out of which to make them. As far as the handling of water and other noncorrosive liquids is concerned, reciprocating pumps are in use at the present time that have been in continuous operation for fifty years with only occasional replacement of worn parts. Such pumps if properly cared for should last indefinitely.

Reciprocating pumps comprise several types. The first and perhaps the most common is the direct-acting steam pump which is made both single and double. These direct-acting pumps have no flywheel to carry them by dead center, but depend on the mechanical operation of the steam valve to reverse the flow of steam to the steam piston, this being accomplished by a suitable device on the piston rod which actuates the steam valve for the piston either directly or through the aid of a steam relay. The pump is therefore double acting—that is, it pumps on both strokes of the piston. On the single pump the piston actuates its own steam valve, while on the double or duplex pump one piston actuates the steam valve on the other cylinder, and vice versa. The discharge from a direct-acting pump is therefore decidedly pulsating, and it is necessary to provide some means to equalize the flow and to prevent water hammer. This is done by means of an air chamber which absorbs the shock by the compression and expansion of air in it.

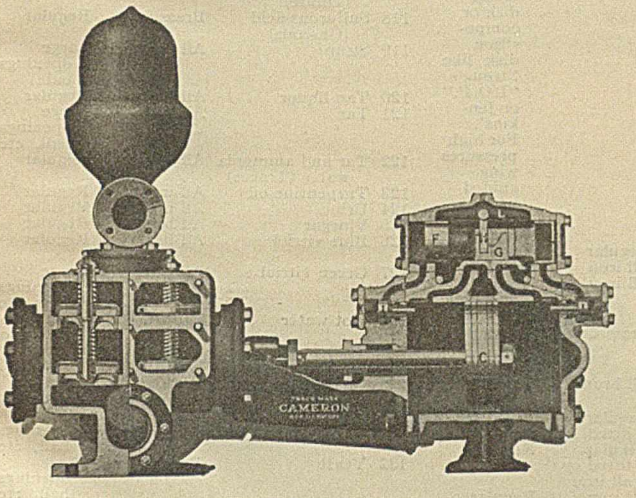

FIG. 1—SINGLE DIRECT-ACTING PUMP

The foregoing figure shows the essential features of the single direct-acting pump.

In this particular pump the valve-actuating relay is operated by the piston itself, instead of the piston rod as is usually the case. The water valves are clearly shown, the inlet valves below, and the outlet valves discharging into the air chamber above. The chief advantage of the single direct-acting steam pump lies in its extreme simplicity and reliability. The steam consumption is also low, as the piston must travel to the end of its stroke before it can reverse. The flow from the pump is, of course, extremely pulsating.

In the case of the double or duplex pump, the valve motion is such that one side finishes its stroke and waits for its valve to be moved by the other side of the pump before it can start on its return stroke. This makes the discharge of the pump nearly continuous and the air chamber is frequently unnecessary. As one or the other of the steam valves is always open, the pump will always start whenever the steam is turned on. This is not the case with a single pump, which must be started by hand. The duplex pump is therefore used where automatic starting is required.

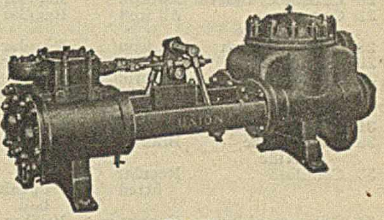

FIG. 2

Fig. 2 shows a duplex pump of the usual type.

Reciprocating pumps have the advantage that they will raise the liquid by suction to the pump, it being unnecessary to prime them. The distance that water can be raised depends upon the temperature and the altitude. Fig. 3 shows the lift possible at sea level for varying water temperature. It will be noted that when the water is at a temperature of 168° F. or more it must flow to the pump from above.

Reciprocating pumps are made of a number of materials, for handling various liquids. The table which follows was collected by the Goulds Manufacturing Company and represents the best available practice at the present time. It will be of interest to chemical manufacturers that the manufacturers of this type of pump do not guarantee the life of the pump when handling chemicals, the purchaser assuming the risk.

A single direct-acting steam pump constructed of Duriron is available which has a capacity of 15 gal. per min. at a pressure of 75 lbs. per sq. in. This pump is especially suitable

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[1] Received October 25, 1922.

[2] Contribution No. 36 from the Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

Table I—Materials for Special Service Pumps

No.	Liquid to be Pumped	Material Used	Valves
1	Acetic acid (Concentrated)	Lead or phosphor bronze	Regular disk, etc.
2	Acetic acid (Diluted)	Enamel	Regular
3	Acid mine water	High lead bronze	Regular
4	Alcohol (Crude)	All bronze brass, also cast iron	Regular
5	Alkaline liquid	Enameled	Regular
6	Alkaline water	All iron	Regular
7	Aluminium sulfate	Brass fitted	Regular
8	Ammonia, ammonia water	All iron	Regular
9	Aniline water	All iron	Regular
10	Beer	All bronze	Regular
11	Beer wort	All bronze	Regular
12	Beet juice (Thin)	Brass fitted	Regular
13	Benzine, benzene	All iron	Regular
14	Bichloride of mercury	All iron	Regular
15	Cachaza (Sugar mill by-product from which rum is made)	Brass fitted	Large openings, ball
16	Calcium brine (Pure)	Regular	Regular
17	Calcium chloride, adulterated with sodium chloride	Bronze fitted	Regular
18	Calcium acid sulfate (Concentrated)	All bronze	Regular
19	Calcium acid sulfate (Diluted)	Brass fitted	Regular
20	Cane juice	Brass fitted	Regular
21	Carbonate of sodium	All iron	Regular
22	Carbonic acid gas in water	Regular	Regular
23	Caustic carbonate of soda (Boiling)	All iron	Regular
24	Caustic chloride of magnesium (Hot)	Hard lead	Regular
25	Caustic chloride of sodium	All iron	Regular
26	Caustic cyanogen	All iron	Regular
27	Caustic manganese	All iron	Regular
28	Caustic potash	All iron	Regular
29	Caustic soda	All iron	Regular
30	Caustic strontia	All bronze	Large openings, ball
31	Caustic sulfide	All bronze	Regular
32	Caustic zinc chloride	Brass fitted	Regular
33	Cellulose	Regular fitted	Large openings, ball
34	Chlorate of lime	Copper is best then bronze and cast iron	Rubber or bronze
35	Chloride of lime	Enameled	Large openings, ball
36	Chlorine and water	Enameled	Regular
37	Chlorine (Dry gas)	Copper-nickel-manganese-alloy	Regular
38	Citric acid	Regular	Regular
39	Coal-tar oil	All iron	Regular
40	Copperas	All iron	Large openings, ball
41	Copper sulfate	All bronze	Regular
42	Creosote oil	All iron	Regular
43	Cyanide of potassium	All iron	Regular
44	Cyanogen	All iron	Regular
45	Cyanogen slime	All iron	Ball
46	Diffusion water	Neutral	Regular
47	Dish water	Regular	Regular
48	Distillery wort	All bronze	Regular
49	Fatty acids heated over 55° C.	All bronze	Regular
50	Ferric hydroxide	All bronze	Regular
51	Ferrous chloride	Ebonite liner	Regular
52	Ferrous sulfate	All iron	Large openings, ball
53	Fuel oil	Brass fitted	Regular
54	Gasoline	Brass fitted	Regular
55	Glue (Hot)	Brass fitted	Large openings, ball
56	Glycerol	All bronze	Regular
57	Gun-cotton brine	All bronze	Large openings, ball
58	Hydrochloric acid	Enamel	Regular
59	Hyposulfite of soda	Lead lined, no zinc	
60	Iron pyritic acid	All bronze	Regular
61	Lard (Hot)	All bronze	Regular
62	Limewater	All iron	Large openings, ball
63	Linseed oil	All iron	Large openings, ball
64	Lye, caustic	All iron	Regular
65	Lye, salty	Brass fitted, preferably bronze	Regular
66	Lye solution containing sand	All iron	Disk
67	Magnesium acid sulfate (Concentrated)	All bronze	Regular
68	Magnesium acid sulfate (Dilute)	Brass fitted	Regular
69	Magnesium chloride (Hot)	Hard lead	Regular
70	Marsh gas	Regular fitted	Regular
71	Mash	Brass fitted, preferably bronze	Large openings, ball
72	Milk	Iron or bronze	
73	Milk of lime	All iron	Large openings, ball
74	Mine water	High lead bronze	
75	Molasses	Bronze fitted	Large openings, ball
76	Muriatic acid	Enameled	Regular
77	Naphtha	Brass fitted	Regular
78	Crude naphtha	Regular	Regular
79	Nitric acid (Concentrated)	Lead	Regular
80	Nitric acid (Dilute)	All iron	Regular
81	Crude oil—asphaltum base oils must be heated in order to pump. Paraffin base oils can be pumped without heating		Special valves for ordinary pressures—metal disk or composition disk like Strong's "I.O.P." or Jenkins'. For high pressures wing guided with leather face
82	Mineral oil	Regular	Regular
83	Vegetable oil	All iron	Regular
84	Purifying oil	All iron	Large openings, ball, etc.
85	Paraffin (Hot) (Melts from 45°–65° C.)	Brass fitted	Regular
86	Peroxide of hydrogen	All bronze	Regular
87	Petroleum	Regular fitted	
88	Petroleum ether	Regular fitted or all iron	Regular
89	Potash	All iron	Regular
90	Potassium chloride	All bronze	Regular
91	Potassium nitrate—caustic solution of saltpeter	All iron	Regular
92	Rape-seed oil	Regular	Regular
93	Sal ammoniac	All iron	Regular
94	Salt brine	All bronze	Large openings, ball, etc
95	Salt water—up to 3 per cent salt	Brass fitted	Regular
96	Salt water—over 3 per cent salt	All bronze	Regular
97	Sewage	Brass fitted	Large openings, ball, etc.
98	Soap water	All iron	Regular
99	Soda	All iron	Regular
100	Soda ash	All iron	Regular
101	Sodium bicarbonate	All iron	Regular
102	Sodium sulfate	All iron	Large openings, ball, etc.
103	Starch	Brass fitted	Large openings, ball, etc.
104	Sugar	All bronze	Large openings, ball, etc.
105	Sulfate of lime	All bronze	Large openings, ball, etc.
106	Sulfide of hydrogen	Regular fitted	Regular
107	Sulfide of sodium (Hot)	All iron	
108	Sulfolignic salts (Concentrated)	All bronze	Regular
109	Sulfolignic salts (Diluted)	Brass fitted	Regulat
110	Sulfur in water	*Bronze fitted	Regular
111	Sulfuric acid (Concentrated)	*All iron	Large openings, ball, etc.
112	Sulfuric acid (Concentrated) (Hot) 60° Baumé	All iron or clay	Regular
113	Sulfuric acid (Concentrated) (Hot) 40° Baumé	*Phosphor bronze	Regular
114	Sulfuric acid (Dilute)	Hard lead	Large openings, ball, etc.
115	Sulfuric acid fuming (Nordhausen)	*Regular fitted	Large openings, ball, etc.
116	Sulfurous acid (Concentrated)	Enameled	Regular
117	Sulfurous acid (Dilute)	All bronze	Regular
118	Sulfurous acid (Gaseous)	Brass fitted	Regular
119	Sirup	All bronze	Large openings, ball,
120	Tan liquor	All bronze	Regular
121	Tar	All iron	Large openings, ball, etc.
122	Tar and ammonia water (Traces)	All iron	Regular
123	Turpentine oil	All iron	Regular
124	Urine	All bronze	Regular
125	Vinegar	All bronze	Regular
126	Blue vitriol	All bronze	Regular
127	Green vitriol	All iron	Large openings, ball, etc.
128	Hot water	Bronze fitted	Special hot water or metal disk
129	Oily water	Regular	Regular
130	Wine	All bronze	Regular
131	Wood pulp	Brass fitted	Large openings, ball, etc.
132	Yeast	Brass fitted	Large openings, ball, etc.
133	Whiskey	All bronze	

Material marked thus * is used, but will not wear any great length of time.

for filter-press work for solutions carrying abrasive solids. It is, however, single acting.

For very corrosive solutions, which cannot be handled readily with the usual metal installations, there is available a hard-rubber reciprocating pump, of which Fig. 4 is an example. This is a double-acting steam pump which has a capacity up to 100 gal. per min. and for pressures up to 30 lbs. per sq. in.

Reciprocating steam pumps are rated by the diameters of their steam and water cylinders, and their stroke. Thus, a pump listed as 5 × 3 × 6 has a 5-in. diameter steam cylinder, a 3-in. water cylinder, and a piston stroke of 6 in. The efficiency of direct-acting steam pumps varies with the length of the stroke, the efficiency for short strokes of 3 or 4 in. being about 40 per cent, while for strokes of 24 in. the efficiency may run as high as 80 per cent. They are made for all capacities and pressures.

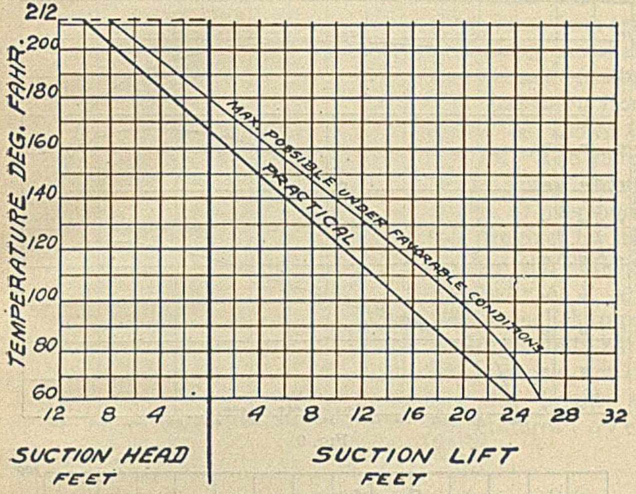

FIG. 3

Reciprocating pumps are also made to be power driven, usually by means of gearing. A very common and satisfactory form is the single-acting triplex pump of which Fig. 5 is an example.

These pumps are of the plunger type, and since the plungers are driven by cranks set 120 degrees apart, the flow is uniform and fairly free from shock. Air chambers are provided, however. Special attention must be paid to the glands which prevent leakage past the plungers.

CENTRIFUGAL PUMPS

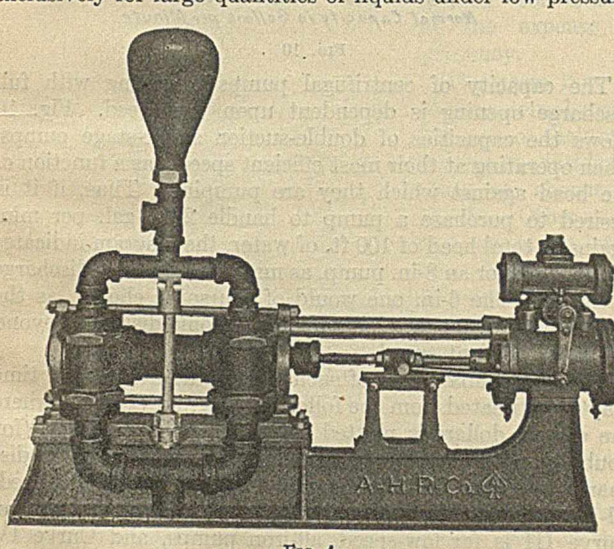

FIG. 4

Until recent years centrifugal pumps have been used exclusively for large quantities of liquids under low pressure heads. Modern designs have so improved them, however, that they are now available for any amounts of liquid up to almost any head—i. e., 300 ft. of water for single-stage pumps, while multi-stage pumps are available up to ten stages. As a consequence of this, centrifugal pumps are rapidly replacing reciprocating pumps in a great many industries.

In the centrifugal pump the liquid is delivered at high velocity from the rapidly revolving vanes of an impeller. The liquid is then taken through passages of gradually increasing cross section in which its velocity head is changed to pressure head. These passages may be of the volute or spiral type, or they may consist of diffusion vanes. In the former case the pump is called a volute pump and in the latter case it is called a turbine pump.

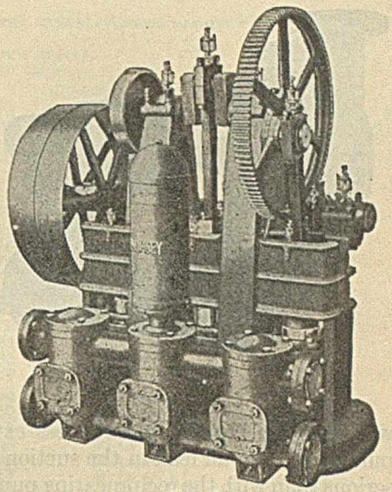

FIG. 5

The chief difference in the performance of the centrifugal and the reciprocating pumps lies in the character of the discharge. In the case of the latter throttling the discharge will build up the pressure against which the pump is delivering and place an additional load upon the pump, as a consequence of which either the pump will stop or something will break; while in the case of the centrifugal pump, throttling the discharge merely has the effect of decreasing the flow without materially increasing the load. In fact, the load on the motor will drop off until, when the discharge is completely closed, the impeller will be revolving inside its casing, doing no work but the friction of churning of the liquid caught inside of the casing. This will eventually develop enough heat to cause the liquid to boil unless the pump is stopped or the heat removed to the surroundings.

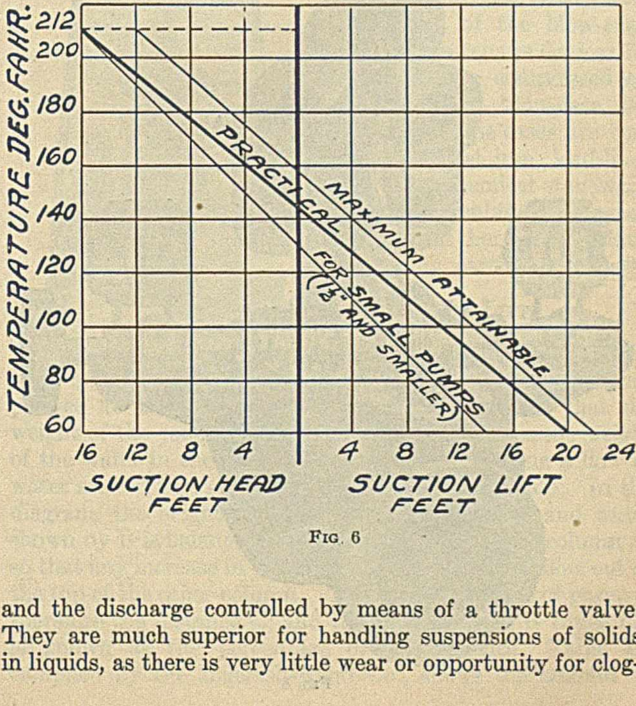

FIG. 6

Centrifugal pumps are, then, ideal for most of the uses in chemical plants, being run at constant velocity by direct connection with a motor or from a constant speed pulley, and the discharge controlled by means of a throttle valve. They are much superior for handling suspensions of solids in liquids, as there is very little wear or opportunity for clogging. Where solids in suspension are to be handled, the impeller is of the open type, while with clear liquids the closed impeller is used, the latter being more efficient. Centrifugal pumps are not suitable for filter-press work.

The one disadvantage of centrifugal pumps is the fact that they must be primed to function, and it is either necessary to place the pump below the source of supply of liquid to be pumped, or to prime the pump by hand from a pressure line each time it is to be started up. It is therefore useless for automatic systems without complicated attachments unless placed below the source of supply. After priming, they will draw up liquids but to a less extent than reciprocating pumps, and an air leak in the suction line will be much more serious than with the reciprocating pump. Fig. 6 shows the suction for water as function of temperature, plotted as before.

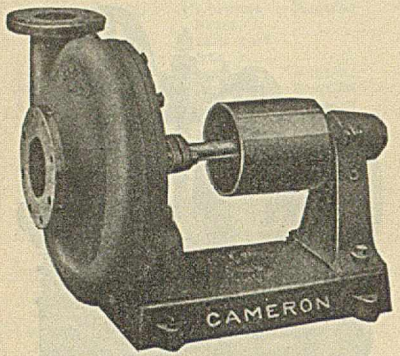

FIG. 7

Single-stage centrifugal pumps are made either single-suction or double-suction. In the case of the former the liquid enters from one side of the impeller only, as is shown in Fig. 7. These single-suction pumps are much less expensive than double-suction pumps, but on account of the lateral thrust upon the shaft there must be provided a thrust bearing that will not give trouble through wear or friction due to lack of sufficient lubrication, especially in the larger sizes. On the other hand, the double-suction pump theoretically should have its thrust equalized, but on account of the inequalities in manufacture it is advisable to provide a thrust bearing for these also, though of much less rugged construction. The single suction pumps are advised for heads of 100 ft. or less, preferably less than 50 ft.

For higher heads and for more efficient operation the double-suction pump should be used, an example of this type being shown in Fig. 8. This is a pump of the volute type, with the top of the casing open to show the enclosed impeller.

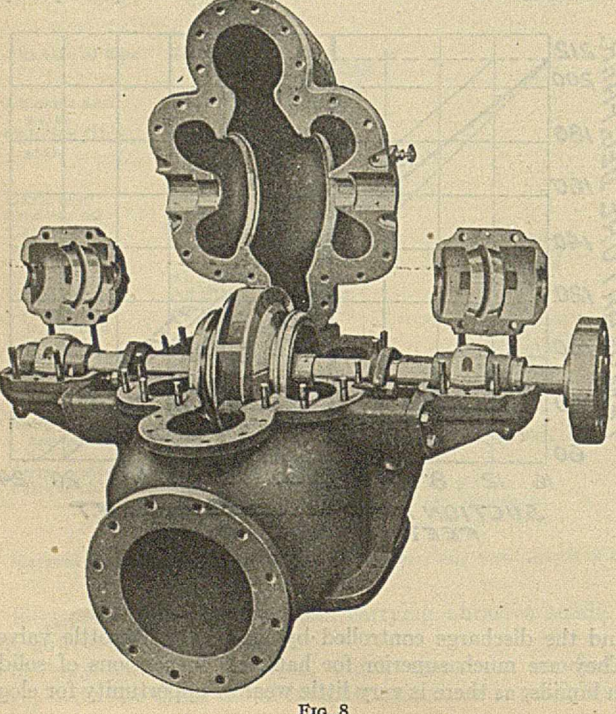

FIG. 8

The characteristics of the centrifugal pump are well shown in Fig. 9, which is a double-suction pump with a 5-in. discharge opening, running at a speed of 1700 r. p. m. It will be noted that at the point of maximum efficiency the efficiency is over 75 per cent, a figure quite comparable with those for reciprocating pumps.

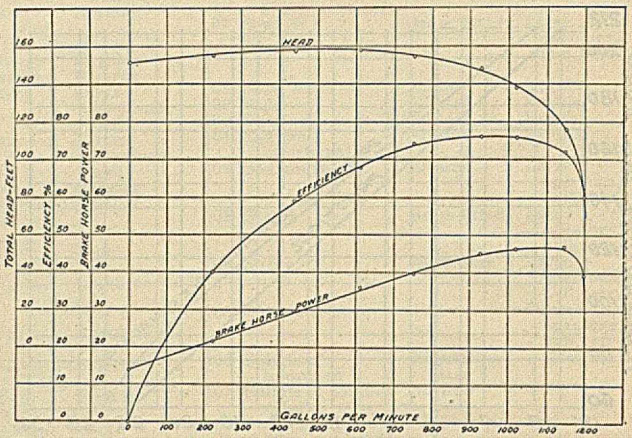

FIG. 9

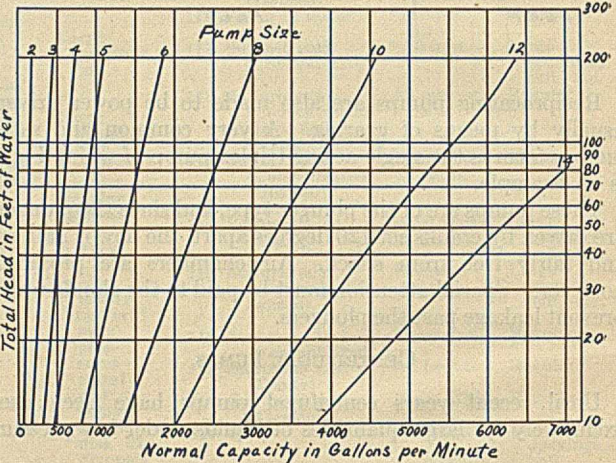

FIG. 10

The capacity of centrifugal pumps operating with full discharge opening is dependent upon the speed. Fig. 10 shows the capacities of double-suction single-stage pumps, when operating at their most efficient speeds, as a function of the head against which they are pumping. Thus, if it is desired to purchase a pump to handle 2000 gal. per min. against a total head of 100 ft. of water, the diagram indicates either a 6-in. or an 8-in. pump, as measured by their discharge openings. The 6-in. one would of course be chosen, as the efficiency does not drop off rapidly for some distance beyond the most efficient speed.

The approximate cost of such a pump at the present time may be estimated from the following diagram (Fig. 11) where the cost in dollars is plotted against the size of pump (for double-suction pumps), the size being the diameter of the discharge opening. In this diagram Curve I is for high-speed, all-iron pumps, Curve II is for high-speed, all-bronze pumps, Curve III is for low-speed, all-iron pumps, and Curve IV is for low-speed, all-bronze pumps. These costs do not include motors or driving pulleys. Single-suction pumps range about half of these costs for the same size.

Centrifugal pumps are made of a large variety of materials for use with all kinds of chemical solutions. Among the more notable of these are hard rubber, hard lead, Duriron, chemical stoneware, and Monel metal. Centrifugal pumps have a tendency to leak at the shaft stuffing boxes. This is of little importance in handling water, but when corrosive liquids are being pumped it may be a matter of considerable moment. The Antisell packless pump of hard lead overcomes this difficulty for sulfuric acid by making the shaft vertical and feeding the impeller from above, as shown in Fig. 12. The hard-rubber pump shown in Fig. 13 overcomes this trouble by removing the leakage as rapidly as it collects through the pipe, 20. Incidentally, hard rubber should not be used for liquids at temperatures over 55° C.

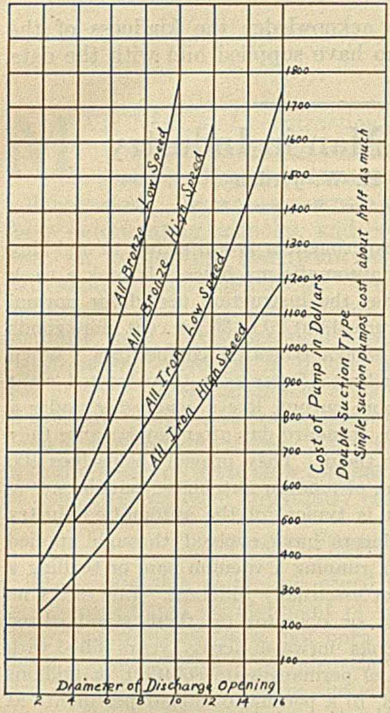

FIG. 11

ROTARY PUMPS

Rotary, or gear, pumps have two intermeshing gears revolving in a casing, the liquid being caught between the teeth of the gears and carried against the higher pressure. Since the operation of the gears is positive, the pumps resemble reciprocating pumps in that the discharge cannot be throttled without stopping the pump. Variable discharge is obtained either by varying the speed of the pump or by by-passing parts of the liquid, the latter method being usually the one used, thus gaining convenience at the expense of efficiency.

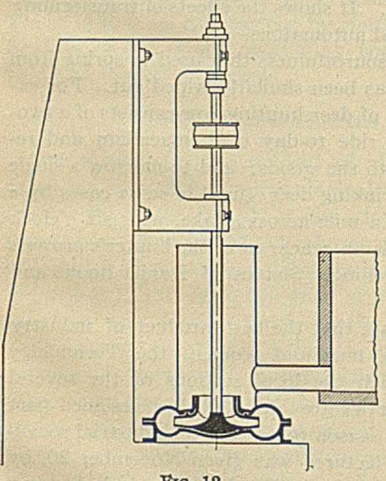

FIG. 12

The gears may be of the external meshing type, or they may revolve one inside the other as shown in Fig. 14. Other modifications of the latter type have eccentric rotors with sliding strips which entrain the liquid by sliding around the inner surface of the pump casing.

The efficiency of these pumps is high. Fig. 15 shows the curves for a 100-gal. pump of the type shown in Fig. 14. As a rule, these pumps are not suitable for pumping suspensions of solids on account of the excessive wear on their bearing surfaces. Some of them have readily replaceable bearing surfaces, however, and are used for such work. Rotary pumps give steady and continuous flow, and after having been used once do not require priming. They are constructed in all sizes and for pressures as high as 600 lbs. per sq. in., and are particularly adapted for handling thick liquids that would clog the ordinary reciprocating pump.

EGGS, BLOW-CASES, OR ELEVATORS

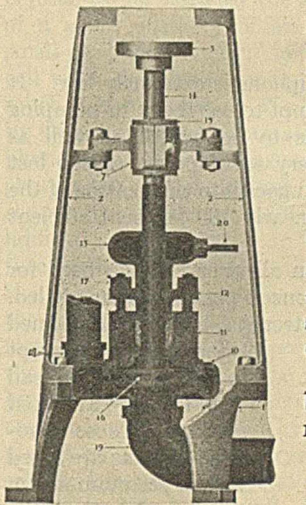

FIG. 13

The direct displacement of liquids, especially acids, by means of air under pressure has been used for many years in chemical plants, and the equipment is well known. Recent improvements have been in the construction of the blow-cases and in the automatic devices for turning on the compressed air as soon as the blow-case becomes full. The cases are constructed of cast iron, lead-lined cast iron, or chemical stoneware. It would doubtless be possible to obtain them of any material for any particular purpose.

AIR LIFTS

The principle of the air lift is illustrated in Fig. 16. Compressed air is blown into one side of a U-tube so that the weight of the combined water and air is less than the weight of the water in the other arm of the tube, causing a flow of water around through the bottom into the light side. In the diagram, the height of the mixed column of air and water shown by B is balanced by the height of the solid column A, so that any increase in the height of A will cause a flow out of the top of the other column. The effective height of pump is therefore the distance C, and the ratio of A to B times 100 is known as the percentage of submergence. Table II, compiled by the Ingersoll-Rand Co., shows the amount of

TABLE II—AIR LIFT TABLE

Formula for cu. ft. free air actual per gal. for various lifts with constants for different ratios of submergence and table showing customary allowable percentages of submergence and the best ratio.[1]

The ratio of volume of air to water raised is expressed by the formula:

$$V_a = \frac{h}{C \log \frac{H + 34}{34}}$$

where

V_a = Cu. ft. free air per min. actual required to raise 1 gal. of water
h = Total lift in feet
H = Running submergence in feet
C = Constant as given in table

CONSTANTS

Submergence, per cent...	75	70	65	60	55	50	45	40	35
Constant "C".........	366	358	348	335	318	296	272	246	216

CUSTOMARY ALLOWABLE AND BEST SUBMERGENCES

Lift in Feet	Customary Allowable Percentage Submergence	Best Percentage Submergence	Air Compressors
20	55 to 70	65 to 70	Single
30	55 to 70	65 to 70	
40	50 to 70	65 to 70	
50	50 to 70	65 to 70	
60	50 to 70	65 to 70	
80	50 to 70	65 to 70	
100	45 to 70	65 to 70	
125	45 to 65	65	
150	40 to 65	60 to 65	
175	40 to 60	55 to 60	
200	40 to 60	55 to 60	Compound
250	40 to 60	55 to 60	
300	37 to 55	50 to 55	
350	37 to 55	50 to 55	
400	37 to 50	45 to 50	
450	35 to 45	40 to 45	
500	35 to 45	40 to 45	
550	35 to 45	40 to 45	
600	35 to 45	40 to 45	
650	35 to 45	40 to 45	
700	35 to 40	40	

[1] Copyright, 1921, by Ingersoll-Rand Company.

NOTE: In the original formula the constants "C" were based on the lift and best submergence. There was no correction offered for submergences under the best. Recognizing the necessity for a set of constants that would correct the formula for different ratios of submergence within the limits of what is considered good practice, the author revised the constants "C" to meet this demand.

air required for pumping water by this method. The air pressure required may be found by measuring the submergence of the air pipe in feet before the pumping starts and multiplying by 0.434, giving the required pressure in pounds per square inch.

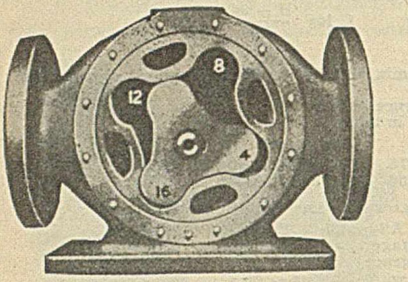

FIG. 14

The advantage of the air lift is its great simplicity and reliability. It is particularly effective for handling solutions containing solids in suspension, as there are no moving parts with which the solids come into contact. The cost of the installation is practically confined to the compressor, the lift itself being of simple and inexpensive construction.

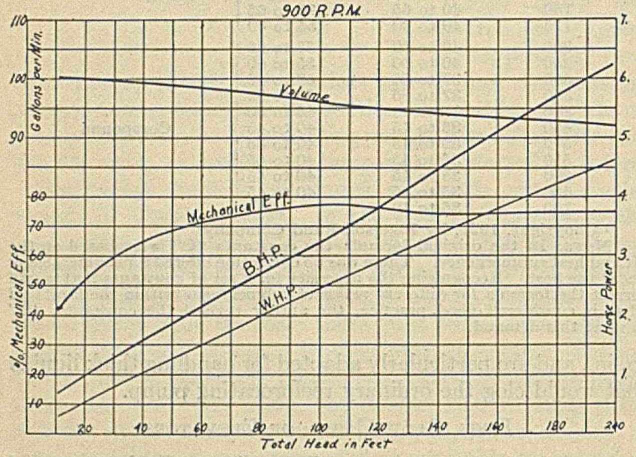

FIG. 15

SIPHONS

The mechanical efficiency of siphons is extremely low. It is therefore not advisable to attempt to use them for pumping alone. But where the liquid is to be heated as well as pumped, the steam siphon is very satisfactory, as the lost mechanical efficiency of the steam goes into the heating of the liquid, rendering the apparatus nearly 100 per cent efficient from the energy standpoint.

Steam siphons are available in all sizes. When used for very dilute acids, the ordinary bronze siphon is recommended. When the acid has appreciable strength, however, lead-lined siphons are used except in the cases where lead would be attacked readily. These lead-lined siphons are fitted with a platinum steam nozzle to lengthen the life of the apparatus, as platinum offers more resistance to erosion than the lead.

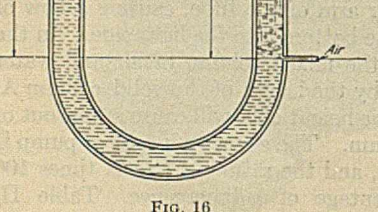

FIG. 16

Siphons of this type are very satisfactory in practice, requiring practically no attention. This fact has its drawbacks, however, as the lead lining should be replaced in periods of from two years to two months, depending on the duty of the siphon, and lack of attention may permit the wear to extend beyond the lining to the body of the siphon itself and require complete replacement.

ACKNOWLEDGMENT

The writer wishes to acknowledge the kindness of the pump manufacturers who have supplied him with the data for this article.

The Iron Man in Industry

By **H. W. Jordan**
133 STOLP AVE., SYRACUSE, N. Y.

In a recent efficiency experiment a group of fair to middling idiots were set at work on automatic machines. It took a week to train them, or six times the instruction period for normal workers. But they soon turned out 20 to 30 per cent more goods per day than their high-school educated competitors. When the machines were speeded up 15 per cent they trotted right along with 15 per cent more output, like a coach dog under a wagon. They kept up this standard day after day because they had no brains to hamper them. They proved themselves 100 per cent efficient operators of modern automatic machines.

This actual experiment is typical of the automatic industry which chemists and engineers have evolved through applied science. Titration of iron, running a vacuum pan, or tending a Bessemer converter, is not essentially different. Life offers no adventure to the chemist or operator on these standardized processes. He merely looks forward across years filled with hundreds of cubic meters of permanganate solution, or millions of tons of sugar and steel, to a pension of $66.67 per month at age of 65. His only thrill is the haunting suspicion that the pension may have a string on it.

"The Iron Man in Industry," a book written by Arthur Pound and published by the Atlantic Monthly Press, is a most able, recent analysis of the social, intellectual, and spiritual effects of modern industry. It vividly portrays the results of specialized, narrow routine in office, plant, and yard, where the broadly generalized handicrafts that were our industries prior to 1880 have become obsolete. It shows the effects of transforming skilled craftsmen into stolid automatons.

Much of the personal resourcefulness that used to spring from leisure hour occupations has been similarly wiped out. For example, the primitive sport of deer hunting now consists of a two-hundred mile automobile ride to-day over macadam and reenforced concrete roads into the woods; and to-morrow a single daybreak rifle shot at a drinking deer (fired in some cases by a hired guide), a quarter of a mile across a lake, with six o'clock dinner back home and solemn rehearsal of the hunter's prowess at the city club that evening. Shades of Daniel Boone and Kit Carson!

In appreciation of the fact that the best product of industry is versatile, clear-thinking men and women, the Technology Club of Syracuse, in which the local sections of the several American engineering societies are affiliated, has assigned part of its lecture evenings this season to a study of industrial sociology. The first of these lectures was given November 20, by Mr. Arthur Pound, on his subject, "The Iron Man in Industry." The following noon he addressed the Syracuse Kiwanis Club, an audience of 200 young business men. That evening he spoke before the Syracuse Community Forum.

"It is the function of engineering to develop the forces of nature for the utmost benefit of mankind." We can use our engineering responsibilities in no more practical way than by applying social industrial science to study of the effects of automatic machine industry upon the mind and character of the workers from president to titer boy, and by giving wide publicity to that study.

Problems of Corrosion[1]

By B. D. Saklatwalla[2]

VANADIUM CORPORATION OF AMERICA, BRIDGEVILLE, PA.

MATERIALS of construction, such as metals, are exposed in service to manifold agencies and forces causing their deterioration, which we collectively call *corrosion.* We are concerned with the final result of these deteriorating agencies, and consequently our interest from an engineering standpoint in analyzing these forces individually has been remote. We have, therefore, up to the present time attacked the problem of corrosion experimentally in a purely practical way, and our efforts toward counteracting corrosion in metals have consisted, more or less, of empirical elimination of certain impurities or additions of different elements in homeopathic or allopathic doses to the known engineering alloys. This method of working has not only made progress slow but has led to a conglomeration of indefinite and even apparently contradictory information.

ENERGY CHANGES IN FORMATION OF ALLOYS

The application of mathematical physics to metallurgical problems through development of metallography, in recent times, has revealed to us, not only the complex structure of the engineering alloys, but also the equally complex energy changes taking place during the solidification or "birth" of these alloys. These energy changes and the conditions under which they occur have a bearing on the physical properties of the individual structural particles forming the solidified alloy. As examples of the phenomena influenced by these changes may be mentioned—the growth of crystals, the distortion of crystal faces, the orientation of their surfaces, the formation or absence of an intercrystalline "cement" medium, internal crystal cohesion, surface adhesion between adjacent crystals, and surface tension of the crystal skin. These influences are exerted by energy changes prior to solidification of the metal, and may therefore be designated as being of "prenatal" origin.

PHYSICAL PROPERTIES IMPORTANT

Our studies on the subject of alloy corrosion have been more or less along morphological rather than histological lines. No doubt a study of the alloy as a whole is of importance, but the study of the inherent physical properties of the individual aggregate constituents is undoubtedly much more important. The morphological study has led to the exploitation of our existing theories—the electrolytic theory, the oxide theory, and the colloidal theory. The accelerative corrosive influence of a galvanic current produced by two heterogeneous elements in the presence of an electrolyte, the corrosive action ascribed to chemical activity of the necessary presence of oxygen, the protective action furnished by certain films of oxide, the dependence of corrosion on the catalytic action of colloids formed during the reaction, are all phenomena of a more or less secondary origin. They undoubtedly play a great part in corrosion action, but their influence can be masked by influences of a more inherent nature. Our experience with development of noncorrosive alloys has proved that such is the case. For instance, the electrolytic theory demands that the more homogeneous and pure the metal is the more noncorrosive it should be. The addition of copper to pure iron, however, instead of promoting corrosion renders it noncorrosive.

It is more or less self-evident that corrosion of a metallic alloy submerged in a gas or liquid is the chemical interaction between the solid and gas or liquid phase. The phenomena in such cases are rather complex, as the varying physical factors influencing the reaction are numerous. Consequently, the resultant reaction velocity, or, in other words, the practical rate of corrosion, will be the algebraical sum of all the physical influences and the resultant chemical effects. We can thus see that, while the addition of another foreign element to a pure metal may set up a greater galvanic action, it might produce other physical results in the characteristics of the aggregate particles themselves, lowering their inherent chemical activity so that the algebraic sum of chemical actions might be on the side of lower corrosion. Hence, we see the importance of the study of the physical nature of the constituent aggregates and the forces governing their reaction activity. Such study will undoubtedly enable us to discern and control the components constituting the resultant corrosion.

PHENOMENA OF SOLIDIFICATION

In order to grasp the significance of these "prenatal" influences for the study of corrosion, an insight into the phenomena occurring during the process of solidification is necessary. According to a theory first propounded by Quincke, crystallization starts by the separation out of the fluid magma of a small quantity of an immiscible liquid phase. This small quantity of "oily," immiscible liquid serves to form the cell walls or bubbles for the other liquid phase present in a much larger quantity. We have thus a structure designated by Quincke as "foam formation." As in the case of all foam phenomena, surface tension of the liquid phases plays a great part at this instant, determining the number, size, shape, etc., of the crystalline particles when subsequent solidification takes place. In this foam stage, as the temperature further decreases, several nuclei or points of crystallization, constituting crystalline skeletons for the building up of the final solid crystals, are formed. The number and arrangement of these nuclei determine the form and dimensions of the growing crystals. The growth continues until checked by the presence of neighboring crystals, the mother liquor continually diminishing by solidification and being displaced by the growing crystals, until the last traces of it solidify between the crystal surfaces, forming an amorphous intercrystalline "cement." Here again we can readily see that in the filling of capillary spaces by an amorphous "cement" surface tension will play a prominent part.

The size and geometric form of the final solidified crystals and their free surface-energy properties, such as adhesion, solution pressure, adsorption, etc., are dependent on this characteristic of surface tension. The property of surface tension between two liquids or a liquid and a solid is a manifestation of the degree of stability of the free molecular energy equilibrium. Very slight changes in the physicochemical reactions taking place during solidification, such as can be ascribed to the addition of another element to the molten magma, or the presence of a foreign phase as a non-

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[1] Received October 6, 1922.

[2] General Superintendent.

metallic inclusion, will cause a disturbance in this equilibrium, tending to produce different physical properties in the crystal aggregates finally solidified. A study, therefore, of the surface tension phenomena of the crystal aggregates might lead to valuable explanation of the inherent noncorrodibility of the known alloys and to the systematic discovery of newer ones.

CONCLUSION

The purpose of the foregoing remarks is by no means to set up the property of surface tension as the "philosopher's stone" of corrosion. Undoubtedly galvanic action, oxidation, protective films, etc., play an equally important part. The aim in these remarks is to direct attention to a channel of research hitherto neglected from the corrosion standpoint.

For a methodical study, the problems of corrosion may be systemized into two main groups—morphological and histological. Our previous work has all been preponderantly morphological. We might also base our division on characteristics of "prenatal" and of "postnatal" origin. The characteristics of the first nature will be such as the effect produced by the formation of definite chemical compounds by proportioning the constituents of the alloying elements, and structural changes produced through addition of small quantities of alloying or purifying agents. As characteristics of "postnatal" origin we may mention change in corrodibility produced by adequate heat treatment, mechanical work, surface polishing, etc.

In the preceding remarks one phase of the corrosion problem has not been touched—namely, the study of protective coatings, such as paints. As this method of protection in no way has a bearing on the properties of the metal to be protected, it does not come within the scope of the metallurgical aspect of the problem. The study of protective coatings is, no doubt, a fertile and extensive field of research in its own way.

Control of Industrial Processes by Light-Sensitive Means[1]

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Considerations of advancing labor costs and of the difficulty of obtaining skilled operators in chemical and industrial works have forced more and more strongly on manufacturers the necessity and desirability of replacing human agencies, wherever possible, by automatic means. The ready success of the thermostatic control of the temperature of kilns, furnaces, and buildings indicates the trend toward the elimination of manual control. Variations in electrical conductivity and in the specific gravity of solutions are other agencies which have been employed to effect automatic control of industrial processes.

It is suggested that another agency may be made a powerful means of solving many of the most difficult problems in the control of industrial processes. This agency is the extremely remarkable property of light of producing electrical effects, such as changes of resistance or electrification of certain substances when it strikes them. It is the purpose of this paper to attempt to outline the possible field of application of this agency to the control of industrial operations and processes and to suggest means for the accomplishment of such control.

ALTHOUGH the literature on the subject of photo-electricity comprises over seven hundred papers published since the discovery by Hertz in 1887 of the action of light on the discharge of electricity and a perhaps even greater number of articles on photo-resistance effects, the research in this field has been devoted largely to the important bearing of photo-electric action on theories of radiation and subatomic phenomena. Applied photo-electricity must still be considered a comparatively neglected subject. While scientific applications of light-sensitive cells to stellar photometry,[2] and—among other applications—the photophone of Bell, the automatic lighting of buoys, the electrical transmission of photographs, the control of torpedoes, and the ingenious optophone of Fournier d'Albe for enabling the blind to read, have reached varying degrees of practicability, only relatively few industrial applications have been proposed. While also a few attempts to effect control in certain directions are evidenced by proposed applications to the regulation of the luminosity of vacuum-tube lamps,[3] the regulation of voltage,[4] and the control of ultraviolet lamps in the sterilization of water,[5] the field of application to the control of manufacturing processes, especially in chemical industry, appears to have been practically neglected.

TYPES OF PHOTOSENSITIVE CELLS

A brief reference to the various types of photosensitive cells will indicate how their properties may be utilized. These distinctive properties consist in all cases of variations of electrical characteristics when subjected to light. While no cell yet devised exactly duplicates the color sensitiveness of the human eye, or can be used, without special means, for the direct measurement of color, nevertheless a rather wide choice of characteristics is available. These cells are broadly classified as selective or nonselective, according as they respond only to certain ranges of wave lengths or to the total amount of radiation.

Of the latter type important examples are the bolometer, the radiomicrometer, and the thermopile, none of which shows increased sensitivity to radiation of a particular region of the spectrum.

Of the selective class one of the oldest types is the selenium cell, in which the conductivity of a thin layer of the lead-gray modification of selenium, formed by slow cooling at 217° C., is increased by exposure to light. In one form this cell consists of a coating about 0.0001 in. thick forming a high-resistance conductor between two series of metal plates, usually German silver, each series being clamped together as shown in Fig. 1, to form an electrode of the cell. The cell is heat-treated to drive out all moisture and occluded gases. These precautions are necessary on account of the suscepti-

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922. Chemical and other applications of the methods referred to in this paper are subjects of patents pending.

[2] Kunz and Stebbins, *Phys. Rev.*, [2] **7** (1916), 62.

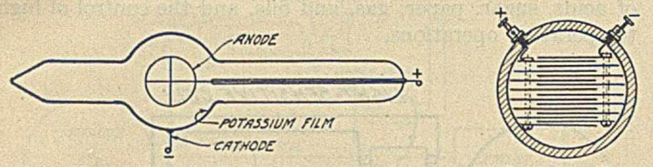
[3] Moore, U. S. Patent 856,483 (1917).

[4] Moskowitz, U. S. Patent 1,150,953 (1915).

[5] Pratt, U. S. Patent 1,208,830 (1916).

bility of selenium to the injurious effects of moisture in the air.

The increase in conductivity is explained by Pfund[6] as being due to the emission of additional electrons by resonance set up within the atom, these electrons having the properties of free electrons during the absorption of light. Although a certain lag in the recovery of the original resistance occurs, selenium cells capable of detecting fluctuations of several hundred per second are readily constructed.



Alkali-Metal Cell Selenium Cell

Fig. 1—Diagrams of Light-Sensitive Cells

Another important type of cell illustrative of the selective class, is the alkali-metal, or photo-electric, cell developed largely through the efforts of Elster and Geitel in Germany, and of Kunz and Ives in this country. In this type of cell, when light strikes the negatively charged surface of the metal, electrons available for carrying current are thrown off, the effect being proportional to the intensity of the light. It is well known that certain wave lengths of light affect certain cells of this type more than others, and it is of interest to note that in general these cells are sensitive only to a limited range of wave lengths, the maximum sensitivity of the most electropositive elements occurring with radiation of the greater wave lengths. Thus, the maximum sensitivity of sodium occurs in the blue, while most of the less electropositive metals and the nonmetals respond only in the ultraviolet. To increase the sensitiveness, such cells are generally filled at low pressure with an inert gas such as argon or helium, or with hydrogen, so that, by applying a sufficiently high potential, ionization by collision and consequently a greatly amplified current are produced. The formation of a hydride on the surface also greatly multiplies the photo-electric current. By the use of 3-electrode vacuum valves, or audions, it is possible to further increase the current to 2 or 3 milliamperes, which is sufficient to operate a relay.

Another type of cell of more recent development, whose sensitivity, on the other hand, extends into the infra-red, is the so-called "thalofide cell,"[7] containing a sensitive surface of slightly oxidized thallium sulfide. On account of the extremely high resistance of this cell, the current is preferably amplified by means of a vacuum valve to a magnitude sufficient to operate a relay.

Several other types of light-sensitive cells have been devised, depending on the Becquerel effect, involving the illumination of the negative electrode of a cell containing an electrolyte, and on the Hertz effect, involving the illumination of the negative terminal of a spark gap to facilitate the passage of the spark.

The sensitiveness of photosensitive cells is obviously one of some concern, especially where exact colorimetric control is required. It may suffice to show that the photoelectric cell has proved entirely adequate for the photometry of light from the most distant stars. It is probable that the sensitiveness of specially designed cells may be made quite equal, or superior, to that of the human eye.

Reliability of Method

The next point to be considered in the evaluation of such a method of control is its reliability. Attention will doubtless be called to the fatigue, mentioned frequently in the literature, of certain cells under prolonged illumination. This effect in the earlier types of cells has been shown to be due largely to such extraneous effects as presence of moisture and occluded gases, and has been largely eliminated in the more recently developed cells. Any difficulty, however, with regard to photo-electric fatigue can be readily avoided by the arrangement of the apparatus in such a manner that the continuous sample is compared as to its optical quality or qualities with a standard sample of the desired composition through the use of a common source of light, so that any difference in the samples will produce a difference in the relative resistances of the cells and operate the control through the medium of a relay suitably installed in a Wheatstone bridge arrangement.

The infinitesimal quantity of luminous energy required to produce an appreciable effect, the ease and certainty with which the light may be controlled, and the comparative independence of other conditions in the operation of the current-varying substance, are characteristics of the selenium, thalofide, and alkali-metal cells which lend themselves readily to the immediate solution of many industrial and chemical problems involving control of production.

Such problems, on examination, generally resolve themselves into checking and maintaining within certain limits, throughout all steps of the process, the following characteristics of the intermediate and final products:

1—Quantity of product or number of production units.
2—Form or shape of product.
3—Quality of product.
  (a) Chemical composition.
  (b) Physical properties.

Applications

In the following discussion it is proposed to indicate means for applying light-sensitive cells to the control of these factors affecting production in such a manner that variations in such factors will produce variations in the intensity or character of light or radiation which will photo-electrically operate suitable means for automatically exercising control over the process. The general method is to produce such a change in the intensity or character of the illumination of the cell as to produce a corresponding change in the current sufficient to operate a relay, which in turn controls the appropriate valves, switches, or other means necessary to effect the desired operation.

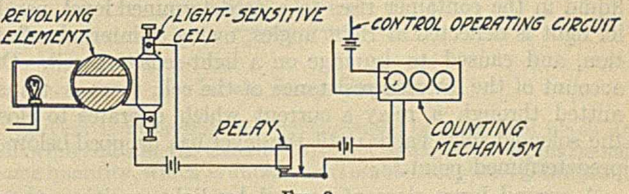


Fig. 2

Among the properties of the final or intermediate products which may be utilized for this purpose are the following:

1—Absorptive power for white or mixed light.
2—Selective absorptive power for light of various colors.
3—Index of refraction.
4—Power of scattering light.
5—Rotation of the plane of polarization of plane polarized light, or change of pattern of other forms of polarized light.
6—Dispersion of light; spark, flame, and absorption spectra.
7—Reflective power for white light, or for light of various colors.
8—Intensity of emission of light at a given temperature.
9—Phosphorescence and fluorescence.
10—Combinations of the foregoing.

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[6] *Phys. Rev.*, [1] **28** (1909), 324.

[7] Case, *Ibid.*, [2] **15** (1920), 289. U. S. Patents 1,301,227 (1919) and 1,316,350 (1919).

The choice of the method of control will obviously depend on the nature of the factor it is desired to control. In the case of the control of the quantity or physical form of the product, directing purely mechanical operations, the actuation of the light-sensitive cell can in many cases be most readily effected by simple obstruction of white light, due to the opacity of the product.

While the first two classes of control, involving the quantity and the form or shape of the product, are applicable to a wide range of mechanical engineering and production problems, mention of a few typical applications that have been the subject of study will indicate their possible usefulness in the field of chemical industry. Following the foregoing classification of types of control according to factors of quantity, shape to be governed, or quality, the field of possible application of the control of the quantity of a product may first be considered.

This group of applications is concerned with the control of operations or processes in such manner that when a predetermined dimension or quantity of production has been reached any desired step in the cycle of operations will take place. Such steps may be the opening or closing of valves, starting or stopping of machinery, operating alarms or indicating devices, or any mechanical or other operation.

As illustrating the method of accomplishing these objects, the accompanying diagrams will serve to show particular applications. The device indicated in Fig. 2 utilizes a combination of means for the projection of approximately parallel light rays through a hole in a rotating element of a machine so that a light-sensitive cell will be illuminated twice for each revolution, with a counting device adapted to respond to the electrical impulses transmitted by the cell through a relay. This counting device is arranged to close a circuit when a certain number of impulses have been received and to automatically reset to repeat the cycle. The circuit closed by the "counting" mechanism may contain any such electrical device as a solenoid valve for shutting off the supply of material to a machine, or a mechanism for performing any such function as stopping or starting a machine, closing or moving containers, or effecting such operations as would otherwise be accomplished through the medium of gearing, cams, or an attendant.

Another typical application is that to the measurement and flow of liquids, Fig. 3 representing a method of controlling the level of liquids of high refractive index. This comprises the use of a container with a hollow transparent prism attached thereto by pipes and so arranged that when the liquid in the container rises to a predetermined level, parallel light is deflected at right angles, owing to internal reflection, and caused to impinge on a light-sensitive cell. On account of the lowered resistance of the cell, there is transmitted through a relay a current which operates to close the solenoid inlet valve until the level has dropped below a predetermined point.

A second large class of control by light-sensitive means comprises the governing of operations or processes in such a manner that a variation in the form or shape of the material in process or of the final product, or of the path of motion causes a predetermined step in the cycle of operations to take place. Such operations may be the starting or stopping of machines, the regulation of the characteristics of electric currents, the operation of alarms or indicating devices, or the accomplishment of any similar desired object.

Although a discussion of the many groups of applications of this class investigated is beyond the scope of this paper, it may be mentioned that these include automatic examination and sorting of articles in process of manufacture as to size and shape, automatic stops, controlling and recording the character of mechanical movements, safety devices, interlocking devices for the prevention of operations out of their proper sequence, and the control of electrical characteristics.

The third class, that of control of the quality of the product, offers an almost endless variety of applications in chemical industry. A partial list has been prepared by the writer, of the large number of possible applications of this type of control in over a hundred important industries, including such varied processes as the manufacture and purification of acids, sugar, paper, gas, and oils, and the control of high temperature operations.

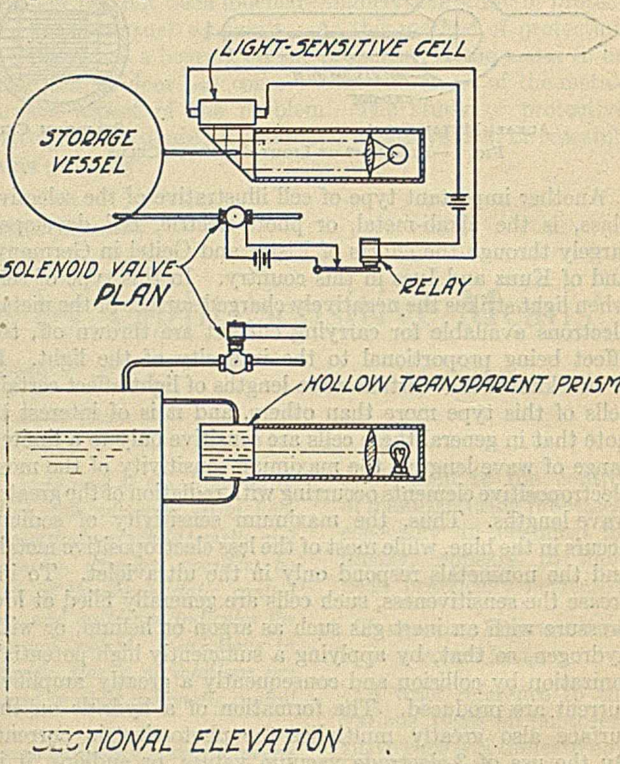

Fig. 3

In the control of the quality or the constitution of the product, the choice of the method of control will depend mainly on the degree in which the substance possesses optical qualities differentiating it from other substances, or the ease with which it can be caused to produce, through the action of a reagent, a distinctive optical test.

Of this class, an illustration of the regulation of chemical operations in which the production of an opaque test, stain, or coloration by the action of a suitable reagent serves sufficiently to identify the substance to be produced, or the impurity to be avoided, may be found in the protection of catalysts, as, for instance, in the contact process for the manufacture of sulfuric acid. In this case, as is well known, the platinum catalyst is very susceptible to "poisoning" by even minute traces of arsenic in the burner gases. The visual detection of arsenic by observation, through a window in the burner gas main, of its presence as a white cloud has been found ineffective and unreliable. The method, proposed and shown diagrammatically in Fig. 4, employs the Marsh test for arsenic in connection with a light-sensitive cell so arranged that when arsenic is present a black stain will be produced on a transparent water-cooled cell interposed between the cell and a source of light. The light will then be cut off, operating, on account of the consequent increase in resistance of the cell, a relay controlling a 3-way valve for the purpose of by-passing the gas for further treatment, thus preventing the arsenic from reaching the catalyst.

chamber. Means are provided for periodically removing the stain with bleaching-powder solution and restoring operation when the impurity has been removed. Arrangements for using other tests for arsenic have also been devised.

The selective absorption of colored substances for monochromatic radiation affords another very direct means for detecting and eliminating impurities. An apparatus for this purpose is illustrated diagrammatically in Fig. 5. For instance, if it is assumed that the undesirable constituent is ferric iron, ammonium thiocyanate might be employed as the reagent. By the use of a color filter excluding red rays, the light-sensitive cell will be normally subjected to light only of other colors. When, however, ferric iron is present in the sample, a red coloration, capable of transmitting only or chiefly red rays, will appear in the transparent vessel. As no red rays are present in the incident light, it will be totally cut off from the light-sensitive cell, thus increasing the cell resistance and operating, through a relay, the appropriate valve for by-passing the product for further treatment. For simplicity in illustration, this device is shown as operating continuously. In practice, however, the apparatus will be arranged for intermittent operation, with provision for flushing out the cell after each test. The control of processes involving the neutralization of acid or alkaline solutions by the use of the selective absorption of indicators is but one of the large number of subgroups of possible application of selective absorption.

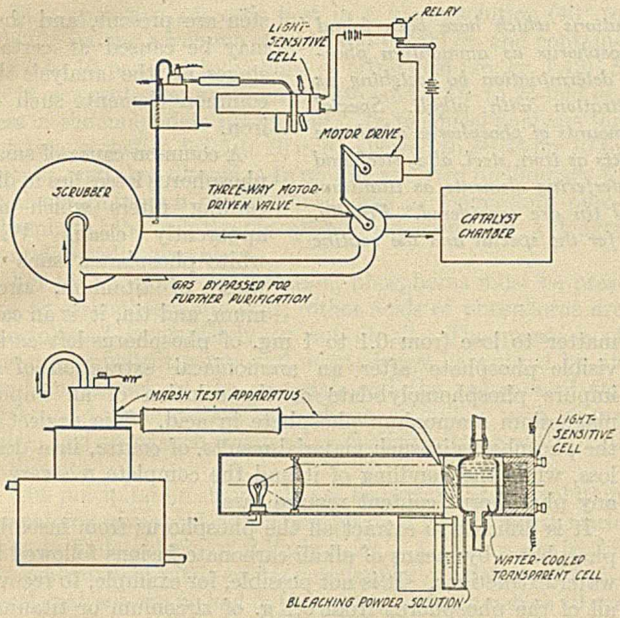

FIG. 4

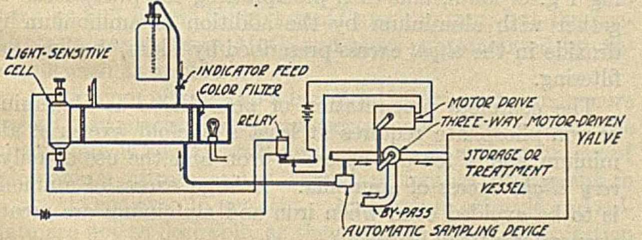

FIG. 5

Considerable attention has been devoted, especially by Houston, Hutchinson and Hurlbut, and Prideaux, to the study of the relation between the wave lengths and absorption coefficients of a limited number of inorganic and organic substances over considerable ranges of concentration and temperature. Further determinations of absorption coefficients, especially for various chemical indicators, would appear to be a contribution immediately useful in the design of control apparatus.

In cases where it is found that a substance is not completely specified by any of the foregoing properties, it will be found in many cases that a combination of tests, such as a color test with a reagent, and of the index of refraction will serve to completely identify the substance.

Among other possible applications studied, which do not come entirely within any one of the foregoing classes, may be included those of combinations of the preceding methods of control with automatic specific gravity regulation in such processes as oil distillation where both specific gravity and color of the product are of importance, replacement of complicated mechanical movements, by electrical devices controlled by light-sensitive means and of the utilization of the photo-electric method in connection with a suitable optical pyrometer for the control of high temperature operations.

It will be observed that in most of the foregoing cases, apparatus in common use is adapted to the control of the process, with only such alterations as are necessary to make the testing or checking process a continuous one. Among the more usual means for checking the chemical composition of substances are chemical reagents and indicators, the polariscope, the colorimeter, the refractometer, and the spectroscope, while such physical properties as tensile and compressive strength, hardness, density, structure, temperature, and pressure are checked by testing machines, the scleroscope, the hydrometer, the microscope, the pyrometer, and the manometer. A study of these means of checking properties of substances shows that the greater number of them, especially those for checking chemical composition, may be registered by optical means in such a manner as to provide the appropriate impulse through the medium of the photosensitive cell to operate an electric relay.

The complete development of the possibilities of process control through light-sensitive means involves the selection or development of analytical tests most suitable for affecting light-sensitive cells, the improvement of photosensitive cells, and the solution of such chemical or mechanical problems as might arise in the application of the control to the actual process. The suggestion is ventured that such development of this field may prove an inexhaustible source, not only of industrial improvements, but also of lateral scientific results of fundamental value.

News from Canada

Success is attending the development of acetylene black at Shawinigan Falls, the Canada Carbide Company having marketed some quantity, which is finding a favorable reception by the paint trade.

The power concentration of the St. Maurice valley will, we are advised, shortly be reinforced by development at Les Gres, a fall about half-way between Three Rivers and Shawinigan. This is expected to develop in the neighborhood of 200,000 additional horse power for the Shawinigan Water and Power Company.

The Canadian China Clay Company at St. Remi, Quebec, has been investigating the possibilities of colloidal treatment of kaolin, and as a result is disposing of considerable quantities in the rubber industry. The suspension of the clay by colloidal means permits of the removal of impurities providing a specially adaptable clay for incorporation.

Col. F. M. Gaudet, C.M.G., who has been Technical Executive Officer of the Honorary Advisory Council for Research, has resigned from that body and has joined the staff of the Canadian Industrial Alcohol Company.

Notes on the Determination of Phosphorus[1,2]

By G. E. F. Lundell and J. I. Hoffman

Bureau of Standards, Washington, D. C.

This paper describes the precautions which have been found desirable in the separation of phosphorus as ammonium phosphomolybdate, and its subsequent determination by weighing as magnesium pyrophosphate or titration with alkali. Special attention is paid to the moderate amounts of phosphorus which are present in such metallurgical products as iron, steel, alloy steel, and bronze; and the effects of such interfering elements as titanium, zirconium, vanadium, arsenic, and tin are considered. Finally, there are presented tested methods for the special and the routine analysis of these materials.

PRACTICALLY all methods for the determination of phosphorus in minerals, rocks, ores, and metallurgical products call for a preliminary separation of the phosphorus as ammonium phosphomolybdate, [$(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$]. A considerable number of methods for the subsequent treatment of the phosphomolybdate have been proposed. These can be divided into two classes—those requiring a pure phosphomolybdate of definite composition, and those requiring a reasonably pure phosphomolybdate of any composition. Practically all the methods are of the first type and include such as involve the weighing of the dried or ignited precipitate, the precipitation and weighing of the molybdenum as lead molybdate, the reduction and subsequent titration of the molybdenum with standard permanganate solution, and the titration of the molybdic acid with standard alkali solution. There are very few methods of the second type and the method calling for final weighing of the phosphorus as magnesium pyrophosphate is the only one in general use.

The complete deposition of phosphorus as ammonium phosphomolybdate is often delayed, and under some conditions prevented, by such elements as vanadium in the quinquivalent condition, titanium, zirconium, and fluorine. The purity of the phosphomolybdate precipitate is often a matter of doubt. It is well known that the first three elements named, as well as silicon and arsenic, are carried down completely, or in part, by the precipitate. The researches of Hundeshagen[3] and others have demonstrated that the composition of ammonium phosphomolybdate varies with such factors as temperature, concentration of the molybdate reagent, and the acidity of the solution.

From the foregoing it is evident that an accurate or even a routine determination of phosphorus, particularly in many metallurgical products, is not as simple a matter as many texts lead one to expect. It has therefore been considered desirable to gather and publish the following observations which have been made and methods of analysis which have been found desirable at the Bureau of Standards and elsewhere for the determination of the moderate amounts of phosphorus to be found in such materials as iron, steel, alloy steel, and phosphor bronze. Although no methods are given for such material as minerals, rocks, and ores, the data indicate what precautions are necessary.

A. General Considerations

I. Cause of Phosphorus Losses Prior to the Phosphomolybdate Precipitation

Losses are chiefly occasioned by the neglect or improper treatment of insoluble compounds obtained during the course of the analysis. These frequently contain phosphorus, and they are often caused by titanium; they will be encountered when such elements as zirconium or tungsten are present, and they may be caused at certain stages of the analysis by common elements such as iron.

A common cause of small phosphorus losses lies in discarding filters which are apparently clean. With white phosphates such as those of titanium, zirconium, and tin, it is an easy matter to lose from 0.1 to 1 mg. of phosphorus left as invisible phosphate after an ammoniacal extraction of an impure phosphomolybdate or the solution of an impure magnesium ammonium phosphate in acid. The neglect of the phosphorus in such material results, of course, in a dead loss, while the handling of it and the complete recovery of any phosphorus content require care.

It is difficult to extract all the phosphorus from insoluble phosphates by means of alkali carbonate fusions followed by water extractions. It is not possible, for example, to recover all of the phosphorus from 0.1 g. of zirconium or titanium phosphates by two careful carbonate fusions followed by water extractions.

Compounds containing phosphorus must not be subjected to protracted fusions with alkali pyrosulfate in open crucibles and at unnecessarily high temperatures.[4] Negligible losses occur in short fusions when crucibles are tightly covered and only sufficient heat for proper fusion is used. Such fusions may, however, give rise to meta- or pyrophosphates, which must be converted to orthophosphate before further treatment.

Phosphorus is precipitated with tungstic acid, and the recovery of it from small amounts of tungstic acid is carried out as with the nonvolatile residue after the purification of silica. With larger amounts of tungsten the phosphorus is more conveniently recovered and the tungsten at the same time eliminated by dissolving the tungstic acid in ammonium hydroxide, slightly acidifying with hydrochloric acid, adding 1 g. of alum, and then precipitating the phosphorus together with aluminium by the addition of ammonium hydroxide in the *slight* excess prescribed by Blum,[5] boiling, and filtering.

The complete precipitation of phosphorus as aluminium or iron phosphate requires at least a fivefold excess of aluminium and a tenfold excess of iron and the use of only a *very slight* excess of ammonia. A large excess of ammonia is to be avoided even when iron and aluminium are greatly preponderant.

As mixtures of sulfuric and phosphoric acids lose phosphorus when heated at high temperatures to complete expulsion of sulfuric acid, any hydrofluoric acid treatment of silica containing phosphorus should be done with nitric instead of sulfuric acid and the hydrofluoric acid expelled by repeated treatment with it. In this connection it is imperative that any final evaporation of phosphoric-sulfuric acid solutions be carried on at as low a temperature as possible and be stopped

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[1] Received June 6, 1922.

[2] Published by permission of the Director of the Bureau of Standards.

[3] *Z. anal. Chem.*, **28** (1889), 164.

[4] W. F. Hillebrand and G. E. F. Lundell, *J. Am. Chem. Soc.*, **42** (1920), 2609.

[5] *J. Am. Chem. Soc.*, **38** (1916), 1282.

as soon as fumes of sulfuric acid appear.[4] No losses of phosphorus occur under such conditions, or when nitric, hydrochloric, or hydrofluoric solutions containing phosphoric acid are evaporated to dryness.

II. THE PRELIMINARY SEPARATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE

This operation succeeds best in a warm solution (40° to 60° C.) having a volume of from 100 to 200 cc. and containing 5 to 10 per cent by volume of nitric acid (sp. gr. 1.42), 5 to 15 per cent of ammonium nitrate, and a 15- to 25-fold excess of the molybdate precipitant. In technical analyses the solution is shaken for 5 to 10 min., allowed to settle for 10 to 30 min., and then filtered. In umpire analyses preliminary to final determination of the phosphorus as magnesium pyrophosphate, the solution is allowed to stand for a longer period, usually over night.

For the foregoing precipitation, phosphorus must be present as orthophosphoric acid; other acids of phosphorus are precipitated incompletely or not at all. The presence of the quinquivalent compound must always be assured by an oxidizing attack of the material, and the presence of the ortho acid made certain by preliminary boiling with strong nitric acid or by such means as an oxidizing fusion with alkali carbonate.

The precipitation should always be performed in a solution containing nitric acid, as the precipitate is less soluble in nitric than in hydrochloric or sulfuric acids. A wide range in the concentration of nitric acid is permissible. Satisfactory technical analyses can be had in the presence of as much as 10 per cent by volume of hydrochloric acid or 5 per cent by volume of sulfuric acid, through the use of double the amount of molybdate reagent ordinarily employed (100 cc. as against 50 cc.) and a longer precipitation period (30 min. as against 15 to 20 min.). In the case of hydrochloric acid, *complete* precipitation is obtained when the solution is allowed to stand over night; complete precipitation is not possible with sulfuric acid, which must be avoided or used sparingly and then converted into ammonium sulfate in accurate analyses. Hydrofluoric acid retards the precipitation of phosphomolybdate and causes the formation of a more soluble precipitate; both difficulties can be entirely prevented by converting the acid to fluoboric acid by the addition of borax or boric acid.

The temperature of the solution has a decided bearing on the precipitation. Precipitation at low temperatures (10° to 20° C.) is slow and the precipitates are difficult to filter and wash. Precipitations at 40° to 50° C. are more rapid and the precipitates are in better condition. Higher temperatures, such as 80° to 90° C., give rapid precipitation, but the precipitates are richer in MoO_3 and more contaminated by elements such as arsenic.

Ammonium nitrate has a beneficial effect, as it causes more rapid precipitation and a coarser grained precipitate. The precipitate is slightly soluble, however, in a large excess of ammonium nitrate and it should preferably be present in amounts not over 15 per cent. Ammonium chloride and sulfate are not as desirable, as they tend to delay precipitation and have slightly greater solvent action on the precipitate. Their presence in reasonable amount is not harmful if a greater excess of the molybdate precipitant is used.

A large excess of the molybdate precipitant is required. This excess varies from 10 times the theoretical amount in a nitric acid-ammonium nitrate solution of pure orthophosphoric acid, to a 15- to 25-fold excess in ordinary solutions, and a 40- to 60-fold excess in solutions containing substances that retard the precipitation. The molybdate precipitant ordinarily employed contains approximately 5 per cent of molybdic acid, 5 to 10 per cent of ammonium nitrate, and 20 to 25 per cent by volume of nitric acid; the reagent used in the experiments hereinafter described was prepared as described by Blair,[6] except that the equivalent amount of 85 per cent molybdic acid was employed instead of the pure molybdic anhydride specified. The source of the molybdic acid is usually 85 per cent molybdic acid, although the 100 per cent anhydride and ammonium molybdate are sometimes specified. It has been stated by Johnson[7] that the phosphomolybdate obtained through the use of a molybdate reagent prepared from unignited molybdic acid has different properties from that obtained from a reagent prepared from the ignited anhydride; the former is more crystalline, easier to filter, but more soluble in a dilute nitric acid wash as contrasted with the latter, which is extremely finely divided, very difficult to filter, but less soluble in dilute acid. This fact has apparently not received the attention that it deserves. Johnson's statements have been confirmed at this Bureau. In order to obtain a proper phosphomolybdate, Johnson recommends that the molybdate reagent be prepared from a mixture of the two. The same author[8] has also recommended an ammoniacal solution of ammonium molybdate and ammonium nitrate as a substitute for the nitric acid mixtures ordinarily used.[9] Such a solution is easily prepared, is stable, and is used with no change in precipitation procedure save the addition of a little nitric acid before the addition of the reagent.

The filtering of the precipitate must be carried out through a filtering medium of close texture. This renders the operation a rather slow process if it is carried out by gravity through paper. More rapid filtration and more efficient washing can be had by suction through asbestos or paper pulp.[10] It is difficult to wash out all acid from paper fiber, and this is the chief source of the "blank" in determinations of phosphorus by the alkalimetric method.

The precipitate is always washed with cold solutions which necessarily differ according to the final disposition of the phosphomolybdate. A solution containing 1 to 2 per cent by volume of nitric acid is usually first employed in order to prevent hydrolysis of salts of such elements as iron and tin. Some analysts[11] prefer to add ammonium nitrate to the nitric acid wash, while others[12] add both ammonium nitrate and molybdate reagent. Baxter[13] used a 10 per cent ammonium nitrate solution for phosphomolybdates which were to be dried at 300° C. and weighed. A 1 per cent nitric acid solution has proved perfectly satisfactory at this Bureau except in cases where salts which are very easily hydrolyzed—as, for example, tin—are present; here a 1.5 per cent solution is used. As the phosphomolybdate is slightly soluble in any

[6] "The Chemical Analysis of Iron," 8th ed., J. B. Lippincott & Co., p. 54. "Weigh 100 g. of pure molybdic anhydride, mix it thoroughly in a beaker with 400 cc. of cold distilled water and add 80 cc. of strong ammonia (0.90 sp gr.). When solution is complete, filter and pour the filtered solution slowly with constant stirring into a mixture of 400 cc. of strong nitric acid (1.42 sp. gr.) and 600 cc. of distilled water. Allow to settle for 24 hrs. and filter."

[7] "Chemical Analysis of Special Steels, etc.," 3rd ed., J. Wiley & Sons, Inc., p. 315.

[8] *Ibid.*, p. 323.

[9] Johnson's directions for preparing the solution are as follows: "Into each of four 800-cc. casseroles weigh 55 g. of ammonium molybdate and 50 g. of ammonium nitrate, and add 40 cc. of ammonium hydroxide (0.95 sp. gr.). Dilute each to 700 cc. with water. Heat for about 30 min., stirring once in a while until all salts are in solution. Combine the contents of the four beakers by pouring into a large bottle; then dilute to 4000 cc. with water. Let stand over night. Filter the insoluble material through double 15-cm. papers. *Do not wash.* The clear solution thus obtained should remain clear indefinitely."

[10] S. L. Jodidi and E. H. Kellogg, *Biochem. Bull.*, **5** (1916), 87.

[11] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey, Bull.* **700**, 178.

[12] H. S. Washington, "The Chemical Analysis of Rocks," 3rd ed., J. Wiley & Sons, Inc., p. 218.

[13] *Am. Chem. J.*, **28** (1902), 298.

acid wash solution, strong acid solutions and excessive washing are to be avoided. Where phosphorus is to be determined gravimetrically as magnesium pyrophosphate, only slight washing is necessary; in other methods final washing must be had with other media, as for instance with 1 per cent potassium nitrate in the alkalimetric method.

It has already been stated that certain substances, such as nitric acid and ammonium nitrate, are desirable in a molybdate precipitation, and that others, such as hydrochloric and sulfuric acids and their ammonium salts, are less desirable. Very undesirable elements are fluorine, vanadium in the quinquivalent state, titanium, and zirconium, which delay the precipitation and contaminate the precipitate that is formed. Arsenic and silicon also contaminate the precipitate but delay the precipitation to a lesser extent. Complete precipitation of *impure* phosphomolybdate can be had in the case of fluorine by the addition of borax or boric acid, and in solutions containing reasonable amounts of the other compounds provided a considerable excess of the molybdate precipitate is used and sufficient time (6 to 24 hrs.) for precipitation is allowed. The interference of vanadium can also be entirely overcome by reducing the vanadium to the quadrivalent condition before the treatment with molybdate and carrying on the precipitation at approximately 20° C. for 30 min. or longer.[14]

Organic compounds are ordinarily regarded as objectionable, although moderate amounts (0.1 to 0.3 g.) of certain organic compounds such as citric and tartaric acids, which have been recommended to prevent the precipitation of iron, have not been found objectionable at this Bureau.

III. Final Determination of Phosphorus by Weighing as Magnesium Pyrophosphate

It is evident that correct determinations of phosphorus can be obtained only by methods which call for solution of the phosphomolybdate and reprecipitation of the phosphorus as a pure compound of definite composition. By far the most satisfactory of such methods calls for solution of the washed phosphomolybdate in dilute ammonium hydroxide, reprecipitation of the phosphorus as magnesium-ammonium phosphate, and ignition of this to the pyrophosphate. In this method the composition of the phosphomolybdate is immaterial; it is only necessary that all the original phosphorus be present as orthophosphate in the solution which is treated with magnesia mixture, and that the resulting magnesium-ammonium phosphate be pure and of definite composition.

As the quantitative presence of phosphorus can be assured by adherence to the precautions cited under I and II, the quantitative presence of phosphorus in the solution to be precipitated by magnesia mixture depends on proper methods of dissolving the phosphomolybdate. The customary procedure consists in treating the phosphomolybdate with dilute ammonium hydroxide. This succeeds well with pure precipitates and those containing arsenic, vanadium, and tungsten. It fails with precipitates containing iron (often present), and such elements as titanium, zirconium, and tin. These elements are to be expected in varying amounts at this point if they were present in the original material, and their phosphates are undoubtedly the insoluble white phosphorus-bearing compounds which are occasionally mentioned in the literature.[15] Sometimes they can be dissolved by the addition of a few crystals of citric acid to the ammoniacal solvent, or by final treatment of the filter paper with a dilute solution of hydrochloric and citric acids. In accurate analyses, however, the ammoniacal solution should be filtered until absolutely clear, previously adding an electrolyte and boiling if necessary, and the well-washed paper ignited, fused with a little alkali carbonate, extracted with water, and the acidified and boiled extract added to the main filtrate. As has already been stated, it is to be noted that sodium carbonate fusions of large amounts of insoluble phosphates, followed by water extraction, are by no means satisfactory.

A pure magnesium-ammonium phosphate of definite composition can be easily obtained from ammoniacal solutions of small amounts of pure ammonium phosphomolybdates, provided the solutions—preferably of a volume not to exceed 50 to 75 cc.—are slightly acidified with hydrochloric acid, treated with 0.2 to 0.5 g. of citric acid, a 5- to 10-fold excess of magnesia mixture, and then carefully neutralized with ammonium hydroxide (sp. gr. 0.90), slowly added dropwise and with constant stirring until the precipitate begins to form and then in an excess of 3 to 5 per cent by volume. A 3- to 4-hr. digestion period is ordinarily sufficient, but a 24-hr. period does no harm and is desirable when small precipitates are involved. Special precipitation procedures, such as precipitation in boiling solution, have not been found necessary at this Bureau. The most desirable washing solution is one containing 3 to 5 per cent by volume of ammonium hydroxide (sp. gr. 0.90). No advantage is gained by using stronger washes or ones containing ammonium nitrate. The precipitate may be ignited either wet or dry, and in either platinum or porcelain. The chief precaution in igniting the precipitate lies in first *warming* until any water in the paper or precipitate is given off, then *slowly charring* the paper without actual flaming in an oxidizing atmosphere, then igniting at as low a temperature as possible, and with the lid placed to allow circulation of air, until the carbon has been destroyed and the residue is white, and finally at approximately 1000° C. with the crucible covered to constant weight.

Solution of the magnesium-ammonium phosphate in nitric acid followed by evaporation to dryness and careful ignition does no harm. Under no circumstances can the *ignited* pyrophosphate be dissolved in nitric acid, evaporated, and again ignited; moistening of the ignited pyrophosphate with nitric acid and ignition usually does no harm and rarely any good.

Various formulas are given for the preparation of magnesia mixtures. Practically all these call for a solution containing magnesium chloride (free from calcium), ammonium chloride, and dilute ammonium hydroxide. Solutions of this type attack glass containers, and therefore it has been proposed by Kuhnt[16] that the ammonium hydroxide in the formulas be omitted, as solutions free from it are without action. As the addition of magnesia mixture should leave the solution acid, there is no need for an ammoniacal solution, and accordingly the magnesia mixture used in this work contained 50 g. of $MgCl_2.6H_2O$ and 100 g. of NH_4Cl per liter of water.

In case the original material contains elements such as arsenic, tin, vanadium, silicon, titanium, zirconium, and large amounts of iron, the magnesium-ammonium phosphate will undoubtedly be contaminated unless steps have been taken for their removal. Tungsten causes no trouble, as it forms no insoluble compounds, in the ammoniacal solution used. Contamination by tin, vanadium, iron, titanium, and zirconium can be entirely prevented by a double precipitation in the presence of ammonium citrate. In this case the first precipitation is carried out as above with the exception that 3 to 5 g. of citric acid, a 25- to 50-fold excess of

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[14] J. R. Cain and F. H. Tucker, *Bur. Standards, Tech. Paper* **24**; This Journal, **5** (1913), 647.

[15] W. F. Hillebrand, *U. S. Geol. Survey, Bull.* **700**, 178; H. S. Washington, *Ibid.*, p. 218.

[16] *Chem.-Ztg.*, **44** (1920), 586.

magnesia mixture and a 12- to 24-hr. cold precipitation period are necessary. When much citric acid is used, more magnesia mixture is needed, particularly when vanadium is present. The first precipitate is dissolved in dilute hydrochloric acid and then reprecipitated as in the case of pure solutions after the addition of 1 to 3 cc. of magnesia mixture and 0.2 to 0.5 g. citric acid. In case the original material was rich in titanium or zirconium, these elements may have come down in small part with the first precipitate as phosphates in spite of the citrate present. In such cases it is desirable to ignite the paper—even though it looks clean after the hydrochloric acid extraction—in a small platinum crucible and then to fuse any residue with a pinch of sodium carbonate, extract with a little water, and add the filtered extract to the main solution. The efficacy of the method is illustrated in Table I.

TABLE I—EFFECT OF CITRIC ACID IN THE PRECIPITATION OF MAGNESIUM AMMONIUM PHOSPHATE

Expected G.	$Mg_2P_2O_7$ Found G.	Contaminant Present G.	REMARKS
0.1048	0.1048	None	
	0.1048	None	
	0.1044	0.005 Fe	
	0.1049	0.005 Al	
	0.1044	0.005 Ti	Precipitate contained less than 0.2 mg. TiO_2
	0.1048	0.005 Ti	
	0.1043	0.005 Zr	Zirconium is the most difficult to keep in solution. 0.005 g. represents the upper limit
0.0105	0.0107	0.005 V	Precipitate contained less than 0.2 mg. V_2O_5. In the absence of citric acid very erratic values were obtained
	0.0104	0.020 Sn	
	0.0107	0.250 Zn	Same value obtained without use of citric acid

Contamination by arsenic and silicon cannot be so easily avoided. As molybdenum is always present and is apt to contaminate the final precipitate, the most satisfactory procedure for the elimination of arsenic, where time is a minor consideration, lies in a preliminary precipitation with magnesia mixture as above, followed by solution of the precipitate in acid, elimination of arsenic and molybdenum by precipitation with hydrogen sulfide, and reprecipitation of the phosphate as in pure solutions. A more rapid and quite satisfactory separation of small amounts of arsenic can also be had by adding ammonium bromide to the hydrochloric acid solution of the first precipitate and then boiling to a small volume.

Silicon, which may be introduced from the original material with reagents, or by attack on glassware, is ordinarily not separated until the pyrophosphate has been weighed. This is then dissolved in dilute acid and any silica determined in the usual manner and deducted.

IV. FINAL DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

This is by far the most important and widely used method for the rapid, routine determination of such small amounts of phosphorus as are found in iron, steel, and bronze. It is not satisfactory for large amounts of phosphorus such as are found in phosphate rock. In this method the ammonium phosphomolybdate is usually first washed with cold dilute nitric acid, 1 to 2 per cent by volume, and then with a cold neutral 1 per cent solution of potassium nitrate. The precipitate is then dissolved in an excess of standard alkali solution and the excess determined by titration with standard acid in the presence of phenolphthalein as indicator. The reaction can be expressed by some such equation as the following if we assume that the washed precipitate has the indicated formula:

$$(NH_4)_3PO_4.12MoO_3+23NaOH=11Na_2MoO_4+(NH_4)_2MoO_4+NaNH_4HPO_4+11H_2O$$

Phenolphthalein is not an ideal indicator for the titration on account of its sensitiveness to carbonic acid and behavior in the presence of ammonium salts. No other indicator has, however, proved as satisfactory in general practice. The interference of carbon dioxide can be avoided by proper preparation of the alkali solution, and the amount of ammonium salts is usually too small to have any serious disturbing effects. In the case of large amounts of phosphorus, some methods call for the addition of an excess of standard alkali, boiling to expulsion of ammonia, and then titration.

It is apparent that this method is dependent on the complete recovery of phosphorus as a pure compound of definite composition. As has been noted, this requires attention to such factors as acidity, concentration of the precipitant, and temperature of the solution, as well as the absence of such elements as quinquivalent vanadium, titanium, zirconium, and arsenic.

It is idle to discuss the proper method of calculating the phosphorus titer of the standard alkali solution, as it is plain that the only proper procedure lies in the adoption of a definite method of analysis and standardization of the alkali solution by means of like material of known phosphorus content (as determined gravimetrically) carried through all the steps of the method. In coöperative analyses of this Bureau's irons and steels, the alkali solution is standardized against the Bureau's standard benzoic acid and its phosphorus titer then calculated on the basis of 23 molecules of sodium hydroxide to one atom of phosphorus. This is done in order to provide data which have a common basis, and the results so obtained after a molybdate precipitation at 40° C. by the method to be described are surprisingly close to the true phosphorus values.

The interfering substances have been mentioned above. As has been stated, vanadium, titanium, and zirconium tend to delay the precipitation of the phosphomolybdate and to contaminate the precipitate; the first effect is aggravated in this method, as the precipitation period (usually 10 to 20 min.) is short. As the impurities may also cause consumption of standard alkali, the errors are sometimes compensating. Arsenic, which delays the complete precipitation of phosphorus at 10° to 20° C., contaminates the precipitate in traces at these temperatures and in practically complete amount at 60° to 90° C.; with arsenic, therefore, the general trend is toward high values. As has been pointed out, the interference of vanadium can be avoided by previously reducing it to the quadrivalent condition and then precipitating for a slightly longer period at a lower temperature. High values are caused by excessive amounts of sodium salts such as may be introduced through sodium carbonate fusions. These are occasioned by the formation of a phosphomolybdate containing an excessive amount of molybdic and nitric acids, and are more marked in pure solutions than in the presence of considerable iron.

In normal runs by the alkalimetric method, practically the same values are obtained whether the phosphomolybdate is filtered off after 15 min. or 12 hrs. For example, runs with two different low silicon steels at 15-min., 30-min., 2-hr., and 12-hr. periods gave 0.0245, 0.0249, 0.0260, and 0.0265 per cent phosphorus, respectively, with the one steel, and 0.298, 0.301, 0.306, and 0.306 with the other. The slightly higher values in the longer periods are ascribed to changes in the composition of the precipitate rather than to more complete deposition. A 15-min. precipitation is sufficient for alkalimetric determinations except in abnormal solutions such as those containing reduced vanadium or hydrochloric acid, where at least 30 min. are necessary.

(*To be concluded*)

Contamination of Water Samples with Material Dissolved from Glass Containers[1,2]

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THE SOLUBILITY of glass in water was suggested by Lavoisier[3] in 1770 as a probable explanation of certain results obtained by earlier experimenters who had assumed that distilled water held for some time in glass vessels did not contain any dissolved mineral matter. References to other articles on this subject and reports of tests of the durability of glass are given in a bibliography by Turner[4] prepared in connection with studies by Cauwood, English, and Turner[5] on the resistance to reagents of vessels made from different types of glass. These studies, like those of Nicolardot,[6] and of Walker and Smither,[7] were made with reference to the quality of chemical glassware developed in England, France, and the United States to take the place of the ware formerly imported. All these authors refer to papers by Mylius[8] and by Foerster,[9] who published some of the earlier comprehensive studies on the resistance of glass to reagents. Solubility tests are included in the series of articles by Peddle[10] on the development of various types of glass.

The necessity for tests of alkalinity of glass ampuls and other containers for medicines has been noted by Bührer[11] and by Kroeber[12] who describe the precipitation of medicinal agents by alkali dissolved from glass containers.

The requirements of glass for bottling purposes are discussed in an article by Frink,[13] in which he gives the results of tests on the solubility of different bottles. Analyses of the glasses are also given. Turner[14] reports tests of a number of English bottles and Bitting[15] gives data on the solubility of some American bottles treated with distilled water and with dilute acid.

The results reported by Frink, by Turner, and by Bitting have one feature in common. The bottles were nearly all either good or bad. Few were intermediate in character. Some bottles tested by Turner gave up one hundred times as much alkali as the more resistant ones. Nearly all of those tested by Bitting were quite resistant but the few that were not gave up about ten times as much alkali. This characteristic appears in some of the tests of chemical glassware. As would be expected, the glasses with higher percentages of alkali are usually the ones that give up the largest quantities. This is undoubtedly well known to the manufacturers.

Glass bottles are the best containers for samples of water, provided they happen to be good bottles. Even the best glass is slightly soluble in water and poor glass may be so soluble as to affect seriously the composition of a sample held for only a few days. Some bottles of the latter kind that had been received in the Water Resources Laboratory were filled with distilled water, tap water, and a solution of sodium carbonate (about 0.5 g. per liter), and the contents examined from time to time over periods of from 7 to 15 mo. At the same time bottles made of ordinary good bottle glass were tested in the same way. The results for 8 mo. are shown in Figs. 1, 2, and 3. The upper part of each figure shows the data for the good bottles and the lower part shows the poor ones.

In water analysis the bicarbonate, carbonate, and hydroxide radicals are determined by titration of the alkalinity with standard acid, generally with phenolphthalein and methyl orange indicators. This regular determination was made on samples from the bottles and all the results were calculated to bicarbonate (HCO_3). The original value for bicarbonate was subtracted, and the remainder, the alkalinity in parts per million taken up from the bottle, was plotted against the time in months that the solution had been in the bottle (Fig. 1). It is obvious that the increase in alkalinity is due to sodium hydroxide and this is evident from the actual titrations which show decreasing values for bicarbonate and increasing hydroxide, with the carbonate increasing to a maximum and then decreasing.

Filtered samples of the solutions were evaporated to dryness and weighed after heating for 1 hr. at 180° C. These results are shown in Fig. 3. Silica in the residues was determined in the usual manner and the results are shown in Fig. 2.

Two samples of tap water and one sample of distilled water that had been in poor bottles for 12 and 15 mo., respectively, were analyzed by the regular procedure followed in the Water Resources Laboratory, which is practically that of the Standard Methods of the American Public Health Association. These results are given in the table, together with an analysis of tap water made at the time the bottles were filled.

The results plotted in Figs. 1, 2, and 3 show that the good bottles did not give up enough soluble material in 6 or 7 mo. to affect an analysis seriously, except for the silica taken up by the sodium carbonate solution. No determination of total solids was made on this sample, but the increase must have been considerable. Alkalinity and silica in the distilled water and tap water in the poor bottles increased nearly as much in one month as in six. The sodium carbonate solution showed a more regular increase in silica content and the few samples of distilled water and of tap water tested after 15 mo. had considerably more silica than at the end of 6 mo.

The fact that tap water or distilled water can take up 20 or 40 parts per million of silica from a bottle in a month shows the importance of this question in connection with water analyses and at the same time suggests a simple test for sample bottles. If distilled water held in a bottle for a month at ordinary room temperature has not dissolved more than one

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[1] Received June 28, 1922.

[2] Published by permission of the Director, U. S. Geological Survey.

[3] *Memoires de l'Academie des Sciences*, **1770**, 73, 90.

[4] *J. Soc. Glass Tech.*, **1** (1917), 213.

[5] *Ibid.*, **1** (1917), 153. Further studies reported in *Ibid.*, **2** (1918), 219, 235; **3** (1919), 129, 228; **6** (1922), 17, 30.

[6] *Compt. rend.*, **163** (1916), 355.

[7] *Bur. Standards, Tech. Paper* **107** (1918).

[8] *Z. Instrumentenk.*, **8** (1888), 267; *Z. anorg. Chem.*, **55** (1907), 233; **67** (1910), 200.

[9] *Z. anal. Chem.*, **31** (1892), 241; **33** (1894), 299, 381; *Ber.*, **25** (1892), 2494.

[10] *J. Soc. Glass Tech.*, **4** (1920), 3, 299; **5** (1921), 72, 195, 201.

[11] *Schweiz. Apoth. Ztg.*, **56** (1918), 285.

[12] *Pharm. Zentralhalle*, **59** (1918), 223, 233; *Schweiz. Apoth. Ztg.*, **59** (1921), 369, 382.

[13] *Trans. Am. Ceram. Soc.*, **15** (1913), 706.

[14] *J. Soc. Glass Tech.*, **3** (1919), 37.

[15] *Glass Industry*, **2** (1921), 235.

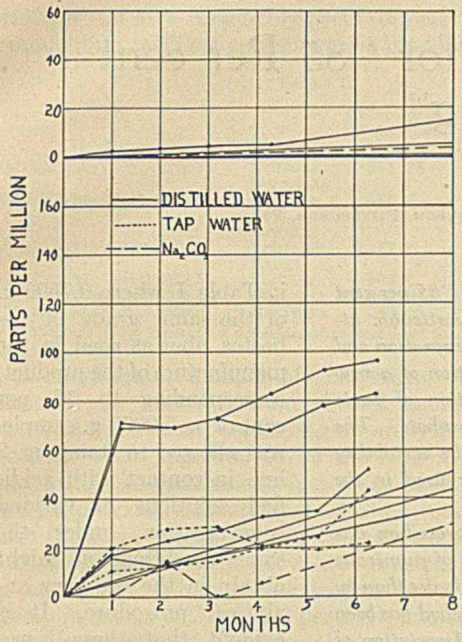

FIG. 1—ALKALI DISSOLVED FROM GOOD BOTTLES (UPPER) AND FROM POOR BOTTLES (LOWER) EXPRESSED AS HCO_3

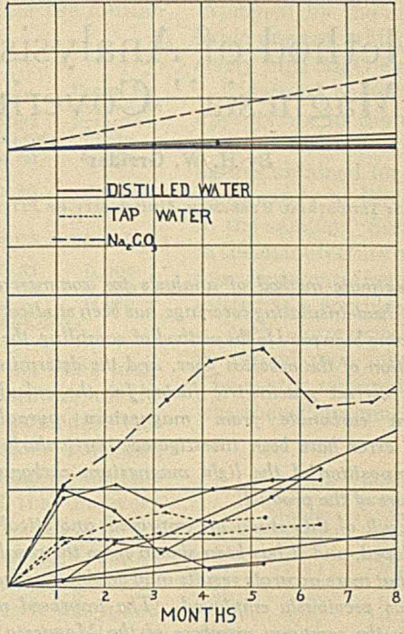

FIG. 2—SILICA (SiO_2) DISSOLVED FROM GOOD BOTTLES (UPPER) AND FROM POOR BOTTLES (LOWER)

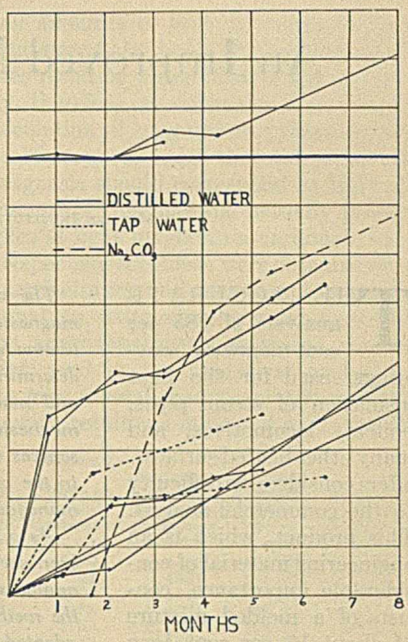

FIG. 3—TOTAL SOLIDS (T. S.) DISSOLVED FROM GOOD BOTTLES (UPPER) AND FROM POOR BOTTLES (LOWER)

or two parts per million of silica, the bottle is likely to be satisfactory for water samples. An unfit bottle can be detected by titration of the water that has stood in it for a few hours or a week.

The table of analyses shows that the large effects on an analysis are in the silica, sodium, and alkalinity. The changes in carbonate and bicarbonate in the tap water correspond almost exactly to the change in sodium. The results in the table are in complete agreement with those obtained occasionally when a sample has been analyzed that has stood too long in a poor bottle and a later check sample has been procured in a good bottle and examined promptly.

ANALYSES SHOWING SOLUTION OF MATERIAL FROM POOR GLASS BOTTLES (PARTS PER MILLION)

	TAP WATER			Distilled Water 15 Months in Bottle[2]
	As Drawn[1]	1 Year in Bottle No. 1[2]	1 Year in Bottle No. 2[2]	
Silica (SiO_2)	8.2	39	53	142
Iron (Fe)	0.15	0.15	0.15	Trace
Calcium (Ca)	18	19	18	1.1
Magnesium (Mg)	4.3	3.3	3.2	0.2
Sodium and potassium (Na + K)	2.2	18	24	22
Hydroxide radical (OH)	0	0	0	2
Carbonate radical (CO_3)	0	24	31	34
Bicarbonate radical (HCO_3)	52	41	41	0
Sulfate radical (SO_4)	19	21	22	3.5
Chloride (Cl)	4.0	4.0	4.0	Trace
Nitrate radical (NO_3)	3.9	3.9	3.8	Trace
Total dissolved solids at 180° C.	91	150	177	208

[1] Analyzed by C. S. Howard.
[2] Analyzed by H. B. Riffenburg.

Most natural fresh waters contain an excess of carbon dioxide, and therefore the regular analysis shows the presence of bicarbonate and no carbonate or hydroxide. A few natural waters are deficient in carbon dioxide and some have dissolved from rocks enough sodium silicate to show hydroxide, but these last are very rare. If an analysis of a natural water shows a large proportion of carbonate or any hydroxide, and the silica is over 30 to 40 parts per million, there is ground for suspicion that the sample contains dissolved glass. Further investigation may show the presence of 50 or 60 parts per million of silica in a natural calcium bicarbonate water or larger quantities in a natural sodium silicate water, but more frequently it will be found that the high silica and the hydroxide come from solution of the container.

CONCLUSION

Samples of water in good bottles will not dissolve enough glass in a month to cause any detectable change in the ordinary mineral analysis. No significant change will be caused in 6 mo. Samples in bad bottles a week, and sometimes only a day, may dissolve enough glass to change the character of the water as shown by an analysis.

The greatest changes are the increase in silica and sodium, and the change of the alkalinity from bicarbonate to carbonate and hydroxide with an increase of total alkalinity corresponding to the sodium.

Bottles may be tested for resistance to solution by filling with distilled water and examining the solution after a month. Titrations with acid and determination of the total solids and the silica will show the extent of the action.

Navy's Recognition of Chemists Urged

On December 1, Charles L. Parsons appeared before the Naval Wage Board, Admiral Strauss, chairman, to discuss the status of chemists in the Navy and to urge that professional chemists be given a professional standing in Navy service. Under present regulations the Navy is the only place in the United States where chemists are paid wages on a daily scale, and it is believed that they should be paid an annual salary, promoted to grades carrying titles to indicate their professional status, and, in general, be treated in a manner becoming to men who are professional and technical specialists. Dr. Parsons gave in some detail the training required and the custom elsewhere in recognizing the profession of chemistry. He stated that in view of the support which the Navy gave chemical research during the war and its appreciation of the work of chemists, it seemed incompatible for it to continue its present policy with respect to chemists.

The editor of THIS JOURNAL followed with further statements along the same general lines. It is hoped that early action on the part of the Board may change the present unsatisfactory condition.

The University of Washington, Seattle, Wash., has announced the 27th annual winter mining session, to continue from January 4 to March 21, 1923. No previous training is required for entrance. The expenses of the courses consist of laboratory deposits for material actually used and a university fee of $20. The course in ceramics includes the study of clay-testing lime, plaster, cement, brick, stoneware, whiteware, refractories, glaze studies, clay technology, and terra cotta manufacture.

An Improved Method of Analysis for "85 Per cent Magnesia" Covering[1,2]

By H. W. Greider[3]

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

The proximate method of analysis for commercial "85 per cent magnesia" heat-insulating coverings has been studied, particular attention having been paid to the method of sampling, the separation and determination of the asbestos fiber, and the determination of a new and more correct gravimetric factor for the calculation of basic magnesium carbonate from magnesium pyrophosphate. The sources of error have been investigated, particularly the variability in the composition of the light magnesium carbonate used in the manufacture of the product.

As a result of this study an improved analytical procedure has been developed, and it has been shown from the results of numerous analyses that more accurate results may be obtained by its use than by the methods previously employed. The improved method has been adopted by the company members of the Magnesia Association of America for use in their laboratory examination of "85 per cent magnesia" products, to replace the differing methods previously employed, with the object of securing more consistently uniform results.

THE ACCURATE analysis of "85 per cent magnesia" coverings, used for the heat insulation of steam pipes, boilers, locomotives, and many other heated surfaces, offers considerable difficulty to the commercial analyst. This product, which is an engineering material of considerable importance, consists of a molded mixture of about 15 per cent long fiber asbestos and 85 per cent light magnesium carbonate, from which fact is derived the commercial designation of the material. The asbestos may vary in the product of different manufacturers from about 8 per cent to 23 per cent, and is used to give the material greater structural strength. For the most efficient combination of mechanical and heating insulating qualities, it is usually considered that the material should contain not less than 10 per cent of asbestos fiber, nor less than 85 per cent of light magnesium carbonate. The magnesium carbonate used in this material is manufactured commercially in this country by the rapid heating, under carefully controlled conditions as to concentration and rate of heating, of a solution of magnesium acid carbonate.

The usual method of analysis for "85 per cent magnesia" involves dissolving the magnesium carbonate from the sample with dilute hydrochloric or acetic acid and filtering off the asbestos fiber; the iron oxide, alumina, lime, and magnesia then being determined in the filtrate. The factor 0.8723 has usually been employed to convert the magnesium pyrophosphate, obtained in the gravimetric determination of magnesia, to the basic magnesium carbonate present in the original sample, assuming the empirical formula $4MgCO_3.Mg(OH)_2.5H_2O$ as representing the composition of the magnesium carbonate.

It has been found in this study of the analytical method that there are two principal sources of error in the procedure as ordinarily carried out. The first error results from the fact that the Canadian serpentine asbestos fiber, which is almost invariably used in the manufacture of 85 per cent magnesia, is somewhat soluble in water and considerably more soluble in dilute solutions of acids, so that a part of the fiber is lost as a result of the acid treatment and subsequent washing of the fiber, introducing into the solution, also, small amounts of magnesium ion from the dissolved asbestos, which are later precipitated in the determination of magnesium carbonate. The magnitude of these losses is shown in Table I, where 0.7500 g. of the same grade of asbestos fiber as used in the manufacture of the product, corresponding to 15 per cent of a 5.0000 g. sample, was allowed to stand for 2 hrs. in contact with acidified solutions of varying concentration under the same conditions as might obtain in the ordinary analytical procedure. It is evident that these losses are quite large when even a small excess of a dilute acid is present, and that it is desirable to filter and wash the fiber as promptly as possible after complete solution of the carbonate has been effected. The presence of more than a very slight excess of acid in the solution at any time should, therefore, be avoided.

Table I

Sample	Solution	Loss in Weight of Fiber Per cent	Net Loss Corrected for Hygroscopic Moisture Per cent	Net Loss Per cent of Total Analysis
1	200 cc. distilled water, just acid to methyl orange	2.07	1.54	0.23
2		2.73	2.20	0.33
			Av. 1.87	Av. 0.28
3	200 cc. distilled water, 10 cc. 5 per cent acetic acid	4.13	3.60	0.54
4		3.75	3.22	0.48
			Av. 3.41	Av. 0.51
5	200 cc. distilled water, 5 cc. 0.1 *N* HCl	6.0	5.47	0.82
6		6.56	6.03	0.90
			Av. 5.75	Av. 0.86
7	200 cc. distilled water, 10 cc. 0.1 *N* HCl	6.60	6.07	0.91
8		6.22	4.69	0.71
			Av. 5.38	Av. 0.81

The second source of error, and a much more important one, is that light magnesium carbonate, as produced by American manufacturers, does not have exactly the composition required by the empirical formula given above, and therefore the gravimetric factor for magnesium pyrophosphate is in error by an amount corresponding to the variation from that formula of the actual composition of the material. In any case, the accuracy of a determination of this character is insufficient to justify the use of a factor calculated to four decimal places, for a substance whose composition is known to be variable.

There is abundant evidence in the literature to prove that basic magnesium carbonate is quite variable in composition, by whatever process it is manufactured, but that the most uniform material is obtained by the heating of a magnesium acid carbonate solution. The variability in the composition of this material is indicated by the formulas in Table II, deduced by several investigators who prepared the light carbonate under different experimental conditions. It is evident, therefore, that it will not be possible to determine a factor for use in the analytical procedure which will give accurate results for *every* commercial sample of this product, and it was the purpose of this investigation only to determine one

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[1] Received May 27, 1922.

[2] This improved method of analysis was developed as the result of an investigation conducted for the Magnesia Association of America, at the Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

[3] Industrial Fellow, Mellon Institute of Industrial Research.

which would give reasonably accurate results for the routine examination of 85 per cent magnesia products.

TABLE II

FORMULA	AUTHORITY	Calculated Molecular Weight	MgO Per cent	Factor for Magnesium Pyrophosphate
$3MgCO_3.Mg(OH)_2\ 3H_2O^1$	Fritsche Berzelius	365.28	44.05	0.820
$4MgCO_3.Mg(OH)_2.5H_2O^1$	H. Rose Brill Kraut	485.6	41.50	0.872
$4MgCO_3.Mg(OH)_2.4H_2O$	Fritsche Kraut	467.6	43.05	0.840
$4MgCO_3.Mg(OH)_2.6H_2O^1$	Steffens	503.6	40.03	0.904
$5MgCO_3.2Mg(OH)_2.7H_2O^1$	Beckurts	664.24	42.50	0.852
$3MgCO_3.Mg(OH)_2.4H_2O$	Beckurts	383.28	42.1	0.860

[1] Prepared by heating a solution of magnesium acid carbonate.

A considerable number of analyses of 85 per cent magnesia blocks obtained from several manufacturers of the material were made, employing an analytical procedure embodying what appeared to be the best available methods, and using the gravimetric factor for basic magnesium carbonate previously mentioned. It was found that in every case the total results for the analysis were from 2.5 to 4.2 per cent in excess of 100 per cent. Inasmuch as the amounts of ferric oxide and alumina hardly exceed traces, and lime is rarely in excess of 2.5 to 3.0 per cent, and since it was found that the error introduced by the asbestos fiber loss due to acidification and washing was much too small to account for so great a discrepancy, it seemed obvious that this error must be chargeable to the magnesium carbonate which makes up the greater part of the sample. It was also demonstrated that no decomposition of the samples took place in the determination of hygroscopic moisture by heating for 24 hrs. at 105° C., since magnesium carbonate showed no continuous loss in weight beyond the 2.5 per cent of moisture usually present, unless heated to temperatures in excess of 250° C.

The percentage of magnesium oxide in several samples of technical light magnesium carbonate was, therefore, determined by igniting them to constant weight, after first drying at 105° C., to free them from hygroscopic moisture. Table III shows that these samples contained from 43.4 to 43.9 per cent of MgO, where the previously assumed empirical formula would require only 41.5 per cent; and that the basic magnesium carbonate calculated, corresponding to the MgO obtained, varied from 104.5 to 105.6 per cent. This finding seemed to account for the high analytical results previously obtained, since, if the MgO obtained is, as here shown, approximately 5 per cent in excess of the calculated amount, the factor used, 0.8723, must also be in error by approximately that per cent. The factor 0.8723, corrected from the average of the foregoing analyses, would thus become 0.832.

TABLE III

SAMPLE	MgO Corresponding to Formula: $4MgCO_3.Mg(OH)_2.5H_2O$ Per cent	MgO Obtained Per cent	Basic Magnesium Carbonate Calculated Corresponding to MgO Obtained, Per cent
1	41.5	43.4	104.5
2	41.5	43.7	105.0
3	41.5	43.4	104.5
4	41.5	43.9	105.6
5	41.5	43.55	104.8
6	41.5	43.5	104.7

Further evidence of the fact that the percentage of magnesium oxide in this material exceeds that required by the formula $4MgCO_3.Mg(OH)_2.5H_2O$ was obtained by a titration of the basic magnesium carbonate. When the dry material is suspended in water, and a measured excess of 0.05 *N* HCl is added and the liquid warmed until all the magnesium carbonate has dissolved, the excess acid then being titrated back with 0.05 *N* NaOH, using methyl red indicator, it is found that the basic magnesium carbonate shows an alkalinity (MgO) which is 5.8 per cent in excess of that required by the formula above. This discrepancy is too great to be explained by the small amounts of lime, alumina, and iron oxide present, which statement also holds true for the excessively high MgO figures resulting on ignition of the samples.

It seemed necessary, therefore, to determine a new factor appropriate to the calculation of magnesium pyrophosphate to basic magnesium carbonate, in order that the analytical figures obtained for magnesia should correspond at least approximately to the amount of this material actually present in the sample. Samples of light magnesium carbonate used in the manufacture of 85 per cent magnesia were obtained from four representative manufacturers, and each sample was submitted to a complete analysis, using samples weighing 0.4000 g. each, corresponding approximately in magnesia content to the aliquot solution used in the analytical procedure. The factor required to give a total analysis of 100 per cent was then determined, with results as indicated in Table IV.

TABLE IV

SAMPLE	Hygroscopic Moisture Per cent	Alumina and Ferric Oxide Per cent	Lime as Calcium Carbonate Per cent	Weight of Magnesium Pyrophosphate Grams	Total of Analysis Using Factor 0.8723	New Calculated Factor for $Mg_2P_2O_7$
1*a*	2.36	0.43	0.80	0.4588	103.69	0.8380
1*b*	2.49	0.42	0.94	0.4591	104.05	
2*a*	2.66	0.45	3.03	0.4546	105.24	0.8275(?)
2*b*	2.80	0.43	2.68	0.4534	104.81	
3*a*	3.40	0.72	1.65	0.4504	103.97	0.8375
3*b*	3.31	0.72	1.83	0.4495	103.89	
4*a*	2.51	0.38	1.93	0.4556	104.02	0.8352
4*b*	2.47	0.44	2.03	0.4522	104.29	

It will be noted that, with the exception of the second sample, the factor values obtained agree rather closely. The analyses show that the second sample contains a considerably greater percentage of lime as calcium carbonate than any of the others, which suggests that it was manufactured under less carefully controlled conditions of precipitation, which, in turn, may account for its different composition. This result was, therefore, discarded and the factor finally adopted was the rounded average of the other three values, or 0.837. Subsequent to the determination of this factor and the development of the improved procedure, it was learned that a new factor had also been independently determined and adopted in the laboratory of one of the large manufacturers of magnesium carbonate. This factor, 0.8371, is practically identical with that determined in this investigation and was found to give good results in that laboratory.

A considerable number of analyses have been made, using this new factor for magnesium pyrophosphate, on various samples of 85 per cent magnesia prepared in different ways and employing improvements in the several steps of the procedure which were suggested as a result of the experimental study of the sources of error. Typical analyses obtained in this way are given in Table V. Examination of these data shows that quite good agreement can be obtained on duplicate analyses made by this method, considering the variability in the composition of the material itself and the difficulties in obtaining and preparing a satisfactory uniform sample. The sum of the separate analytical figures approximates 100 per cent as closely as could be expected with a material of this character. It should be noted here that 85 per cent magnesia from the manufacturer whose magnesium carbonate sample gives the low factor indicated in Table IV was found to give satisfactory total analysis with the new average factor adopted above. The procedure recommended for the examination of 85 per cent magnesia is given below.

RECOMMENDED PROCEDURE

PREPARATION OF SAMPLES—From each lot of the material 10 fragments are cut, using a very sharp, thin-bladed knife (such as a leather or rubber knife), taking great care to slice the asbestos fibers off clean and avoid pulling them out of the sample block in which they are imbedded. Each fragment is trimmed down with this knife to a cubical shape, surfacing each face of the cube free from projecting asbestos fibers. The entire sample is thoroughly crushed and mixed and is then, if necessary, quar-

TABLE V—ANALYSES OF "85 PER CENT MAGNESIA" COVERINGS BY THE IMPROVED METHOD (USING NEW FACTOR)

No.	METHOD OF PREPARING SAMPLE	Asbestos Fiber Per cent	Hygroscopic Moisture Per cent	Alumina and Ferric Oxide Per cent	Lime as Calcium Carbonate Per cent	Basic Magnesium Carbonate Per cent	Total of Analyses Per cent	CALCULATED TO DRY BASIS Asbestos Fiber	Magnesium[1] Carbonate
I	2 large cubes cut from opposite ends of same block, each cube surfaced free from projecting asbestos fiber. Entire sample thoroughly crushed and mixed	16.9	3.02	....	1.2	78.65	99.77	17.42	82.35
		16.4	....	....	2.3	77.95	99.67	16.9	82.75
II	2 cubes cut from opposite ends of block, prepared same as Sample I	16.7	2.84	0.40	2.71	77.26	99.91	17.2	82.7
		16.8	2.78	0.52	2.37	77.55	100.02	17.28	82.75
III	5 cubes cut along length of block, prepared same as Sample I	14.0	2.50	0.56	3.39	79.28	99.73	14.35	85.4
		14.55	2.80	0.52	2.86	78.70	99.48	14.95	84.55
IV	10 cubes, each 2.5 g., cut along length of block, prepared same as Sample I	16.0	2.82	0.66	2.50	77.55	99.53	16.47	83.05
		16.6	2.88	0.42	2.61	77.25	99.76	17.1	82.72
V	10 cubes, each 2.5 g., cut from another block, prepared same as Sample IV	10.2	1.30	0.38	1.46	87.0	100.34	10.33	90.0
		9.93	1.38	0.44	1.43	87.5	100.47	10.04	90.5
VI	*New block* 10 cubes cut at intervals along block, prepared same as Sample V	9.76	2.52	0.24	0.21	87.6	100.3	10.46	89.8
		9.81	2.38	0.26	0.18	87.85	100.5	10.50	89.95
VII	*New block* 10 cubes cut at intervals along length of block sample, prepared same as Sample VI	19.76	1.98	0.20	0.25	77.7	99.89	20.6	79.25
		19.99	1.88	0.20	0.18	77.65	99.90	20.73	79.15

[1] Includes the impurities in the commercial basic magnesium carbonate, ferric oxide, alumina, and lime as calcium carbonate.

tered down to a 25-g. sample, which is stored in a straight-side, wide-mouth glass jar with an aluminium screw top. Just before taking the sample for analysis the closed jar is shaken thoroughly. In removing the material from the sample jar it is simply shaken out and is not handled with the fingers or any tool which might exert a pinching action and cause separation of the asbestos and magnesium carbonate.

HYGROSCOPIC MOISTURE—A 2-g. portion of the sample is placed on a weighed watch glass and dried at 105° C. to constant weight. The loss in weight is taken as hygroscopic moisture.

FIBER—A 5-g. sample is taken for the chemical analysis. 100 cc. of water and 2 drops of methyl red indicator are added and approximately N HCl is slowly added, with stirring until all the magnesium carbonate has dissolved and *a permanent pink color has just appeared*. (This will ordinarily require about 125 cc.) The asbestos fiber is immediately collected by filtering through a dried, weighed Gooch crucible, and is quickly and thoroughly washed with cold water. The crucible and contents are dried at 110° C. and weighed, the increase in weight being taken as fiber. (If greater accuracy is desired here, the weight of fiber so obtained may be corrected by a blank determination on a sample of the asbestos used in the manufacture of the product, to determine the loss in weight of the fiber due to the treatment with dilute acid and the subsequent washing.) In any case, the filtration of the fiber should be carried out as rapidly as possible, and the least possible excess of acid necessary to dissolve the magnesia should be used, to minimize this source of error.

IRON OXIDE AND ALUMINA—To the combined filtrate and washings from the fiber determination 85 cc. of 10 per cent HCl are added and the solution is brought to boiling. Dilute NH_4OH is slowly added to slight excess after the addition of 2 drops of methyl red indicator solution; the solution is boiled for a minute or two to coagulate the precipitate and expel the excess of ammonia. The precipitate, which consists of the hydroxides of aluminium and iron, is filtered off, washed with a hot 2 per cent NH_4Cl solution and, if the determination of iron oxide and alumina is desired, is ignited and weighed as $Fe_2O_3 + Al_2O_3$.

LIME AS CALCIUM CARBONATE—The combined filtrate and washings obtained above are brought to boiling and made slightly acid with HCl. About 25 cc. of a saturated (4 per cent) solution of ammonium oxalate, or an equivalent amount of a more dilute solution, are then added and the solution made slightly alkaline with NH_4OH. In order to avoid inclusion of excessive amounts of magnesia with the calcium oxalate precipitate, it is imperative that the volume of the solution from which it is precipitated should be not less than 500 cc. After boiling for 5 min. the solution is allowed to cool, and when thoroughly cold the bulk of the solution is decanted through a filter and the precipitate then collected on the filter and washed two or three times with cold water, using about 50 cc. of water each time. The filtrate and washings are set aside for the magnesia determination. The precipitate on the filter is dissolved in hot dilute (10 per cent) HCl, about 60 cc. being required, and is returned to the beaker in which the precipitation was made, the filter being thoroughly washed with cold water. This solution and the washings are combined and brought to boiling, a few cc. of ammonium oxalate solution are added and then dilute NH_4OH in slight excess. When cold the precipitate of calcium oxalate is collected on a filter, washed with cold water, dried, ignited over a blast lamp to constant weight, and weighed as CaO. From this weight, using the factor 1.78, the calcium carbonate present in the original sample is calculated. It is especially important that the double precipitation of calcium oxalate be carried out when accurate results for lime are desired, in order to avoid the inclusion of magnesia with the lime in the calcium oxalate precipitate.

The combined filtrates, but not the washings from the last lime precipitation, are made up to 1000 cc. in a standard flask. A 100-cc. aliquot is employed for the determination of magnesia.

MAGNESIA—A 100-cc. portion of this solution is acidified with HCl and diluted to about 400 cc. A sufficient quantity—15 cc., of a saturated solution of sodium ammonia phosphate to precipitate all the magnesia is added, and also a considerable excess of ammonia. The solution is thoroughly stirred until precipitation is complete and is allowed to stand at least 12 hrs. in the cold. The bulk of the liquid is then decanted through the filter; the precipitate on the filter is washed back into the beaker and dissolved in the smallest possible amount in dilute HCl. A few drops of phosphate solution are added and then ammonia in slight excess, with stirring, as before. After standing 6 hrs., the precipitate is filtered off and washed with dilute ammonia (1:10). It is then dried, detached from the paper and the latter burned in the weighed crucible in which the precipitate is to be ignited and weighed. The ash from the paper is strongly ignited and the precipitate itself is then placed in the crucible, heated gently at first, and when ammonia is no longer evolved, the heating is increased to a full blast and continued for at least 20 min., cooling, weighing, and reigniting until constant weight is obtained. The residue is magnesium pyrophosphate and it is calculated to basic magnesium carbonate in the original sample by the following factor:

Weight $Mg_2P_2O_7 \times 0.837$ = Weight basic magnesium carbonate, instead of the factor 0.8723, corresponding to the ordinarily assumed composition of light magnesium carbonate, $4MgCO_3.Mg(OH)_2.5H_2O$. The total of the analyses above should approach closely to 100 per cent if the complete procedure is followed.

A method recently published by Griffin[4] for the analysis of 85 per cent magnesia seems to be inaccurate in two respects. The factor used for the conversion of magnesium pyrophosphate to basic magnesium carbonate is 0.8723, corresponding to the formula $4MgCO_3.Mg(OH)_2.5H_2O$. This introduces into the results a large positive error, as has been shown by the data above, which, however, is partly offset by a negative error resulting from the fact that in the determination of asbestos fiber the analyst is directed to ignite the asbestos before weighing as fiber. The chrysotile asbestos fiber used in 85 per cent magnesia contains about 14 per cent of water, which it loses on heating to the ignition temperature, and, therefore, in a sample containing 15 per cent of asbestos the minus error thus introduced into the total of the analysis may be as great as 2.1 per cent.

In cases where satisfactory total analyses cannot be obtained by the use of the corrected factor determined above, it will be necessary for the analyst to have recourse to a complete ultimate analysis of the product, involving the determination of hygroscopic moisture, total loss on ignition, total CO_2, and the calculation of the CO_2 equivalent of the CaO and

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[4] "Technical Methods of Analysis, as Employed in the Laboratories of A. D. Little, Inc.," by R. C. Griffin, New York, **1921**, p. 62.

MgO found in the sample, as well as the calculation of the water of constitution of the basic magnesium carbonate, by difference. This method will, of course, give very accurate results, but owing to the large number of analytical operations and calculations involved, it is not one well suited to the routine analytical examination of the material.

Studies on Manganates and Permanganates[1]

II—The Effect of Composition, Temperature, and Moisture on the Reactions Involved in the Manufacture of Potassium Manganate

By H. I. Schlesinger, V. T. Jackson,[2] and E. E. Cordrey

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The experimental results published in the first paper of this series[3] dealt chiefly with the effect produced upon the yield by changes in the relative amounts of potassium hydroxide and manganese dioxide in the preparation of potassium manganate by the usual process. Although one or two questions of interest in connection with that phase of the work are cleared up by the results now to be reported, the present paper deals chiefly with the influence of temperature and of moisture on the yield and on the velocity of the reaction. Both of these conditions have been found to influence the course of the reaction in such a manner that the results are of theoretical and especially of practical importance in connection with the manufacture of potassium manganate and hence of potassium permanganate.

MATERIALS AND PROCEDURE

THE MATERIALS used in the investigation were potassium hydroxide, containing 86 per cent KOH and 5.5 per cent of potassium carbonate, and Kahlbaum's precipitated manganese dioxide. The latter contained manganese dioxide in amount corresponding to 44.2 per cent of manganese, as determined by analysis with ferrous ammonium sulfate, and lower oxides of manganese corresponding to 5.3 per cent of manganese. It contained only traces of impurities other than water. In particular, it was free from alkali, chlorides, and nitrates, which might have affected the reaction. In preparing the mixtures and in carrying out the reaction the procedure of Schlesinger, Mullinix, and Popoff[3] was followed. The rotary kilns were, however, heated electrically, thus permitting more accurate temperature control and decrease in the amount of contamination with carbon dioxide. In many of the runs the mixes were heated in oxygen instead of in air, since this materially reduced the time required for each run, but did not affect the final result.

The progress of the reaction was followed by the same analytical procedure as in the previous work, except that in addition to determining the manganate and total manganese content of samples taken from the mix at various times, we also determined the amount of carbon dioxide absorbed during the runs, especially during the process of remoistening described in the first paper. This analysis was made by acidifying a sample of the mix and then absorbing and weighing the liberated carbon dioxide. While the potassium carbonate formed in the mixes by the taking up of carbon dioxide has no direct effect on the reaction in the range of temperature employed, determination of the carbon dioxide absorbed is, nevertheless, essential to accurate work, since the yield depends upon the relative amount of potassium hydroxide and absorption of carbon dioxide means a loss of the free caustic.[4]

EFFECT OF TEMPERATURE ON YIELD

Four series of experiments, at 415°, 325°, 270°, and 235° C., respectively, were carried out. At the higher temperatures ratios of potassium hydroxide to manganese, expressed in mols of each varying from about 1.5 to about 3.25, were included, while at the lower temperatures only mixtures in which this ratio was above 2 were studied, for reasons which will appear later. For each experiment—i. e., at each "ratio" reported—from 15 to 30 determinations of manganate, 3 of total manganese, and 3 of carbon dioxide had to be made in order to follow the course of the reaction. In some instances the number of analyses greatly exceeded these figures. We have, however, condensed this analytical material into Table I, which deals only with the final data and the results obtained with dry air or dry oxygen. In the first column are given the ratios in mols of potassium hydroxide to manganese, determined as described by Schlesinger, Mullinix, and Popoff, except that a correction is now made for carbon dioxide absorbed during the run; in the second column will be found the *percentage* of potassium manganate contained in the mix when equilibrium is reached, and in the last column the yield that this quantity of manganate represents—i. e., the *percentage* of all the manganese present that has been converted

TABLE I—YIELD OF MANGANATE OBTAINED WITH VARYING RATIOS OF KOH TO Mn AND AT DIFFERENT TEMPERATURES, WHEN THE MIXES ARE HEATED IN DRY AIR OR IN DRY OXYGEN

415° C.			325° C.		
Ratio	Per cent K_2MnO_4	Per cent Yield	Ratio	Per cent K_2MnO_4	Per cent Yield
1.617	76.0	75.8	1.492	73.6	70.8
1.848	78.5	88.8	1.794	83.5	86.9
1.867	81.7	88.2	1.910	85.7	92.5
2.007	77.9	91.4	2.016	85.0	96.9
2.027	79.5	89.7	2.159	81.6	93.0
2.151	69.0	84.4	2.442	63.9	79.4
2.182	63.9	82.4	2.505	62.0	78.6
2.320	62.9	77.0	2.721	52.2	67.5
2.471	58.8	71.9	2.875	48.3	62.9
2.611	50.9	64.8	2.976	41.8	56.5
2.770	44.0	57.6	3.038	41.4	55.9
3.024	39.9	55.2	3.258	40.1	56.7
3.225	39.7	55.5			

270° C.			235° C.		
Ratio	Per cent K_2MnO_4	Per cent Yield	Ratio	Per cent K_2MnO_4	Per cent Yield
2.006	85.3	95.9	2.024	84.7	95.7
2.117	82.7	94.9	2.278	77.2	96.3
2.349	71.5	90.2	2.456	78.7	99.6
2.427	70.4	85.8	2.715	71.2	99.4
2.523	61.7	80.5	3.137	48.8	72.5
2.685	55.4	74.5			

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[1] Received May 8, 1922.

[2] This paper is taken in part from material presented by V. T. Jackson to the faculty of the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Schlesinger, Mullinix, and Popoff, THIS JOURNAL, 11 (1919), 317.

[4] That potassium carbonate itself is without influence in the reaction was demonstrated by adding 0.3 mol of the carbonate to a mix of 2.4 mols of the hydroxide and 1 mol of manganese dioxide and heating the new mixture in a stream of oxygen. The yield of manganate was the same as that obtained in the absence of the carbonate.

into manganate. These data are also graphically represented in Fig. 1. It is self-evident from the reaction equation

$$4KOH + 2MnO_2 + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

that when the ratio of potassium hydroxide to manganese dioxide in mols is less than 2, not all of the manganese dioxide could be converted into manganate. In spite of this we have given in the table for all mixtures the yield based on an assumed possible utilization of all the manganese, because this method is simpler and shows more adequately the amount of manganate obtainable at all concentrations. In order to make the picture of the course of reaction complete, we have added the dotted lines to Fig. 1. These represent a recalculation of the yield in terms of potassium hydroxide converted into manganate for those mixtures in which the manganese dioxide is present in excess—i. e., for ratios less than 2.

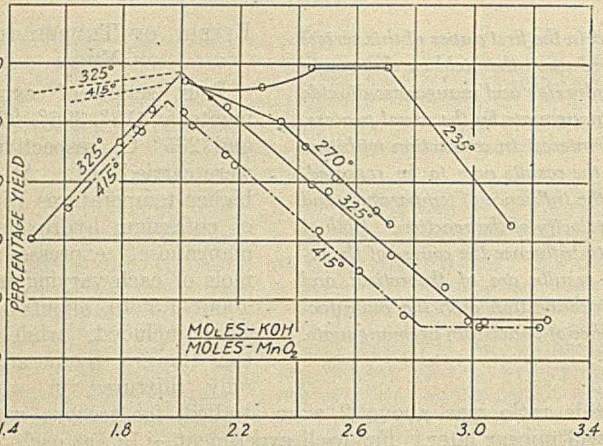

Fig. 1

From the tables, and particularly by reference to the dotted lines in Fig. 1, it will be seen that when the manganese dioxide is present in excess the reaction goes practically to completion. The yield, to be sure, never quite reaches 100 per cent. This can easily be accounted for by the assumption that the lower oxides of manganese, which are present as shown by the analytical data and which have been calculated as taking part in the reaction as if they were manganese dioxide, do not really fully become converted into manganate. Since, at the lower temperatures, the yield is somewhat higher, we may further conclude that there is an equilibrium between manganese dioxide and the lower oxides of such character that at the lower temperatures more of the manganese dioxide is formed from the lower oxides in the mixtures. These conclusions are in agreement with well-known facts about the behavior of the oxides of manganese in the absence of alkalies. Likewise, the results just discussed make clear that when fairly pure manganese dioxide and potassium hydroxide are employed in the reaction, and when allowance is made for the loss of the latter substance by absorption of carbon dioxide, complete conversion of manganese dioxide into manganate is obtained when 2 mols of caustic are used with every mol of the dioxide. The ratio of 2.5 of caustic to 1 of the dioxide, found to be necessary when pyrolusite is the source of the manganese dioxide—as is usually the case in the manufacture of permanganates—is therefore to be explained on the basis of probable impurities present in pyrolusite, as was suggested in the first paper.[3] Finally, the data show that as long as manganese dioxide is present in excess, the yield is very nearly independent of the temperature—at least within the range covered by our experimental work. For this reason we limited ourselves at the lower temperatures to a study of the reaction in the presence of an excess of alkali.

Under these conditions the situation is quite different. The excess of alkali, as has already been shown in the first paper, decomposes the manganate, and the amount of decomposition increases with increase in the amount of potassium hydroxide. It will be observed that the amount of decomposition produced by a given excess of potassium hydroxide is very much smaller at the lower temperatures than it is at the higher ones. Both at 415° and at 325° C. the yield becomes constant after it has fallen to a little below 60 per cent; at the two temperatures below these we have not investigated mixes rich enough in alkali to show this region of constant yield, because such mixes become exceedingly sticky in the rotary kilns at low temperatures and reliable sampling and thorough mixing become very difficult.

One other striking phenomenon is to be noted in connection with the results at the different temperatures. At 415° and 325° C. the curves that show the effect of excess of alkali on the yield are single straight lines, indicating that the amount of decomposition of the manganate is directly proportional to the amount of alkali added. At 270° C., however, the yield at first falls slowly with increasing excess of potassium hydroxide until the excess is about 0.2 mol and the yield about 90 per cent, and then falls off more rapidly; the portion of the curve representing the latter phase of the reaction is *parallel* to the curves for the higher temperatures. At 235° C. the difference in the character of the curve is even more marked—the yield slowly increases until it reaches practically 100 per cent, remains constant with further addition of alkali, and only after an excess of about 0.7 mol of the latter has been added does the yield begin to decrease. The number of experiments at the lowest temperature is not great enough to determine the exact character of this curve, but is sufficient for an interpretation of the results, especially so far as their importance to the manufacture of manganates is concerned.

It is quite clear that the data described in the preceding paragraph cannot be explained satisfactorily as a purely thermal phenomenon. If the effect of temperature were solely one of displacement of an equilibrium between manganate, potassium hydroxide, and the products of the interaction of these two substances, the curves should all be straight lines, as they are at 415° C., and should have their origin at the ratio 2.00 and the yield 100 per cent. Since neither of these characteristics is found for the group of actual curves, it is necessary to search for another explanation of the temperature effect. In this effort we were aided by an observation already mentioned in the first paper of the series. We there called attention to the influence of moisture on the velocity with which equilibrium is attained in the reaction, and to the possibility that moisture might affect the final condition of equilibrium. Further investigation of this matter at the higher temperatures failed apparently to disclose anything more of interest.

At the lower temperatures, on the other hand, it was found that the presence of moisture has a profound influence on the course of the reaction. This can best be brought out by the following illustrations:

A mix in which the ratio of alkali to manganese was about 3.1 to 1.0 was prepared and heated in the ordinary way in air. The yield rose during the first 10 hrs. of treatment at 235° C. to 72.5 per cent. This and the further changes taking place in the material are shown in Fig. 2. It will be noted that, after the first 10 hrs., further heating at 235° C. left the yield practically unchanged, although this treatment was continued for 15 hrs. Equilibrium had apparently been attained. The mix was then heated for a few hours at a temperature above 400° C. and was thereby decomposed to such an extent that the yield fell to 57.5 per cent. The temperature was then again lowered to 235° C. and the heating continued in *dry* air. Fifteen hours of this treatment had no influence on the yield, although before the material had been exposed to the higher temperature the yield had been 72.5 per cent. We next passed air, moistened by allowing it to bubble through boiling water, over the mix at 235° C. In approximately 10 hrs. the yield rose to practically 100 per cent. Finally, the moistened air was replaced by dry air, with the result that the yield again fell to 72.5 per cent, where it became constant.

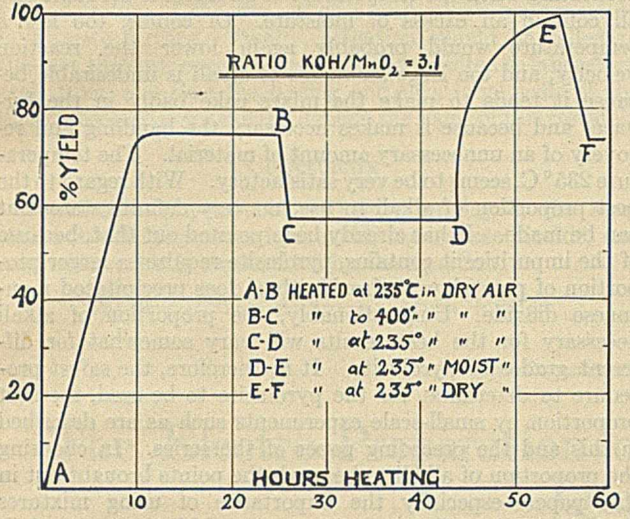

Fig. 2

Apparently, then, there are three conditions of equilibrium corresponding to the same temperature. There is only one explanation for this phenomenon—namely, that the differences observed under the various conditions of carrying out the heating at a given temperature are due to differences in moisture content of the material. A mix of a given composition will, at a certain temperature, say, 235° C., retain a certain amount of moisture when the mix is heated in ordinary air, and in the presence of this amount of moisture will reach a certain yield at equilibrium. If the temperature is raised, some or all of the moisture is driven out of the material and the yield falls. If reheating at the lower temperature is again undertaken, but in dry air, the moisture cannot be regained and the yield cannot rise. If, however, the mix is heated in an atmosphere rich in moisture, it will take up more water than it had originally retained in ordinary air, and the yield will be higher than it originally was. Finally, reheating in ordinary air will cause the mix to lose its excess of moisture and the yield will fall to its original value. The instance cited has been corroborated by others. Only one further illustration need be cited. A mix of ratio 2.5 was heated in ordinary air at 270° C. until equilibrium was reached with a yield of 80 per cent. When the heating was continued in air moistened as described, the yield rose to 98.4 per cent; reheating in dry air again lowered the yield to 80 per cent.

The phenomena which have just been described and their interpretation explain quite satisfactorily the influence which temperature has on the yield in the reaction under discussion. They explain also the difference in the type of curve observed at the different temperatures. When the temperature is low, the large amount of water retained by the mixes makes it necessary to add a fairly large excess of alkali before decomposition of the manganate will begin. Under these conditions the lower oxides of manganese become more completely oxidized to manganese dioxide, and the yield slowly rises until practically all the manganese is converted into manganate. (See curve for 235° C., Fig. 1.) At 270° C., the tendency of the yield to rise on account of the transformation of the lower oxides is partially counterbalanced by the decomposing influence of the excess of alkali, which becomes noticeable earlier than at 235° C. because of the smaller amount of water present. Hence, the yield drops slowly until all the lower oxides have been oxidized to the higher stage. After this phase of the reaction has been completed, there is no longer any factor which masks the decomposing influence of the alkali, and the yield drops off rapidly.

The interpretation which we have given for the effect of temperature on the yield also makes possible an explanation of the difference between our results and those of Sackur.[5] His experiments were carried out entirely with thoroughly dried mixes, and he found that his maximum yield was 60 per cent. We likewise find, in the experiments referred to above, that decomposition of the manganate by use of high temperatures stops when the yield has been lowered to from 55 to 60 per cent. Sackur's conclusions, however, that the possible yield in the manufacture of manganates is on this account limited to 60 per cent, is manifestly incorrect, as has been pointed out both in this paper and in the first one of this series.

Effect of Moisture

The function of moisture in the prevention of the decomposition of manganates by excess of potassium hydroxide cannot as yet be explained in a manner entirely free from objection. One of several possibilities may be suggested. According to Sackur the product formed by heating dry mixes of potassium hydroxide and manganese dioxide in the air or oxygen is a mangani-manganate of the composition $3K_2MnO_4.2K_2MnO_3.3K_2O$. It is readily conceivable, if Sackur's theory is correct, that in the presence of moisture this compound is decomposed into manganate, manganite, and potassium hydroxide, and that the manganite thus formed can be oxidized to manganate. The amount of decomposition of the complex compound would depend upon the amount of water present, and consequently the total yield of manganate would be likewise affected by the presence of moisture. The objection to this explanation is that one would expect to find necessary an excess of 1.2 mols of potassium hydroxide per mol of manganese dioxide, in order to complete the formation of the mangani-manganate postulated by Sackur. In the presence of moisture even more potassium hydroxide should be required, since the moisture decomposes a part of the mangani-manganate formed. But we find that much less potassium hydroxide is actually required. Thus, at 415° C., the decomposition seems to be complete when the excess of the caustic potash is only about 0.8 mol. This difficulty can be avoided by assuming that a mangani-manganate, of some other composition—e. g., $3K_2MnO_4.2K_2MnO_3.K_2O$—is found under the conditions of our experiments. Final decision on this question must await further data.

While to the manufacturer of permanganate, which is usually made from manganate, the yield of the manganate is of great importance, the time required for obtaining the product is, of course, likewise a vital factor. Our results are also of considerable interest in this connection. In the discussion of this point, we are limiting ourselves to the results at 235° and 270° C., for two reasons. From Fig. 1 it is obvious that at the lower temperatures, especially at 235° C., there is a fairly wide range of concentrations, or, better, proportions of the two constituents at which the maximum yield can be obtained; while at the higher temperatures either a relatively slight deficiency or a slight excess of alkali produces a considerable lowering of the yield. Other things being equal, the manufacturer would on this account alone prefer to work at the lower temperature. The second reason for limiting the discussion to the lower temperatures is that at the higher ones our experiments were made almost entirely with oxygen in order to hasten the reaction, whereas at the lower temperatures the experiments were carried out in a current of air,

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[5] *Ber.*, **43** (1910), 381; **44** (1911), 777; *Z. anorg. Chem.*, **73** (1912), 101.

and thus conform more closely to actual manufacturing conditions. In general, at the higher temperatures the reaction seemed to proceed more slowly.

To present the data on the time required for the reactions, Table II and Fig. 3 have been constructed, but only a few characteristic mixes have been taken from the data at hand. It will be recalled, by reference to the first paper, that in many cases it was necessary to remove the mixes from the furnace and to moisten them with water in order to reach a condition of true equilibrium. From the notes in Column 5 of the table, it will be observed that this is not always necessary. Clearly, the process to be practical should be carried out under conditions which make the remoistening unnecessary. Fig. 3 reproduces these data graphically. Crosses indicate remoistening. The solid lines represent the data at 235° C., the dotted lines at 270° C. These curves have been smoothed out. The actual curves present many irregularities, due, in part at least, to difficulties in accurate sampling. Also there is one recurring type of irregularity that is shown neither in the table nor the curves. When the mixes are given the preliminary heating and mixing already referred to, they invariably take up oxygen. In some cases they take up more oxygen than corresponds to the equilibrium condition at the temperature of the main experiment. This is due to difference in moisture content and in temperature at the two stages of the experiment. In certain other respects, also, these data on the time element in the reactions are not strictly comparable for the different runs. During the preliminary heating, the mixes are stirred from time to time by hand. As the excess of water evaporates, the material first becomes sticky and then hard. During this period the stirring is attended by considerable difficulty, and on this account two batches prepared in exactly the same way may enter the rotary kilns with different manganate contents. Consequently, it is not surprising to find that the time required to attain equilibrium for mixes of the same proportion and at the same temperature is not always exactly the same. But these differences are relatively small when compared to the differences found when the composition of the mixture or the temperature of the experiment varies, and therefore definite conclusions about the most favorable conditions for carrying out the process may be drawn from our data.

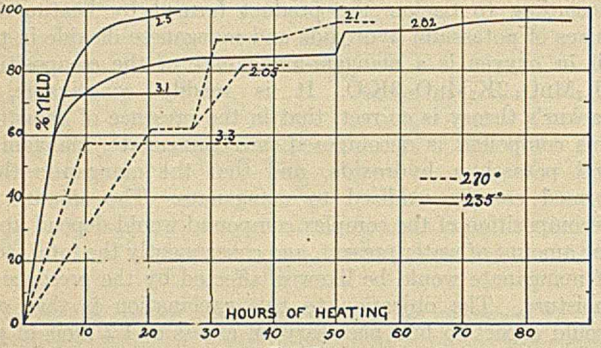

FIG. 3

TABLE II—TO SHOW THE EFFECT OF THE COMPOSITION OF THE MIX AND OF THE TEMPERATURE ON THE TIME REQUIRED TO ATTAIN MAXIMUM YIELD IN DRY AIR

Ratio	Temp. ° C.	Max. Yield Per cent	Time Required Hrs.	NOTES
3.1	235	72.5	7	No remoistening
2.7	235	99	20	No remoistening
2.5	235	99	25	No remoistening
2.3	235	98	55	Remoistened once
2.1	235	96	75	Remoistened twice
3.3	270	58	8	No remoistening
2.5	270	82	35	Remoistened once
2.1	270	95	50	Remoistened twice

These data show clearly that those conditions which favor retention of water by the mixes—namely, low temperature and excess of alkali—also favor rapid attainment of equilibrium. Inspection of Fig. 3 will show that this is true, not only of the final stage in the approach to equilibrium, but that the difference in velocity is noticeable in all stages except during the preheating when the temperature of all mixes is the same and all contain an excess of moisture. Of course, too low a temperature would probably again lower the reaction velocity, and too large an excess of alkali is undesirable because it tends to make the mixes cake badly in the furnaces and because it makes necessary the handling and recovery of an unnecessary amount of material. The temperature 235° C. seems to be very satisfactory. With regard to the best proportion of alkali to use, no very definite statement can be made. It has already been pointed out that, because of the impurities it contains, pyrolusite requires a larger proportion of potassium hydroxide than does precipitated manganese dioxide. Unquestionably, the proportion of alkali necessary for the best results will vary somewhat for different grades of pyrolusite. It is, therefore, the safest procedure to determine, for the pyrolusite to be used, the best proportion by small-scale experiments such as are described in this and the preceding paper of the series. In choosing the proportion of alkali to be used, the points brought out in this paper—especially the importance of using mixtures that will retain sufficient moisture—should be borne in mind. From our data it would seem that mixes containing from 2.5 to 2.75 mols of potassium hydroxide to one of manganese dioxide, or from 1.6 to 1.8 times as much potassium hydroxide as manganese dioxide, both figured to a 100 per cent basis, would be likely to give good results with pyrolusite, although some samples might require even a greater excess of alkali.

DISCUSSION OF RESULTS

The conclusions which have been drawn from the data presented in this paper differ widely in some important respects from what has hitherto been the practice in large-scale preparation of potassium manganate as a step in the manufacture of potassium permanganate. Thus, Ullmann[6] suggests a preheating to 200° to 250° C. and a subsequent continuation of the major part of the reaction at 500° C. According to the views expressed by him, the preheating has the function of preparing a mix which will not sinter and which will readily lose its moisture at the higher temperatures. The procedure as described by Ullmann, so far as we have been able to determine, seems to be quite generally followed in this country as well as abroad. It is quite clear from our data that this procedure is not the most favorable one, and that the theory with regard to the importance of removing the moisture is diametrically opposed to the facts. While we also recommend preheating, we do so only because it prepares mixes mechanically in such a way that they become easier to handle, and we have shown that the subsequent use of high temperatures is decidedly undesirable.[7]

It is fortunate that the changes in the usual procedure, which seem advisable as a result of our data, are of such a nature that they should materially decrease the cost of the manufacture of manganate. For not only do they involve the use of lower temperatures, but they should result also in decreasing the time during which the heat is applied, and increase the yield. Our results also suggest the possibility that the reason why it has hitherto been impossible to obtain

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[6] "Enzyklopaedie der technischen Chemie," 8 (1920), 18.

[7] Bergius and Sackur, German Patent 266,347 (1912), describe a process for the manufacture of manganates in which moist mixes and oxygen under pressure are used. Pressures up to 100 atmospheres and very large excess of alkali are described. We have found the use of oxygen to possess no marked advantage over air, and we have shown the use of high pressures to be quite unnecessary if the proportion of alkali to manganese dioxide is correct.

satisfactory yields of sodium manganate by the analogous process of heating sodium hydroxide with manganese dioxide in air, is that the mixes containing sodium hydroxide do not so readily retain moisture as do those containing potassium hydroxide—a suggestion which is in agreement with the properties of the two alkalies and which we expect to investigate further. Finally, attention should be called to the fact that our experiments have been limited to laboratory scale runs, and that the testing out on a large scale of the ideas presented is considered outside the scope of this research.

Conclusion

1—At the temperatures ordinarily employed, the reaction between potassium hydroxide, manganese dioxide, and oxygen is correctly represented by the equation:

$$4KOH + 2MnO_2 + O_2 \longrightarrow K_2MnO_4 + 2H_2O$$

For pyrolusite or other impure forms of manganese dioxide a larger amount of alkali may be needed to obtain a quantitative yield.

2—Excess of potassium hydroxide decomposes the manganate. This decomposition does not proceed further than to an extent represented by a yield of 60 per cent.

3—The higher the temperature, at least within the interval 235° to 415° C., the greater is the decomposition produced by a given excess of alkali.

4—The presence of moisture either prevents or decreases the decomposition produced by alkali. Moisture also increases the speed with which equilibrium is attained. It is therefore advisable to carry out the reaction at as low a temperature as possible in order to retain the moisture. Suggestions concerning the best conditions for the manufacture of potassium manganate are made and are of such character that they should decrease its cost.

The Electro-Preparation of Solid Alkali Amalgams in Quantity[1]

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In the present work (1) the method and apparatus of Arlt, Nernst, Kerp, and Böttger for the preparation of solid alkali amalgams were simplified and the efficiency greatly increased; (2) the method modified by G. McP. Smith and Bennett was also changed in order eventually to maintain it as the more rapid method; (3) Shepherd's method was modified by the use of different diaphrams, but trouble was experienced through endosmosis and diaphram disintegration; (4) our observations indicate that solid sodium and potassium amalgams are lighter than mercury, contrary to the usual statements in the literature.

Solid amalgams of the alkali metals are of value as reagents in a number of lines of work, so that a rapid and easy method of preparing them in quantity was desired.

Methods of Amalgam Preparation

THE ORDINARY chemical methods of preparation require care to avoid explosive accident. They are usually carried out under xylol,[2] paraffin, or petroleum oil.[3] These substances are difficult to remove completely from the amalgam. Then, too, alkali metal is not always conveniently available. Electro-preparation from salts of the alkali metals is therefore attractive, though it does not appear to give the strong amalgams, which may be produced by chemical methods—i. e., records rarely if ever exist with more than 2.30 per cent potassium, and our results did not exceed this concentration.

Six general methods have been developed for the electro-preparation of alkali amalgams.

(1) Davy[4] "electrified" a wet paste of "barytes and red oxide of mercury" and obtained a solid amalgam on the negative wire.

(2) Berzelius and Pontin[5] used a mercury cathode and a paste of barytes and lime.

(3) Robert Hare (1835)[6] "was the pioneer worker to use mercury as a cathode in industrial and analytical operations." He prepared calcium, barium, and strontium amalgams by electrolysis of the aqueous salt solutions, using mercury as cathode. Hare used $CaCl_2$ for CaO in what he called the "Seebeck, Berzelius, and Pontin" process. His amalgam contained not over 1 in 500 of calcium. Berzelius[7] used a mercury cathode under a "solution of potash and hydrate of potash" for the production of potassium amalgam. Wolcott Gibbs had acted as student assistant to Hare in 1841, and later Gibbs[8] introduced the mercury cathode for metal amalgam production for analysis. This method of Berzelius was used also by Richards and Mueller,[9] with strong cooling for the preparation of solid potassium amalgam of high purity. Later, G. McP. Smith and Bennett[10] efficiently developed this general method and extended it to more elements than had been done until then.

(4) Arlt[11] suggests a stream of mercury falling through a solution of a salt of the alkali-metal, and a protective layer of carbon disulfide or chloroform between the mercury layer and the electrolyte during the passage of the current. Errors in this method were later corrected by Nernst and the method adapted to lecture experiment.[12] It was adapted to laboratory use by Kerp,[13] and Kerp and Böttger.[14] Corrections of impressions left by Kerp as to the relative densities of alkali amalgams and mercury and the composition of amalgams have been given by Withrow,[15] and Bain and Withrow.[16]

(5) Shepherd[17] suspended the mercury cathode in a porous cup at the surface of a sodium salt solution being electrolyzed, to avoid the insulating action of the specifically lighter amalgam which accumulated at the surface of the mercury. He apparently obtained solid alkali amalgams more readily than any predecessor. This method was extended by G. McP. Smith and Withrow[18] to potassium

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[1] Received March 13, 1922.

[2] Reuter, *Z. Elektrochem.*, **8** (1902), 802.

[3] G. McP. Smith, *Am. Chem. J.*, **37** (1907), 512.

[4] *Phil. Trans.*, **98** (1808), 338.

[5] *Ibid.*, **98** (1808), 339.

[6] Edgar F. Smith, "Chemistry in America," **1914**, p. 312, J. B. Lippincott & Co., Philadelphia.

[7] Gmelin, **6** (1851), 97.

[8] *Chem. News*, **42** (1880), 291.

[9] *J. Am. Chem. Soc.*, **29** (1907), 645.

[10] *Ibid.*, **31** (1909), 799.

[11] *J. Soc. Chem. Ind.*, **15** (1896), 908; *Z. Elektrochem.*, **3** (1897), 300; English Patent 15,129 (1896).

[12] *Z. Electrochem.*, **3** (1897), 308.

[13] *Z. anorg. Chem.*, **17** (1898), 300.

[14] *Ibid.*, **25** (1900), 1.

[15] *J. Phys. Chem.*, **20** (1916), 528.

[16] *Ibid.*, **25** (1921), 535.

[17] *Ibid.*, **7** (1903), 29.

[18] *J. Am. Chem. Soc.*, **29** (1907), 321.

and alkali-earth amalgams, and further studied and extended to other salts by Frank and Withrow.[19] Serious contamination with potassium from the porous cup was found.

(6) Moissan[20] and also G. McP. Smith[21] produced amalgams by electrolysis of a complex alkali-mercury salt between platinum electrodes. This method is similar in principle to Davy's work,[4] and particularly to the work of Luckow[22] for making heavy metal amalgams electrolytically, modified by Vortmann.[23] Luckow mixed mercuric chloride with the salt of the heavy metal to be electrolyzed.

Most of the methods given have been slow, and the yields have been low, or small quantities only have been handled. Therefore experimental comparisons of some of the different methods have been made. Notwithstanding the desirable features peculiar to each method, each has disadvantages which may possibly account for inability to secure results sometimes desired in our work.

The Arlt-Nernst-Kerp and Böttger Method

When Kerp modified the Arlt-Nernst procedure, he used as cathode a stream of mercury continuously flowing from a jet-tube into a salt solution. These jets were replaced by others with increasingly larger bore as the amalgam became more viscous. This device was a decided improvement. A little experience with it, however, indicated certain disadvantages for our purpose. Among these may be mentioned:

1—The process is slow, a pressure of only 8 to 10 volts being readily used. In 4 to 5 hrs., only 200 g. of solid amalgam and 800 g. of liquid amalgam are produced.

2—It requires constant attention. The mercury is circulated as often as 150 times, according to Kerp's directions. A continuous stream must be maintained or the tubes clog with crystals.

3—Undue decomposition of the product goes on within the process. The large surface of amalgam below the stream and which does not constantly receive current is reacted upon by the electrolyte, with which it is in contact.

4—The jet tips must be changed as the amalgam becomes more viscous, for comparatively small bore tips were used at the early stages of electrolysis because of the high mobility of the mercury.

5—It is hard to get a stream of mercury of any length. It quickly breaks into drops, making the current irregular and reducing the average current flow.

6—It is difficult to carry out such an operation in an inert atmosphere.

Apparatus—In our work with Kerp's method, we found that the apparatus could be simplified and the method improved in a number of ways.

It was found after slight modification that quite as good results are obtained in the open air as in dry hydrogen. Instead of using larger jet-tubes as the liquid amalgam became more viscous, we finally used one fairly large jet-tube with a stopcock to control the flow, especially in the early stages of operation. The stopcock tube was joined to the jet-tube by means of a rubber stopper. Electrical connection with the mercury stream was obtained by sticking a sharpened platinum wire through the stopper, so that it projected into the mercury stream. This stopcock device permitted a regulation of the size and length of mercury stream not possible with a series of replaceable jets. Breaking into drops was thus placed under constant control. The introduction of this stopcock, however, brought its own difficulty in the form of arcing. During operation, electrolyte worked its way up through the jet to the stopcock, breaking the mercury stream into drops or slugs at this point, and arcing resulted. This was entirely avoided by making electrical contact with the mercury column below the stopcock near the tip (instead of at the top of the same) by another platinum wire hooked over the top of the jet-tube, reaching down through the tube almost to the jet or tip. The electrolysis chamber as first modified was an ordinary small percolator of about 250-cc. capacity with a goosenecked exit tube sealed in the bottom with plaster of Paris. Trouble arising from the migration of electrolyte down into this tube, causing a rise in the level of the mercury in the percolator, was eliminated by inserting a capillary tube and blowing out the liquid. The air was allowed to bubble out through the mercury.

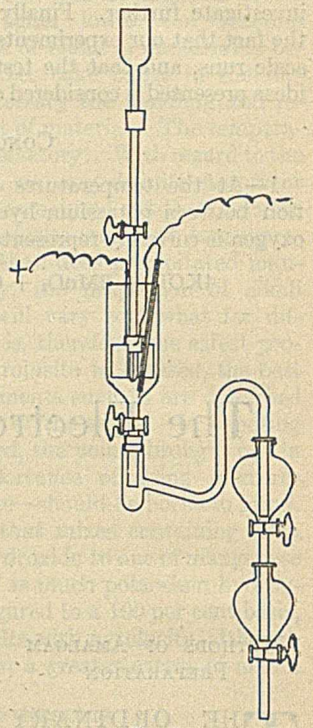

Fig. 1

Various modifications of this apparatus were tried, as later discussion will point out. Fig. 1 shows the modified apparatus in its final form. It is desirable that the delivery tubes be long enough to reach the bottoms of the receiving vessels, as any splashing tends to the formation of impurity, which appears to be a mixture of mercury in high subdivision, oxide, and stopcock grease.

In addition to the contact made with the stream of mercury just before it leaves the jet tip, electrical connection was made with the bottom layer of mercury by means of a platinum wire sealed through the bottom of a glass tube. The connecting of current at the bottom keeps the mercury at the bottom an active cathode, thereby reducing decomposition as well as accelerating production. By this means the process goes on, even if the stream of mercury must be stopped for any reason. With the double electrical contact arrangement, the use of a stopcock in the inlet tube introduces no arcing effect. A long stream of mercury is not so necessary and less attention is thereby required and a constant current can be maintained. A sixfold higher current can also be used, which reduces the time required, and heats the electrolyte to near the boiling temperature. Actual boiling of the electrolyte gives undue evaporation. This heating effect enables a stronger alkali amalgam to be more easily produced than if the mass were becoming pasty or stiff. Thus, when the liquid is subsequently chilled, a higher yield of solid amalgam is produced. The factor of "constant attention necessary" could not of course be dispensed with, although it becomes a less serious matter in view of the great shortening of the total time necessary for reasonable yield with the modified apparatus.

Procedure—In operating the modified apparatus, mercury is placed in the upper reservoir, and the saturated solution to be electrolyzed is placed in the electrolysis chamber.[24] The upper stopcock is then regulated to give a constant stream of mercury through the electrolyte in the separatory funnel. The lower cock is then adjusted to maintain a slight layer of mercury and amalgam at the bottom of the separatory funnel. Both the mercury stream and the layer at the bottom of the chamber are made cathodes during passage of the current, as described above under "Apparatus." The dilute amalgam, which is drawn off from the bottom of the electrolysis chamber and through the receiving vessels, is transferred to the upper reservoir and again passed through the system. This procedure is repeated, making such adjustments of the stopcocks as are necessary from time to

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[19] *J. Am. Chem. Soc.*, **42** (1920), 671.

[20] *Compt. rend.*, **144** (1907), 790.

[21] *Ber.*, **40** (1907), 2946.

[22] *Z. anal. Chem.*, **25** (1886), 113; *Chem. Ztg.*, **9** (1885), 338; *J. Am. Chem. Soc.*, **25** (1903), 884.

[23] *Ber.*, **24** (1891), 2749.

[24] Preliminary heating of the electrolyte saves a little time. Otherwise this is accomplished by the current. Actual boiling is undesirable.

time to maintain the desired rate of flow of the cathode material. When the cathode material has gained the desired alkali content, the product drawn off through the bottom stopcock is cooled and filtered, thereby separating out the solid amalgam from the liquid phase in contact therewith. The current conditions are indicated in the table, the usual current-measuring and control apparatus being used.

EXPERIMENTAL DATA—In the table only typical final results are given. The current readings are direct ones as measured by the usual instruments.

Run	Electrolyte	Mercury G.	Amperes	Volts	Time in Min.	Solid Amalgam Yield, G.
1[1]	Satd. KCl	1,000	Not stated	8–10	240–300	200
2	Satd. KCl	1,000	16	14.0–11.0	30	300
3	Satd. KCl	1,000	13.5–16.5	10.5–12.5	30	183
4	Satd. KCl	1,000	17.0–15.0	10.5	30	183
5	Satd. KCl	890	11.0–15.0	9.0–10.0	30	490
6	Satd. NaCl	1,000	11	6.0–8.0	105	132
7[2]	Satd. NaCl	250	3	6	105	180
8	Satd. NaCl	1,000	20	9.5–6.5	165	250
9	Satd. NaCl	500	10	5.5–5.0	80	None
10	Satd. NaCl	250	3	4.5–5.0	190	180
11	Satd. NaCl	250	3	5.2	140	170
12	Satd. NaCl	250	10	Not stated	Not stated	50(?)
13	Satd. NaCl	250	10	Not stated	30	Not weighed
14	Satd. NaCl	1,000	18.5–21	15–12.2	134	681
15[2]	Satd. KCl	250	3	6	50	150
16	Satd. KCl	1,000	20	12.5–9.5	50	1,015

[1] Reported by Kerp.
[2] Reported by Smith and Bennett.

Potassium Amalgam—In the table, Run 1 shows the results obtained by Kerp. Run 2 shows those obtained with the Kerp apparatus as modified by us to eliminate movable jets by the use of a stopcock, giving the required output in greatly lessened time and much less labor. This modified method actually yields 1.5 times as much solid amalgam as did the original Kerp method, and does it in less than one-eighth the time, or is about twelve times as efficient as the original.

When this apparatus was finally modified by substituting for the percolator and gooseneck a straight-stem separatory funnel, production was over seven times as efficient as that recorded by Kerp (Runs 3 and 4). Some runs were made in hydrogen as suggested by Kerp, but all those recorded here were made in air. Expt. 5 was made with the current taken out at both jet and bottom of the layer of mercury. The product showed no impurity either by sight or chemical inspection. About 2.5 times the amount of solid amalgam was produced in less than one-eighth the time. Therefore, the modified apparatus may be considered about twenty times as efficient as that recorded by Kerp. Since the amperage used is not given in Kerp's original work, it can only be assumed that it corresponded reasonably with ours, as we used the same voltage. At the conclusion of the runs the hot liquid amalgam was always chilled and filtered through a platinum cone under suction to get the solid amalgam.

Sodium Amalgam—Kerp's work was confined to potassium. Even our modified method was not as satisfactory with sodium amalgam as with potassium amalgam, as Run 6 shows, because of the more rapid decomposition of the sodium amalgam. Satisfactory amalgam was obtained, however. The same yield as in Run 6 could be obtained in less time. Frequently during the runs crystals of sodium amalgam could be seen protruding slightly from the surface of the mercury, confirming previous observations by one of the present authors.[15]

THE HARE-BERZELIUS-RICHARDS-MUELLER-SMITH-BENNETT METHOD

It requires much time and labor to set up even our modified form of Kerp's apparatus as herein described. Therefore the Hare-Berzelius method as developed by Smith and Bennett[10] was tried.

This method is extremely simple. 25 g. of mercury are put in a 250-cc. beaker, covered with 50 cc. of electrolyte and electrolyzed, using as an anode a platinum flag electrode, turned parallel to the surface of the mercury. Connection is made with the mercury by a platinum wire, sealed in a glass tube. The amalgam is agitated by shaking until it becomes too thick to shake. Then the crystals are pushed beneath the surface with a flattened glass rod. It seemed that this method would be improved upon by using mechanical agitation to push the crystals below the surface, and to try this an apparatus was devised.

The results which we obtained with this method confirm in general those of Smith and Bennett. We were, however, not always able to check their calculation of current efficiency. Run 7 is a result recorded by Smith and Bennett with their arrangement in which they state a current efficiency of 84 per cent. In Run 8 we changed the method so as to use high current and mechanical agitation. This run was started at room temperature, but, like the runs by Kerp's method, it came to a boil after a time. The speed of the motor was controlled to suit the circumstances. The current efficiency was found to be less than 40 per cent, possibly due to high temperature. Run 9 was therefore undertaken with a lower current—10 amperes—with the result of no solid amalgam after 1 hr. and 20 min. It is evident that as far as the making of amalgam is concerned little advantage results from this mechanical agitation, although it is more convenient. As soon as the amalgam became pasty, the use of a stirrer was of little or no advantage. The use of a solenoid suggests itself but was not tried.

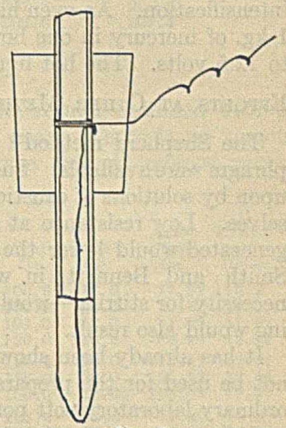
FIG. 2

Runs 10 and 11 were made to duplicate exactly Smith and Bennett's condition. No trouble was encountered in confirming their results, though it will be evident that sodium amalgam is much more difficult to prepare by this method than is potassium amalgam, if one refers to Smith and Bennett's potassium results (Run 15).

Run 12 was made under the same conditions except that a higher current was used. Again no solid amalgam was obtained. On chilling the liquid, however, a little separated out (50 g.). The electrolyte came to the boiling point in this run.

It was concluded, therefore, that the use of a higher current to reduce the time heats the liquid so that the sodium amalgam is decomposed about as fast as the crystals form. Runs 13 and 14 were made to find out the effect of cooling the electrolyte on the production of solid sodium amalgam.

In Run 13 the electrolyte was cooled by being circulated through a glass worm packed in a freezing mixture of ice and salt. A siphon with the outlet bent up kept the liquid level sufficiently constant. The results were entirely satisfactory. Solid amalgam was obtained in quantity, but its weight was not determined. The temperature was kept down to the point where the beaker was just perceptibly warm to the hand.

Run 14 shows the result when a higher current was used and the electrolyte kept cool by keeping the beaker in ice water during the run. These results were a great improvement over previous runs and were highly satisfactory. They were 2.5 times as efficient, considering time and yield, as the Smith and Bennett record.

With potassium amalgam, cooling as resorted to by Richards and Mueller was found unnecessary. Smith and Bennett's results (Run 15) show a good yield of solid amalgam obtained in a reasonably short time. However, in Run 16 a much higher yield was obtained by crowding the current density so that the electrolyte came to boiling. At the conclusion tap water was run into the beaker, and the whole mass of amalgam solidified without any liquid remaining. The result with reference to yield and time was 6.7 times as efficient as the results recorded by Smith and Bennett for their conditions, so that the method is quite capable of intensification. An even harder amalgam was obtained from 1 kg. of mercury in one hour, using 19 to 21 amperes at 15 to 12.5 volts. The hot liquid was poured off and chilled.

EFFORTS AT OTHER METHODS OF AMALGAM PREPARATION

The Shepherd method[25] would be ideal if a suitable diaphragm were available. Such a diaphragm should be unacted upon by solutions of caustic alkali or by the amalgams themselves. Low resistance at all times is essential or the heat generated would lower the current efficiency below that of Smith and Bennett, in which case convenience—lack of necessity for stirring—would be the only advantage. Bumping would also result.

It has already been shown[18] that Shepherd's method cannot be used for the preparation of pure amalgams with the ordinary laboratory soft porous cups, since they disintegrate and contaminate the amalgam. In an effort to adapt the method to quantity production of solid amalgams, we tried to find a diaphragm which would stand up under the conditions of temperature and alkalinity, but without success. Solid potassium amalgam was made using an ordinary soft porous cup as diaphragm and cathode container with saturated potassium chloride in one hour with 4 amperes at 13 to 8 volts. The bottom tended to drop out of the porous cups available. Solid sodium amalgams were also obtained, using the same kind of cups, from saturated sodium chloride solutions. The conditions were similar to those mentioned for potassium. These amalgams were contaminated, doubtless from the porous cups. In our efforts to find a more suitable diaphragm material, such things were tried as hardened filter paper alone, and supported by muslin, and alundum cups. Various devices for protecting the diaphragms from chemical action did not save them. About the time solid amalgam was forming the diaphragm would break through. Even an alundum cup was softened on the outside after use for an hour and a half with a saturated $NaCl$ solution and a current of 8 to 9 amperes at 14 to 15.5 volts. However, 103 g. of solid amalgam were produced from 213 g. of mercury. In this run, however, much trouble from endosmosis was experienced.

A number of possibilities for diaphragms suggest themselves, such as glass wool, fabric saturated with mineral oil and supported by metal or other gauze and the like, but they gave little satisfaction though they have not been tried out exhaustively.[26]

An attempt was made to produce electrolytic solid amalgam continuously by clamping a porous cup containing electrolyte in a beaker into which a stream of mercury was delivered at the bottom. It was hoped that the overflow at the top would yield amalgam. The endosmosis and bumping phenomena disrupted the work and it was not continued. It may easily be, nevertheless, that by using cooled circulating brine a strictly continuous and automatic process could be developed, should it be required. When the bottom of the porous cup was sealed by ceresin to the bottom (inside) of the beaker, it was not necessary to hold the cup down, but other sealing material is required to avoid melting by the rising cell temperature. However, it is not necessary to worry over diaphragm troubles, because it is so easy to efficiently make the amalgams in the other ways which we have developed, and nothing further was done in this direction.

RELATIVE DENSITIES OF ALKALI AMALGAM AND MERCURY

All the solid alkali-metal amalgams made were found to float in mercury and even potassium amalgam, which, disintegrated, gave fragments which could be felt at the surface of the mercury and no pieces could be felt at the bottom. Slow cooling of potassium amalgam gave larger crystals which were visible at the surface of the mercury-amalgam solution. Added to pure mercury they disappeared, but a skimming operation with a watch glass at the surface of the mercury recovered most of the amalgam crystals. In Runs 6, 10, 11, and 13, solid sodium amalgam was visible in chunks floating at the surface of the liquid amalgam. These indications confirm the contention previously made[15] that all alkali-metal amalgams are probably lighter than mercury in contradistinction to the sinking of the amalgam recorded by Kerp.[14]

CONCLUSIONS

1—Kerp's method for electro-preparation of amalgams can be greatly simplified and improved by allowing the mercury in the bottom of the cell, as well as that from the flowing jet, to receive current. In this way the current can be increased many-fold, with a corresponding reduction in manipulation and in the time of run.

2—If the current be led out at the tip of the jet-tube, a single jet-tube with a stopcock can be used instead of changeable jets used by Kerp.

3—To produce a pure product it is not necessary to run in an atmosphere of hydrogen.

4—Smith and Bennett's method can be improved by forcing the current, and also—for use in producing sodium amalgam, for which it was none too satisfactory—by cooling the electrolyte strongly. The use of a higher current reduces the time required for individual runs.

5—If a suitable diaphragm could be found, Shepherd's method would undoubtedly be the best.

6—Such a diaphragm would have to be unacted upon by solutions of caustic alkalies, by the amalgams themselves, offer low electrical resistance, and be a nonconductor. No such material was found.

7—Additional evidence shows Kerp's indication that solid amalgam sinks in a mercury amalgam solution to be erroneous.

ACKNOWLEDGMENT

The authors are indebted to Lawrence E. Stout, assistant in industrial chemistry in this laboratory, for help in the preparation of this paper.

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[25] *J. Phys. Chem.*, **7** (1903), 29.

[26] The preparation of alkali amalgams by the Shepherd method has been studied by Müller [*Z. physik. chem. Unterricht*, **28** (1915), 148; *C. A.*, **9** (1915), 2487] using a diaphragm of closely woven canvas. The abstract does not mention the kind of amalgam, but calculations for potassium amalgam show his method to be possibly more efficient, on the basis of time and solid amalgam producible, than the Smith and Bennett record, but also shows that it is less efficient than our results obtained by crowding the current in the Smith and Bennett method.

The Pittsburgh Plate Glass Company is completing at Milwaukee, Wis., the first unit of what will be one of the largest paint and varnish laboratories in the United States. All the scattered paint and varnish laboratories of the company will be consolidated here, as well as the research laboratory and the general offices of the paint and varnish division of the company.

Permanence of the Grignard Reagent[1]

By Henry Gilman and Charles H. Meyers

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THE GRIGNARD REAGENT is extensively used in organic chemistry, particularly for the preparation of the so-called fine or research chemicals. Its industrial applications are now largely in the fields of drug and perfume synthesis. The reagent is generally prepared by adding a solution of the appropriate RX compound in absolute ether to magnesium turnings. The RMgX compound so formed is conveniently used directly after preparation. In connection with a series of investigations which, it is hoped, will extend the general usefulness of the reagent, more especially where reasonably large quantities are used, a study has been made of its permanence.

In a preliminary note[2] mention was made of the permanence of ethereal solutions of ethylmagnesium iodide and phenylmagnesium bromide, both when exposed to daylight and when kept in the dark. It has since been found that this applies to a rather complete series of representative RMgX compounds, some in highly concentrated solutions. All the solutions investigated were protected from the atmosphere, because water, carbon dioxide, and oxygen react with RMgX compounds.

EXPERIMENTAL

The Grignard reagent was prepared in the customary manner—in a 500-cc., 3-neck flask provided with a stirrer having a mercury seal, a reflux condenser, and a separatory funnel. Sufficient ether was used to make about 300 cc. of solution. At the end of the reaction the solution was allowed to stand a few hours in order that any sediment in the reaction mixture might settle. About 200 cc. of the ether solution were then drawn up by suction into a gas collector having a volume of 250 cc. The gas collectors used were of standard type—all-glass cylinders provided on each end with a stopcock. After drawing up the sample, the stopcocks were closed and a piece of rubber tubing fitted with a glass plug was placed on the delivery end to prevent clogging in that part below the stopcock. The containers were held upright on a wooden rack.

A sample was drawn off for analysis into graduated test tubes made from burets, the first few cubic centimeters being discarded. The acid-titration method of analysis was selected. This involves essentially the addition of an excess of standard acid to an aliquot, and then titrating back with standard alkali. The first analysis of each solution was made on the day of preparation.

Inasmuch as the analysis extended over several months, it was necessary to determine if an appreciable quantity of ether diffused or leaked through the glass stopcocks. For this purpose two special all-glass collectors were made. These collectors were essentially counterparts of those used, with the exception that an upper portion was constricted to a diameter of 1 cm. This portion was graduated to 0.2 cc. and gave the total volume of the container from 200 cc. to 220 cc. A solution of ethylmagnesium iodide in ether, containing about 10 g. per 100 cc., was drawn into the two containers. The volumes of these solutions were read at intervals over a 4-mo. period. The following data indicate that the changes in volume, presumably due to a loss of ether, are of no serious moment.

Date	Temp. °C.	C_2H_5MgI I Cc.	C_2H_5MgI II Cc.
2-28-22	24	209.3	211.0
4-2 -22	24	208.5	209.6
5-24-22	23	207.8	208.0
6-26-22	24	208.0	207.4

DATA

The following table records the results obtained over a time interval exceeding one-half year. There is no reason for doubting that the permanence extends over a much longer period.

RMgX Compound	Date	Aliquot of RMgX	Acid[1] Cc.	Base[2] Cc.	Acid-Base Cc.	G. RMgX per 100 cc.
CH_3MgI	12-8 -21	20.65	100.65	17.0	77.97	16.2
	2-9 -22	21.35	106.2	20.0	79.52	16.0
	3-31-22	22.93	101.0	12.0	84.99	15.92
	6-19-22	23.2	100.0	10.9	85.46	15.83
C_2H_5MgBr[3]	1- 5-22	21.25	128.45	13.0	111.11	18.01
	2- 9-22	23.4	156.0	26.0	121.32	17.86
	3-31-22	22.7	150.0	23.65	118.45	17.97
N-C_4H_9MgBr	12-10-21	22.55	101.4	18.0	77.39	14.31
	2- 9-22	20.2	104.7	27.0	68.68	14.17
	3-31-22	23.1	100.0	15.8	78.92	14.24
	6-19-22	21.55	101.0	20.4	73.79	14.27
N-C_4H_9MgBr	12-11-21	11.95	151.9	15.0	131.89	46.0
	2- 9-22	15.6	204.9	25.0	171.55	45.84
	3-31-22	19.8	250.0	23.8	218.25	45.95
	6-19-22	18.13	250.0	37.8	199.6	45.89
iso-$C_5H_{11}MgBr$	12-13-21	18.90	100.35	34.0	54.99	13.18
	2- 9-22	20.2	101.9	32.0	59.21	13.28
	3-31-22	22.5	100.0	25.9	65.45	13.18
	6-19-22	22.88	101.0	25.25	67.32	13.33
cyclo-$C_6H_{11}MgBr$	1- 4-22	22.0	101.7	37.0	52.34	11.52
	2- 9-22	20.3	102.8	41.0	48.11	11.48
	3-31-22	22.45	100.0	35.1	53.18	11.47
	6-19-22	22.4	100.0	34.8	53.58	11.58
C_6H_5MgBr	1-10-22	19.8	104.8	31.0	63.45	15.02
	2- 9-22	17.9	104.3	35.0	57.6	15.07
	3-31-22	23.3	100.0	18.7	75.05	15.09
	6-19-22	22.88	100.0	19.45	74.05	15.16
C_6H_5MgBr	1-10-22	13.8	151.2	31.0	109.85	37.29
	2- 9-22	14.7	154.0	28.0	116.65	37.18
	3-31-22	22.12	200.0	17.85	176.19	37.32
	6-19-22	18.48	200.0	38.6	148.5	37.65
$C_6H_5CH_2MgCl$	1-11-22	20.45	53.4	24.0	21.38	4.08
	2- 9-22	18.2	51.7	25.0	18.35	3.93
	3-31-22	23.15	50.0	19.9	24.65	4.15
	6-19-22	24.17	50.0	18.85	24.85	4.01
p-$CH_3C_6H_4MgBr$	12-11-21	19.45	121.25	50.0	54.55	14.16
	2- 9-22	20.15	102.3	35.0	55.61	13.93
	3-31-22	22.7	100.0	27.55	63.25	14.06
	6-19-22	21.8	100.0	29.2	61.05	14.13
α-$C_{10}H_7MgBr$[4]	12-12-21	19.58	59.7	34.0	14.34	4.38
	2- 9-22	19.5	50.65	30.0	10.63	3.26
	3-31-22	23.9	50.0	27.85	12.85	3.21

[1] 0.2584 *N* H_2SO_4, determined by precipitating as $BaSO_4$.

[2] 1 cc. NaOH = 1.334 cc. H_2SO_4.

[3] Container was broken before taking fourth aliquot.

[4] Solid α-$C_{10}H_7MgBr$ separated early from solution. This accounts for the first abnormal drop in concentration of solution, and the clogging which prevented the taking of a fourth aliquot.

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[1] Received July 21, 1922.

[2] This Journal, 14 (1922), 243.

Fatal Accident at Columbia

On November 17, 1922, an accident occurred in the Chemical Engineering Laboratory at Columbia University, killing instantly William E. Spandow and injuring Reginald G. Sloane. Mr. Sloane is apparently now out of danger of any loss of eyesight and probably will have but a slight scar. A number of other students in other parts of the room were uninjured.

Mr. Spandow was of the highest type, both personally and as a student. He was in his third year of graduate work in the chemical engineering curriculum.

The accident occurred during an experiment where diphenylamine was to be made by heating aniline and aniline hydrochloride in an autoclave. The cover of the autoclave gave way with the disastrous results mentioned above.

Electrometric Acidimetry and Alkalimetry without the Use of Hydrogen[1]

By P. A. van der Meulen and Frank Wilcoxon

Rutgers College and the State University of New Jersey, New Brunswick, N. J.

THE VALUE of electrical methods for determining the conditions of solutions and for following the course of reactions is already well established, and the fields of their usefulness are constantly being extended by workers in various branches of science. Böttger[2] and Hildebrand[3] have applied measurements of electromotive force to the determination of end-points in the titration of acids and bases, while Crotogino[4] in a similar manner has titrated oxidizing and reducing agents.

For the titration of acids and bases, some form of the hydrogen electrode, usually of the bubbling type, is used as one electrode of a cell, the other being the mercury of a calomel half-element of known e. m. f. The electrolyte is the solution to be titrated.

Recent articles by Keeler[5] and by Klopsteg[6] have dealt with practical applications of the hydrogen electrode to control of plant processes and to titrations.

The use of the hydrogen electrode involves the necessity of a plentiful supply of hydrogen of a high degree of purity, and in certain solutions the electrode may become "poisoned," as has been frequently mentioned in the literature.

The electrodes require also to be replatinized from time to time, or to be discarded.

Haber and Klemensiewicz[7] have mentioned a method of titration for acids and alkalies in which a glass tube was used as electrode instead of the hydrogen electrode. Satisfactory results were obtained, but only with glass that had been specially treated.

Experiments were undertaken to determine the possibility of using a polished platinum wire, without using hydrogen, in the titration of acids and bases. It was found that such a wire immersed in a solution of acid in distilled water, with a calomel half-cell as the other electrode, gave a fairly stable potential whose value changed as the acid was neutralized, the rate of change being a maximum when an equivalent quantity of alkali had been added.

For measuring potential differences, a potentiometer with mirror galvanometer and scale was used. The titrations were conducted in a beaker, the solution being stirred with an electrically driven stirrer. A small, polished platinum wire was suspended in the beaker so that about 3 cm. were immersed. A calomel half-cell of the saturated type was connected through a salt-bridge to the liquid in the beaker.

In the usual titrations with the hydrogen electrode, the mercury of the calomel half-cell is the positive electrode of the cell. In these titrations, however, the mercury was found to be negative while the platinum wire was positive except when the solution was quite far on the alkaline side of the neutral point. A reversing switch was, therefore, included in the circuit to avoid changing the connections with the potentiometer when titrating acid with alkali.

The method of procedure was as follows: A known amount of standard acid having been introduced into the beaker, distilled water was added to make the volume about 200 cc., the wire and calomel half-cell were introduced and the stirrer started. The titrations were carried out at room temperature (about 20° C.). The voltage was determined after each addition of alkali, and a curve was plotted showing the voltage corresponding to total alkali added.

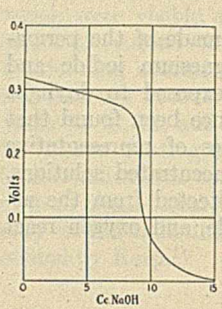

Fig. 1

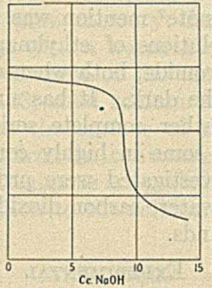

Fig. 2

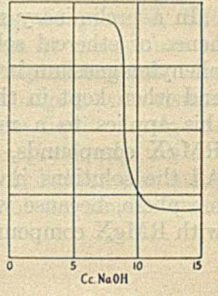

Fig. 3

The maximum change of voltage per 0.1 cc. of standard alkali added in these titrations is nearly 34 millivolts, which should make the location of the end-point a matter of no difficulty. (Figs. 1 and 2, and Tables I and II.)[8]

Table I

Cc. NaOH	Volts	Difference per 0.1 Cc.
0	0.319	0.0006
5	0.291	0.0007
8	0.268	0.0025
8.9	0.245	0.0335
9.1	0.178	0.0290
9.3	0.120	0.0073
10	0.069	0.0014
15	0.002	

Table II

Cc. NaOH	Volts	Difference per 0.1 Cc.
0	0.288	0.0003
5	0.274	0.0006
8	0.255	0.0033
8.9	0.225	0.0337
9.1	0.157	0.0055
10	0.107	0.0012
14	0.060	

It is possible to eliminate the calomel half-cell, and to substitute for it a second beaker containing a solution of alkali in which a second platinum wire is dipped. A titration curve of similar form to the curves in Figs. 1 and 2 will be obtained, but the actual voltages will, of course, be different. The results of such a titration are given in Table III and plotted in Fig. 3.

When it is desired merely to locate the end-point of a titration without following its entire course, the potentiometer is not necessary. A concentration cell is made up consisting of two beakers, one containing the solution to be titrated, and the other a solution whose H-ion concentration corresponds to the desired end-point. These beakers are connected through a salt-bridge, and a platinum wire dipped in each

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[1] Received July 19, 1922.

[2] *Z. phys. Chem.*, **24** (1897), 253.

[3] *J. Am. Chem. Soc.*, **35** (1913), 847.

[4] *Z. anorg. Chem.*, **24** (1900), 225.

[5] This Journal, **14** (1922), 395.

[6] *Ibid.*, **14** (1922), 399.

[7] *Z. physik. Chem.*, **67** (1909), 385.

[8] In these titrations 10 cc. 0.1 *N* HCl were titrated with CO_2-free NaOH. 10 cc. HCl = 9.10 cc. NaOH with phenolphthalein.

TABLE III

(10 cc. HCl titrated with NaOH, using 2 platinum wires)

Cc. NaOH	Volts	Cc. NaOH	Volts
1	0.375	9	0.200
2	0.374	9.2	0.158
3	0.374	9.4	0.138
4	0.378	9.6	0.122
5	0.380	10	0.107
6	0.377	11	0.081
7	0.374	12	0.078
8	0.368	13	0.078
8.8	0.336	14	0.078
		15	0.078

beaker. The wires are connected through a tapping key to the galvanometer. When the deflection of the galvanometer changes direction, the end-point of the titration has been reached. The results of such a titration, using two polished platinum wires, are shown in Table IV. The end-point with phenolphthalein was at 8.15 cc.

TABLE IV

(10 cc. 0.1 *N* HCl titrated with NaOH)

Cc. NaOH	Galvanometer Deflection
0	Right
3.8	Right
7.5	Right
8.1	Right
8.15	Right
8.20	Left

Since the voltages observed with these combinations must be due to selective adsorption of positively or negatively charged ions by the electrodes, it was thought that a cell might be arranged consisting of a single beaker with two electrodes of different materials, and that such an arrangement would give an e. m. f. varying with the H-ion concentration of the solution. This was found to be the case. A beaker containing dilute hydrochloric acid in which were immersed a platinum plate and a graphite rod, gave an e. m. f. that varied as the acid in the beaker was titrated with alkali. A sharp break in the titration curve was always obtained at the end-point, but the curve was somewhat irregular and not reproducible throughout the entire course in duplicate titrations.

In all these titrations the readings obtained depended somewhat on the rate of stirring and the length of time between the addition of alkali and reading the voltage. The location of the end-points, however, was a matter of no difficulty.

Effect of Salts upon the Acid Hydrolysis of Wood[1]

By E. C. Sherrard and W. H. Gauger[2]

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This investigation was carried on in the hope of finding some salts that could be used as catalysts to increase the yield of alcohol formed by the acid hydrolysis of wood.

No close predictions can be made as to the possible effects of an untried inorganic salt, although in general the metals of any one group in the periodic table behave similarly. Magnesium, zinc, and mercury are good examples of this, but, on the other hand, nickel is at some variance with cobalt and iron. Further experimentation is necessary before any conclusions can be drawn in this direction. The experiments with the hydroxy sulfonic acids indicate excellent possibilities in the field of hydrolytic catalysts.

THE YIELD of alcohol prepared by the fermentation of reducing sugars obtained in the acid hydrolysis of wood has been investigated in some detail by Kressmann.[3] He found that with dilute acids he could obtain from white spruce sawdust a maximum of 22.11 per cent total reducing sugars (based on the weight of original dry wood). Of these he was able to ferment 70.38 per cent with a production of 22.55 gal. of alcohol per dry ton. Since the white spruce experimented upon contained 58 per cent cellulose, of which 90 per cent may be converted into reducing sugars,[4] the theoretical yield is 57.94 per cent reducing sugars. Assuming these sugars to be 100 per cent fermentable, a yield of 94.21 gal. of 95 per cent alcohol per dry ton should be obtainable.

The object of the present investigation was to study the effect of added salts with the hope of finding a catalyst that would force the reaction somewhat further or cause a higher per cent of fermentable sugars to be formed. The yield obtained by Kressmann is sufficient to make the process commercially feasible for the large mills in the country. In order to make it more adaptable to the majority of the mills with only an average amount of raw material available, an increased yield in alcohol is desirable. About 70 cooks have been carried out, in which a large number of inorganic salts and two of the naphthalene hydroxysulfonic acids—2-hydroxynaphthalene-6-sulfonic acid and 1,8-dihydroxynaphthalene-3,6-disulfonic acid—were tried.

The same procedure was adopted in all experiments unless otherwise specified, the reaction being carried out in a small bronze autoclave. In each case a mixture of 100 g. white spruce sawdust (dry weight), 200 g. of H_2O, and 2.5 g. H_2SO_4 (100 per cent) to which was added the desired amount of catalyst, was cooked at 115 lbs. steam pressure (175° C.) for a period of 15 min. The method of analysis adopted was the same as that of Kressmann.[4] Owing to inadequate mixing and nonuniform heating during the cook, the results obtained are about 10 per cent lower than those obtainable in the large rotary digester in operation at the laboratory. The data on these experiments are given in Table I.

After the first 29 cooks had been made without any decided increase in the alcohol yield, it was decided to try the effect of adding glucose to the mixture before cooking. The opinion has often been advanced that in this reaction an equilibrium is soon reached at which point the glucose formed by the reaction is decomposed as rapidly as it is formed from the cellulose. Cooks 30 and 31 were accordingly made. It will be noted that in Cook 30, 19 per cent total sugar was obtained over the 10 per cent added, and in Cook 31, 18.65 per cent was obtained over the 20 per cent added. These results indicate that the presence of glucose had little effect on the end-point of the reaction, and also that little decomposition of the added sugar occurred during the period of the cook.

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[1] Presented before the Section of Cellulose Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Chemist and Assistant Chemist in Forest Products.

[3] *U. S. Dept. Agr., Bull.* **983**.

[4] Monier-Williams, *J. Chem. Soc.* (*London*), **119** (1921), 803; **117** (1920), 1489.

TABLE I

Cook No.	Catalyst	Reducing Sugar Per cent	Fermentable Sugars Per cent	Alcohol G. per Kg. Dry Wood	Alcohol Gal. per Ton Dry Wood
Blank	None	21.14	66.0	71.3	21.35
11	0.5 per cent $Fe_2(SO_4)_3$	22.37	65.6	74.96	22.44
12	1.25 per cent $Fe_2(SO_4)_3$	21.97	69.3	70.70	21.15
13	0.5 per cent $CuSO_4$	21.30	67.5	71.90	21.53
14	1.25 per cent $CuSO_4$	21.17	56.7	71.10	21.29
15	0.5 per cent $NaHSO_3$	18.03	61.0	54.90	16.44
16	1.25 per cent $NaHSO_3$	17.81	59.8	53.70	16.09
17	1 per cent $C_3H_6O_3$ para	20.90	63.5	70.60	21.15
18	5 per cent $C_3H_6O_3$ para	21.10	66.4	67.90	20.35
19	0.5 per cent $ZnSO_4$	21.50	63.1	70.70	21.19
20	1.25 per cent $ZnSO_4$	20.06	65.2	76,0	22.78
21	0.5 per cent $K_2Al_2(SO_4)_4$	20.50	68.7	60.87	20.60
22	1.25 per cent $K_2Al_2(SO_4)_4$	18.99	48.4	54.90	16.45
23	0.5 per cent $NiSO_4$	19.87	Sample lost		
24	1.25 per cent Ni SO_4	20.74	62.6	58.00	17.40
25	2.5 per cent $Fe_2(SO_4)_3$	21.47	66.7	70.1	21.00
26	1 per cent H_2O_2	17.68	52.65	46.2	13.82
27	2 per cent H_2O_2	19.42	64.6	54.2	16.2
28	4 per cent H_2O_2	20.02	61.5	61.8	18.53
29	2.5 per cent $Fe_2(SCN)_6$	20.50	62.40	60.1	18.03
30	10 per cent $C_6H_{12}O_6$ (glucose)	29.10	75.10	109.8	32.86
31	20 per cent $C_6H_{12}O_6$ (glucose)	38.65	78.70	151.0	45.20
32	1.5 +1.5 per cent H_2SO_4	23.18	67.80	78.5	23.50
33	1.5 +2.5 per cent H_2SO_4	22.60	88.20	76.5	22.90
34	60 min. at 20 lbs. per sq. in.	7.86	No fermentation made		
35	60 min. at 40 lbs. per sq. in.	18.18	62.80	56.7	17.00
36	1 per cent FeI_2	15.18	59.40	44.5	13.30
37	1.5 +1.5 per cent H_2SO_4	22.89	71.40	83.5	25.00
38	None (residue)	5.63	No fermentation made		
39	0.5 per cent CrO_3	14.82	54.25	40.0	11.95
40	1 per cent $UO_2(NO_3)_2$	15.94	68.60	55.0	16.45
41	0.5 per cent $MnSO_4$	21.02	67.10	70.5	21.10
42	1.25 per cent $MnSO_4$	22.80	63.50	69.3	20.70
43	0.5 per cent $MgSO_4$	21.68	66.20	73.8	22.05
44	1.25 per cent $MgSO_4$	22.14	64.40	69.5	20.80
45	0.5 per cent $CoSO_4$	22.37	66.20	74.2	22.25
46	1.25 per cent $CoSO_4$	22.11	70.10	77.1	23.10
47	1 per cent NaOH	16.59	60.30	49.5	14.80
48	0.5 per cent $MnSO_4$	22.30	65.00	71.8	21.50
49	0.5 per cent $HgCl_2$	20.88	65.70	68.8	20.60
50	1.25 per cent $HgCl_2$	22.74	69.70	79.6	23.85
51	Cl_2	20.00	Not fermentable		
52	0.5 per cent Na_2S	18.85	60.6	56.7	17.00
53	1.25 per cent Na_2S	7.46	24.9	8.98	2.69
54	0.5 per cent $C_{10}H_6 <\substack{(OH)\\(SO_3H)}$	23.17	67.8	78.8	23.60
55	1.25 per cent $C_{10}H_6 <\substack{(OH)\\(SO_3H)}$	23.03	67.7	78.75	23.60
56	0.5 per cent $C_{10}H_4 <\substack{(OH)_2\\(SO_3H)_2}$	21.34	65.6	68.7	20.6
57	1.25 per cent $C_{10}H_4 <\substack{(OH)_2\\(SO_3H)_2}$	21.99	66.9	73.5	22.0
58	2 per cent $C_{10}H_4 <\substack{(OH)_2\\(SO_3H)_2}$	22.82	65.75	71.50	21.35
59	1.8 per cent HCl	21.92	73.0	80.75	24.20
60	2.5 per cent HCl	22.08	74.0	86.40	25.85
61	1.8 per cent H_3PO_4	12.74	40.3	26.10	7.81
62	2.5 per cent H_3PO_4	12.51	40.4	25.00	7.48
63	C_6H_6 – 74.7 lbs. – 30 min.	17.81	46.5	45.30	13.58
64	Ether 111.8 lbs.– 30 min.	16.75	58.4	45.80	13.72
65	C_6H_6 – 93 lbs. – 20 min.	18.38	59.9	50.00	14.97
66	C_6H_6 – 85 lbs. – 20 min.	12.79	49.2	28.14	8.42
67	C_6H_6 – 100 lbs. – 60 min.	17.84	59.4	47.10	14.10

Since little or no decomposition of the glucose occurs under the conditions above, it was thought that a second digestion with an additional quantity of acid might give increased yields. The sawdust was accordingly submitted to a double cooking in the hope of getting an accumulative effect, the sugar produced by the first digestion to be augmented by that produced by the second. Cook 32 was performed on a mixture of 100 parts dry sawdust, 1.5 parts H_2SO_4, and 200 parts H_2O, cooked for 15 min. at 115 lbs. steam pressure, when the mixture was removed from the autoclave, treated with an additional 1.5 parts H_2SO_4, and recooked for 15 min. While a slight increase was noted over the blank, the results were somewhat disappointing, and indicate that the cellulose remaining from the first hydrolysis, as determined by the Cross and Bevan method, is much more stable than that in the original wood. Cooks 33 and 37 were exact duplicates of 32 except that in Cook 33, 2.5 parts H_2SO_4 were added for the second cooking, and in Cook 37 the period of the second cooking was extended to 30 min. This last procedure gave the best results obtained, with H_2SO_4 as the hydrolyzing agent, the alcohol yield being 17 per cent higher than that obtained in the blank runs using simply the standard conditions outlined above.

Cooks made at low pressures and temperatures (34 and 35) for longer periods of time failed to give increased yields. By the use of volatile liquids—ether and benzene—Cooks 63 to 67 were carried out at pressures higher than those obtainable with pure steam at a corresponding temperature. A comparison of Cooks 63 and 34 would indicate that the pressure has a slightly greater effect than the temperature upon the reaction. (The temperature of Cook 63 was about 121° C.)

By using HCl instead of H_2SO_4, under similar conditions of cooking and in the same proportions (per cent by weight), somewhat better sugar and alcohol yields were obtained. Unfortunately, the phosphoric acid cooks were made at a time when the steam pressure was only 100 lbs., so they are hardly comparable. The general indication from the blank cooks made with the three acids, however, is that the acids highest in the dissociation series cause the greatest degree of hydrolysis, indicating a hydrogen-ion catalysis.

In Cooks 47 and 51 the sawdust was given a preliminary treatment in an effort to partially break down the incrusting lignin and render the cellulose more susceptible to the action of the hydrolyzing agents. This preliminary treatment consisted, in the case of Cook 47, of digesting the wood with 1 per cent NaOH for 15 min. at 175° C. or 115 lbs. steam pressure. The preliminary treatment of Cook 51 consisted of subjecting the moist sawdust to the action of a stream of chlorine gas for 30 min., after which it was washed with a solution of sodium sulfite and then water. In the first case the sugar yields were lower than when no preliminary treatment was used, while in the second the presence of the chlorine ion prevented a fermentation of any of the sugars formed.

Table II gives the highest and lowest results obtained with the various salts used as catalysts in connection with H_2SO_4.

TABLE II

Highest Yields: Catalyst	Alcohol per Ton of Dry Wood Gal.	Per cent Increase over Blank	Lowest Yields: Catalyst	Alcohol per Ton of Dry Wood Gal.
None	21.35	0.0	None	21.35
0.5 per cent $MgSO_4$	22.05	3.3	1.25 per cent K_2Al_2 $(SO_4)_4$	
0.5 per cent $Co(NO_3)_2$	22.25	4.2	1 per cent $UO_2(NO_3)$	16.45
0.5 per cent $Fe_2(SO_4)_3$	22.44	5.1	2.0 per cent H_2O_2	16.20
1.25 per cent $ZnSO_4$	22.78	6.7	1.0 per cent NaOH	14.80
1.25 per cent $Co(NO_3)_2$	23.10	8.2	1.0 per cent H_2O_2	13.82
0.5 per cent $C_{10}H_6 <\substack{(OK)\\(SO_3K)}$	23.60	10.5	1.0 per cent FeI_2	13.30
1.25 per cent $C_{10}H_6 <\substack{(OK)\\(SO_3K)}$	23.60	10.5	0.5 per cent CrO_3	11.95
1.25 per cent $HgCl_2$	23.85	11.7	1.25 per cent Na_2S	2.69

The fermentations were carried on by means of a pure culture strain of *Saccharomyces cerevisiae*, isolated from a Hungarian distillery bottom yeast, according to the method of Sherrard and Blanco. The leach liquor was nearly neutralized with $CaCO_3$, concentrated to a 10 per cent solution *in vacuo*, filtered, diluted with an equal volume of a 4 per cent solution of autolyzed yeast, which served as a nutrient, and the acidity adjusted to less than 5 degrees by means of $Ca(OH)_2$. The liquor was then sterilized for three successive days, placed in the constant temperature fermentation room, and allowed to come to the temperature of the room, 88° F. The yeast culture was then added, and the fermentation allowed to proceed for 96 hrs.

Methods for Chemical Analysis of Babbitt Metal Approved by A. E. S. C.

The American Engineering Standards Committee has approved as "Tentative American Standard" the methods for the chemical analysis of alloys of lead, tin, antimony, and copper—otherwise known as Babbitt metal—submitted by the American Society for Testing Materials.

Two methods of analysis are included in the document approved by the A. E. S. C. The first is a quick and fairly accurate method intended for practical or shop use; the second is a slower, more expensive, and more exact method intended for reference purposes or for the settlement of disputed questions.

The approval of the A. E. S. C. was voted on the recommendation of a special committee representative of all the interests concerned with the subjects, of which George C. Stone was chairman.

Furfural Resins[1]

By J. P. Trickey, C. S. Miner, and H. J. Brownlee

The Miner Laboratories, Chicago, Ill.

EARLY in the course of the research work done on furfural, it was discovered that resinous masses were produced when it was treated with various compounds, especially amines and phenols. Stenhouse in 1840[1,*] and Fownes in 1845[2] observed the formation of resinous bodies when furfural was boiled with acids and alkalies. Stenhouse in 1870[3] and Persoz in 1860[4] obtained gummy and tarry substances while working with furfural and aromatic amines and phenols. Claisen in 1887[5] obtained a brown resin of indefinite composition when furfural was treated with β-naphthol in glacial acetic acid solution, using hydrochloric acid as a condensing agent.

In none of these cases was any study reported, either of the reaction or the product obtained, aside from very superficial examinations of physical properties.

Meunier in 1916[6] prepared soluble resins from furfural and aniline in the presence of alkalies. The product was a black resin, soluble in benzene and alcohol. The solution produced a black enamel. He also produced resins from furfural and acetone.

Quite recently (1921) Mains and Phillips[7] extended the work of Meunier, preparing soluble resins from furfural and various aromatic amines, acetone, methylethyl ketone, sodium hydroxide, and furfuramide. All these resins were soluble in benzene, acetone, alcohol, and furfural, forming varnish stains varying in shade from light brown to black.

In 1921 Novotny[8] patented a process for the production of hot molding phenol-furfural resins, using both furfural and furfuramide in their preparation.

Beckmann and Dehn in 1918[9] investigated the phenol-furfural resins, studying the reaction of 24 phenols using acids, acid salts, and alkalies as condensing agents. They report that they obtained their best result from furfural with phenol, raw cresol, guaiacol, carvacrol, and β-naphthol, using equal parts of furfural and the phenol, and 5 per cent of hydrochloric acid, figured on total weight of mix, as the condensing agent.

In this paper a very general survey of the various furfural resins has been made, with special reference to the phenol-furfural type.

PHENOL AND CRESOL

The first work done was on the acid resins reported in the work of Beckmann and Dehn.

Equal volumes of phenol and furfural were mixed and 5 per cent by volume of concentrated HCl, figured on total volume of mix, was added. The mixture immediately turned dark blue and heat was evolved. At the end of 10 min. the mixture congealed and in about 30 min. it was firm enough to remove. It was still soft and about the consistency of cheese. After standing for several hours the resin hardened considerably. On heating for an hour at 100° C. it became very hard and tough.

Similar results were obtained using U. S. P. cresol.

Similar results were also obtained with sulfuric and oxalic acids, although in the case of oxalic acid the reaction was less vigorous and external heat was necessary to cause the reaction to proceed. The test tube was fitted with a reflux tube to keep the concentration of the reaction mixture constant.

The effect of varying the concentration of the acid catalyst was studied, with various mixtures of phenol and furfural. The mixtures of phenol and furfural in per cents were as follows:

Phenol	80	60	50	40	20
Furfural	20	40	50	60	80

The concentrations of HCl studied were 0.2 per cent, 0.4 per cent, and 0.6 per cent, figured as dry HCl on total amount of mix.

The results of these experiments may be summarized as follows:

1—In order to obtain an infusible, insoluble resin, the molecular proportions preferably should be slightly in excess of 1 mol furfural to 1 mol phenol.

2—The resin obtained by an excess of phenol was soluble in acetone and alcohol, and remained a jelly-like mass when cooled, even after it had been heated for a number of days.

3—The resins obtained by use of varying amounts of acid as condensing agent were similar but the time necessary to complete the reaction varied from 2 wks. in the case of 0.2 per cent, to 10 hrs. in the case of 0.6 per cent acid, indicating that the acid catalyst is most effective within a very narrow range of concentration.

ALKALI RESINS

Beckmann and Dehn, in their work on phenol-furfural resins, obtained resins, using sodium hydroxide, sodium carbonate, or ammonia, and heating in a sealed tube to 180° C. The resin obtained was soluble and fusible, the products being brown in color and considered by them inferior to the acid resins. They report that they were unable to obtain infusible resins from phenol and furfural with alkaline condensing agents.

In our experiments we used sodium hydroxide and sodium carbonate as the condensing agents, and found that we could obtain very easily an excellent resin. The resins produced by use of sodium carbonate having properties similar to those obtained by the use of the hydroxide, we used the carbonate in most of our work because of the ease of handling.

Experiments were made using proportions of phenol and furfural as in the acid resins, and it was found that 1 per cent of the monohydrate of sodium carbonate, figured on total weight of mix, gave a reaction mixture that was easily controlled.

The results obtained are summarized as follows:

1—In order to obtain an insoluble resin, the proportions are preferably about 1.25 mols furfural to 1 mol phenol.

2—The resins formed by excess of phenol were solid and brittle when hot, melted easily, readily soluble in acetone, alcohol, and furfural. When heated with enough furfural to bring the molecular proportion up to 1.25 furfural to 1 phenol, they went over to the infusible state. With these resins we were able to produce on a commercial scale excellent cold molded products.

On the basis of these experiments, we find it quite impossible to understand the report of Beckmann and Dehn that they were unable to obtain infusible resins when they used alkaline condensing agents.

To study the effect of ammonia as a condensing agent, furfuramide was used in place of furfural. The resins ob-

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[1] Presented before the Division of Industrial and Engineering Chemistry, at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

* The numbers in the text refer to the bibliography at the end of this article.

tained, even with an excess of furfuramide, were fusible and soluble. After 2 mo. of intermittent heating, the resin was still fusible and soluble.

RESINS WITH ANILINE

A few experiments were made on the basis of the work reported by Mains and Phillips. The results obtained by them, using aniline and furfural, and HCl as the condensing agent, were repeated.

We also prepared resins from aniline, using sodium carbonate. The resins were readily soluble in alcohol and acetone, giving a solution staining wood a reddish brown, very much the color of mahogany.

The resin prepared by Mains and Phillips from furfuramide, by simply heating this compound at 100° C. for 1 hr., was prepared and studied. It was found that this resin was impure furfurin ($C_{15}H_{12}O_3N_2$).

Bertagnini in 1853[10] prepared furfurin by heating furfuramide at 110° to 120° C. for 1 hr., dissolving the resinous mass formed in alcohol, precipitating the furfurin as the double oxalate. This compound is soluble in boiling water and is decolorized by treatment with animal charcoal at the boiling temperature, filtered hot and allowed to crystallize from the filtrate. The furfurin is liberated by action of potassium hydroxide and obtained as a white crystalline compound which we have prepared in considerable quantities.

The furfuramide resin prepared as outlined above was subjected to this treatment, and a very good yield of furfurin was obtained.

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A New Test for Acrolein and Its Bearing on Rancidity in Fats[1]

By Wilmer C. Powick

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IN THE COURSE of a chemical study on the rancidity of fats, what is believed to be a new test for acrolein has been discovered. The test depends upon the formation of a colored condensation product between acrolein and phloroglucine in presence of hydrochloric acid and hydrogen peroxide. The test is best performed as follows:

> To 1 or 2 drops of dilute acrolein solution in a test tube 1 drop of an approximately 3 per cent solution of hydrogen peroxide is added. After about 1 min., 5 cc. of concentrated hydrochloric acid (C. P., sp. gr. 1.19) are added, and the test tube shaken. Finally, 5 cc. of a 1 per cent ethereal solution of phloroglucine are added, and the whole shaken. A deep red color is immediately imparted to the hydrochloric acid phase, which, on spectroscopic examination, shows a well-defined, fairly narrow absorption band in the yellow-green region. In the absence of hydrogen peroxide the red color is not obtained, while when an excess of acrolein is used the condensation product separates as a purple precipitate.

The essential feature in which this test differs from the Kreis test, so extensively employed as an index of rancidity in fats, is in the use of hydrogen peroxide and the spectroscopic examination.

It is to be particularly noted, however, that the color yielded by rancid fats in the Kreis test is spectroscopically identical with that obtained with acrolein in the manner described, and that this color and spectrum are apparently distinctive of the condensation product which in the test described above is formed between phloroglucine and acrolein in the presence of hydrogen peroxide and hydrochloric acid. The saturated aldehydes, whose presence in rancid fats is generally recognized, do not respond to this test, either in the presence or absence of hydrogen peroxide. The next higher homolog of acrolein, crotonic aldehyde, gives a red color with phloroglucine-hydrochloric acid which rapidly disappears on standing, while in the presence of hydrogen peroxide no red coloration is obtained. While a number of other substances, such as vanillin, eugenol, cinnamic aldehyde, aged turpentine, and certain nonrancid cottonseed oils, give a red color in the absence of hydrogen peroxide, the spectra of these colors show general absorption throughout the green-blue-violet part of the spectrum, but no localized band as in the case of rancid fats and of acrolein in the presence of hydrogen peroxide.

It would seem, therefore, that the same substance is responsible for the Kreis test in rancid fats as is formed by the action of hydrogen peroxide on acrolein, and that this substance is different from the reactive substance in certain nonrancid cottonseed oils. It is evident, therefore, that the Kreis test, when followed by a spectroscopic examination, may be used to distinguish rancidity in this product, although it was previously considered to be of doubtful value in this connection.

Whether this substance, which gives the Kreis reaction in rancid fats and is formed by the interaction of acrolein and hydrogen peroxide, is a peroxide of acrolein; whether or not it is derived from oleic acid, as now seems to be the case; and whether it is formed naturally in rancid fats or artificially at the time of making the test—possibly by interaction of oleic acid peroxide with pre-formed acrolein—are questions which are not yet fully answered. Studies on these points are nearing completion, however, and an early publication of the results is expected.

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[1] Received September 28, 1922.

As a result of laboratory tests made in the College of Industries of Carnegie Institute of Technology, Pittsburgh, Pa., under the direction of S. E. Dibble, head of the heating and ventilating department, it has finally been established that clay pipe for drainage and sewerage use is in every way the equal of the more expensive cast iron pipe which has been used heretofore. Not only have Professor Dibble's tests shown that (1) a proper bituminous compound can be used efficiently in jointing a pipe; (2) joints made in the manner developed will stand any pressure that the pipe itself is capable of standing, without any leak; (3) a pipe so jointed can be thrown out of alignment without causing a leakage at the joints; and (4) leaks due to poor workmanship can be repaired easily and quickly; but he has gone further and has published actual chemical analyses of two of the bituminous compounds which he has found to be satisfactory.

Industrial Mold Enzymes[1,2]

By Kokichi Oshima[3] and Margaret B. Church

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A new method for quantitative estimation of protease is described in this paper.

Many strains of the Aspergillus flavus-oryzae group, which were separated from tane-koji used in shoyu manufacture and related industries, showed individually the production of amylase and protease of very widely differing strengths.

Amylase and protease are produced at the same time without any special relation to growth or variety of the fungus employed.

Cultural experiments on various food substances show that the four strains used produce strongest amylase and protease with bran. The ratio of amylase and protease does not seem to change much with the culture medium. Even on soy-bean flour, which contains no starch, strong amylase is produced.

Practically all the intracellular enzymes pass out into the culture medium soon after spore formation. Extracellular enzymes continue to increase as long as the mycelium shows an increase. Their power decreases very gradually.

CERTAIN large industries are entirely or in part dependent upon the activities of mold growth. One of the industries primarily dependent on the growth and enzyme production of the yellow-green molds or fungi classed as the *Aspergillus flavus-oryzae* group, is the soy-sauce manufacture of Japan, China, and neighboring countries. A process dependent directly on mold enzymes which has developed within the United States is the application of certain patented enzymic products in solid, liquid, or concentrated form to the desizing and degumming of textiles. In the case of fabrics woven from cotton, jute, or similar fibers, it is often necessary to oversize the warp threads to facilitate weaving. By treatment with a bath of a suitable enzyme solution, the extra size or starch may be removed from the woven fabric. In the case of the silk industry, such enzymic products are applicable for degumming or separating the two distinct fibers that compose the silk thread spun by the silkworm. An industry in the United States indirectly dependent on the enzymic products available after active growth of this same group of molds on bran or similar materials is the jelly- and jam-making trade of the present time. The increased utilization of pectin from apple pomace in commercial and household jelly-making necessitates that such pectin be as high a grade product as possible. Clarification of the pectin is necessary or a turbid jelly will result. Certain starchy and protein substances need to be changed into other substances that do not cause cloudiness in the jelly. One agent, and possibly the only one, which alone will bring about this desired result, is the combination of the amylolytic and proteolytic enzymes developed by the growth of certain strains of the *A. flavus-oryzae* group of molds. The particular enzymes involved in this and related processes seem to be insufficiently known.

Various investigators have covered certain phases of the question. Previous experiments, however, have been mostly qualitative, in which the presence of an enzymic activity has been determined, but little attention has been given to the comparative activity of different molds. It seems equally important to investigate a series of related molds of industrial value and to obtain a quantitative estimation of their relative ability to produce the necessary enzymic action. Several different molds and many closely related strains are involved in the fermentation processes under discussion. A large number of these strains from the *A. flavus-oryzae* group were brought together for its study. They were secured from the Microbiological Laboratory, U. S. Department of Agriculture, from the laboratory of Dr. J. Takamine, from the Japanese Brewing Station in Japan, and directly from Japanese moyashi. (Moyashi is a mold starter made in large quantities for industrial operations.) A full discussion of this group of organisms under consideration is found in a recent publication of Thom and Church.[11,*]

TABLE I—STRAINS OF MOLDS USED IN ENZYMIC EXPERIMENTS

Culture Number	IDENTIFICATION OF MOLD
18	*Penicillium roqueforti* Thom
3509	*Aspergillus parasiticus* Speare
4235.x.1	*Aspergillus tamari* Kita
130Sc	*Aspergillus effusus* Tiraboschi
4078.Or-5	*Aspergillus Wentii* Wehmer
113	*Aspergillus oryzae* (Ahlb.) Cohn
3565	*Aspergillus tamari* Kita
129	Intermediate form of *A. flavus*
108	*Aspergillus flavus* Link
4328	*Aspergillus flavus* Link
4272.2	*Aspergillus flavus* Link
APa	Form intermediate between *A. flavus* and *oryzae*
APb	*A. effusus* type
AOl	As APa
AO2a	As APa
AO2b	Resembling strain F of Takahashi
AO3a	As APa
AO3b	*A. parasilicus* type
AO4a	As APa
AO4b	As APa
AO5a	As APa
A	As APa
AOold	*Aspergillus oryzae* (Ahlb.) Cohn
AOAb	Form intermediate between *A. flavus* and *oryzae*
AOAc	Form intermediate between *A. flavus* and *oryzae*
AON	Form intermediate between *A. flavus* and *oryzae*
AOK	Form intermediate between *A. flavus* and *oryzae*
AOP	Form intermediate between *A. flavus* and *oryzae*
	Aspergillus ochraceous
APc	Not identified
AOAa	Not identified
AOb	Form intermediate between *A. flavus* and *oryzae*
AO5b	*Aspergillus oryzae*
AO5c	*Aspergillus flavus*

PREVIOUS WORK

A review of previous investigations upon the general subject of the enzymes concerned in such fermentation processes justifies the following summary:

1—The addition of a particular substance to the culture medium does not cause entirely new enzymes to develop but stimulates the production of the particular enzyme that is already normally formed by the organism.[3]

2—Substances that are closely related to the enzymes in their chemical structure appear to be more efficient in stimulating enzymic formation than are substances not closely related. For example, for the production of protease, proteins are the strongest stimulants, followed by peptides, amides, ammonia, and other inorganic nitrogenous substances that are progressively weaker. For amylase, starch is the strongest stimulant, followed by dextrin, maltose, and glucose.[6,13,4]

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[1] Received July 29, 1922.

[2] This work was conducted in the Microbiological Laboratory of the Bureau of Chemistry, U. S. Department of Agriculture, with the assistance of Dr. J. F. Brewster, formerly of the Bureau of Chemistry. The earlier experiments were carried out in the laboratory of Dr. J. Takamine. Photographs by courtesy of Gen-itsu Kita, Kyoto Imperial University, Japan.

[3] Professor of Chemistry in College of Fisheries.

* The numbers in the text refer to the bibliography at the end of this article.

3—Enzymes are present in the mycelium of the fungus in the greatest amount at the period of sporulation of the fungus, and rapidly disappear after that time.

Comparison of Protease Produced by Molds on Several Media

As a preliminary experiment to pick out the strong protease producers from the collection of fungi, the molds were cultivated on skim milk, soy-bean milk agar, and gelatin. Growth of the molds on these artificial high protein media was observed and extent of proteolysis was noted. The breaking down of protein substances in the skim milk and in the soy-bean milk agar was indicated by a change from the opaque appearance in the sterilized medium in both cases to an almost translucent appearance after active mold growth had occurred. This translucent appearance, indicating changes in the proteins composing the skim milk or soy-bean milk agar due to proteolysis, will be complete throughout the tube of medium or only partial, depending on the thoroughness of digestion. Partial or complete digestion of protein in the skim milk or soy-bean milk agar indicates the relative proteolytic strength of the particular mold strain under investigation. The breaking down of protein in the gelatin is indicated by liquefaction. Some strains, like 3565, APa, 4235.x.1, 3509, 108, AO3b, AO5b, AOold, AOK, and the accidental *Aspergillus ochraceous*, were quick sporing forms. This group contained also very strong protease producers, as judged by the indications stated above, whereas 129, AOb, and AON spored quickly but produced weak protease.

Among the strains that produced spores slowly, AO2b, APb, and 130Sc produced strong protease, but AOAc, 113, and 18 were very weak as producers of protease. We should bear in mind that the digestion velocity of these experiments depends upon the rapidity of mold growth and the amount of excreted protease. Judgment as to the relative amount of protease excreted depends on the observed partial or total change in the medium from an opaque to a translucent appearance in the case of the skim milk and soy-bean milk agar, and extent of liquefaction in the case of gelatin. Rapidity of digestion of skim milk and soy-bean milk was much the same for each fungus. The digestion or liquefaction of gelatin, however, differs greatly from either that of skim milk or soy-bean milk. This may be due to the differences in optimum temperature for growth, different adaptability for culture media, and to differences in the nature of the enzymes, protease, and gelatinase. For instance, AOK digested gelatin most quickly, though it was not the strongest in other digestions.

Method for Quantitative Estimation of Protease

The method here used was based mainly on the Fuld-Gross[5] method for trypsin, but it is believed to be more convenient and accurate than the Fuld-Gross method:

Solutions Required—(1) 0.5 per cent casein solution. 2 g. of dry casein are mixed with 200 cc. H_2O + 50 cc. 0.1 *N* NaOH and warmed to 70° to 80° C. After cooling, this is neutralized with 0.1*N* HCl, using phenolphthalein as indicator, on porcelain plate. About 30 cc. 0.1 *N* HCl are required. 3 cc. of 0.1 *N* NaOH are added to make *N*/1500 NaOH reaction and the whole filled up to 500 cc. with distilled water. The casein was made by Hammarsten's method,[1] and the moisture estimated.

(2) Mixture of solution of magnesium sulfate and nitric acid. 4 parts of saturated magnesium sulfate solution are mixed with 1 part of concentrated nitric acid.

Procedure—To 4 test tubes with 5 cc. of 0.5 per cent casein solution immersed in 40° C. water bath add 4 cc., 2 cc., 1.5 cc., and 0.5 cc., respectively, of protease solution. Mix well and after 1 hr. add 0.5 cc. of mixture of solution of nitric acid and magnesium sulfate to each tube.

The limit between incompletely and completely digested tubes can be readily seen. This limit is indicated by a gradation from an opaque appearance in the solution where the digestion is incomplete to a water-white appearance in completely digested tubes. The protease solution may then be diluted in proper ratio to suit the next test. Using the same procedure but with the following quantities, 0.2 cc., 0.3 cc., 0.45 cc., 0.7 cc., and 1.0 cc., the protease is again tested. The closer and finer quantities permit more exact reading of the opacity of the solutions, which is desirable after the preliminary tests. The two points between which opacity changes to water-white permit the proteolytic power of a given mold to be approximated. In order to obtain a safer judgment, 5 cc. of 0.005 per cent casein solution may be used as representing complete digestion. To obtain still more accurate results, the protease solution may be taken with a series of even smaller variations.

To express the proteolytic power, the following unit was devised. If 0.025 g. (or cc.) of original enzymic substance digests completely 5 cc. of 0.5 per cent casein solution (= 0.025 g.) in 1 hr. at 40° C., then the proteolytic value (= P. V.) of this substance is 100.

Fig. 1—Label on Envelope Containing Commercial Mold Ferment (Japanese)

Optimum Reaction of Casein Solution for Protease Action

It was found that there are different optimum reactions for casein digestion by *Aspergillus* enzymes, according to the methods of casein disappearance and amino nitrogen liberation. For the former, the optimum pH is 8.0, for the latter, 6.2. The experimental data are given in another publication.[8]

Comparison of Protease and Amylase Produced by Molds on Wheat Bran

To compare more exactly the enzymic strength of many kinds of fungi, wheat bran was taken as a culture medium, as it contains much starch and also proteins in good condition. Previous experience indicated that various species of *Aspergillus* produced the strongest protease and amylase when growing on wheat bran. To find the optimum conditions of cultivation on wheat bran, various experiments were made with it to determine the influence of moisture, sterilization, culture period, quantity of bran, and temperature on the growth of the fungi.

As a result, the following standard method of cultivation was selected:

Put 5 g. wheat bran in a 200-cc. Erlenmeyer flask, with 5 cc. distilled water. Mix well, plug with cotton, sterilize for 1 hr. with steam pressure of 7 to 8 lbs. After cooling, inoculate with 0.2 to 0.3 g. of *seed* of the desired fungus, shake well, and keep in incubator at 30° C. for a definite period. (To make tane-koji or *seed* of fungi, use same procedure except that 3 g. of bran in 50-cc. flask with 3 cc. of 5 per cent cooked rice extract digested with takadiastase are used as the ingredients on which the mold is grown.) After this period has elapsed add 45 cc. distilled water, mix well, keep the flask in ice water for 3 hrs. and filter through filter paper. With this extract test the enzymic activity and acidity.

Amylase is tested by the author's method,[7] which is based upon the copper-reducing power of the produced sugar and is expressed in Lintner's scale at 40° C. Protease is tested by the new method described above. The enzymic value, both proteolytic and diastatic, expressed by the author's methods is strictly proportional to the enzymic power presented in the sample, but not proportional to the relative values that are generally adapted for mycological experiments.

Of the cultures, AO2b, AO5a, AOAc, APb, 18, and 113 were kept in the incubator for 88 hrs. Even after that period of incubation AOAc, 18, and 113 did not show sporing. All others were kept 40 hrs. in the incubator at 30° C. and all showed complete sporing. Acidity was tested with phenolphthalein as indicator on the porcelain spot plate. In the tests for protease and amylase, the work was completed on the day the cultures were extracted. Therefore, no antiseptics were added. These culture experiments on skim milk, soy-bean milk, agar, gelatin, and bran show that there are great differences in enzyme production, even among the fungi which seem morphologically quite alike.

FIG. 2—INOCULATION OF INGREDIENTS OF SOY SAUCE WITH THE MOLD FERMENT, *Aspergillus flavus*

Strong protease producers are *A. ochraceous*, AOK, AOold, AO5b, AO3b, APb, APa, and 3509. Strong amylase producers are AO1, AO2a, AO2b, AO3a, AO4a, AO4b, AO5a, AO5b, AO5c, AOold, and A. Strong producers of both enzymes are AOold and AO5b. Strong protease and very poor amylase producers are APa, APc, and AOK.

TABLE II—QUANTITY OF ENZYMES PRODUCED BY FUNGI CULTURED ON WHEAT BRAN

Culture Number	Amylase Lintner's Value	Protease Oshima's Value
18	15	6
113	100	8[2]
AOAc	5	8[2]
AOAa[1]	19	36
AOP	31	36
AOb	40	42
AOAb	99	42
AO5a	172	42
AO2b	459	42
108	25	56
4272.2	46	56
AO4b	126	56
AO3a	132	56
AO2a	236	56
3565	31	83
AO4a	135	83
AO5c	210	83
A	236	83
4328	53	100
AO1	262	100
4235.x.1	21	112
3509	25	130
AOold	412	166
AO3b	25	168
A. ochraceous	46	168
APa	25	178
AOK	40	200
AO5b	305	208
APb	13	260

[1] *Aspergillus*, not identified.

[2] Before sporing.

INFLUENCE OF CULTURE PERIOD ON PRODUCTION OF ENZYMES

Some have considered that protease production in the *A. flavus-oryzae* group is later than the amylase production. Using the standard methods of cultivation described here, and varying periods of growth, together with *Aspergillus* strains AOold, APb, and AO3b, the following conclusion was reached—there is no distinguishable point or interval at which protease production begins as compared with amylase production among molds of the *A. flavus-oryzae* group. That great differences in the rate of growth of the molds and in quantitative enzymic production do exist may once more be concluded from this experiment.

CULTURE OF MOLDS ON VARIOUS SUBSTANCES

The kind of material that is best for the production of the strongest enzymes from a fungus was also studied. As it is a general fact that natural culture media are more suitable than artificial ones for the growth of fungi, many natural food substances were collected for the purpose of studying enzymic production by the *A. flavus-oryzae* group of molds. The same procedure as with the standard methods of cultivation was carried out, except that the duration of cultivation and the substances used as media were altered. Strains of *A. oryzae* (AOold), of *A. effusus* type (APb), of *A. parasiticus* (AO3b), and a strain (AO2b) resembling F of Takahashi were used. AOold was a strong protease and diastase producer; APb grew slowly and was a strong protease but weak diastase producer; AO3b grew rapidly and was a strong protease and weak diastase producer; AO2b grew slowly and was a strong diastase but weak protease producer. The following materials were made, as far as possible, of the same fineness:

TABLE III

	MATERIALS	TEXTURE AFTER STERILIZATION
I	Wheat bran	Unchanged
II	Wheat middling	Unchanged
III	Corn meal	Unchanged
IV	Cocoanut meal	Unchanged
V	Peanut meal	Compact mass
VI	Cottonseed cake	Unchanged
VII	Oil extracted soy-bean meal	Compact mass
VIII	Soy-bean meal	Compact mass
IX	Crushed soy-bean	Pebble-like
X	Dried yeast	Paste-like
XI	Ground dried codfish	Unchanged
XII	Casein	Adhered to wall of container

Using the methods already described for amylase and protease estimation, this experiment shows that wheat bran is best, and that strong enzymes may be produced with soy-bean products, if the natural condition of the beans is altered by grinding and cooking. It is regarded of great importance in the making of shoyu-koji that the ingredients present a specific physical condition. The aeration afforded by a comminuted and not packed physical condition of the various substances utilized as culture media or substrata is desirable. A change in the ratio of protease to amylase with a change of medium or substratum seems probable. The very weak strength of the enzymes developing in this case, except from mold grown on wheat bran, makes the majority of these substrata unsatisfactory for further study. On codfish no strains were apparently able to grow. The good growth obtained on yeast makes an interesting problem for further study.

COMPARISON OF AMOUNTS OF INTRACELLULAR AND EXTRACELLULAR ENZYMES

For this purpose an artificial liquid culture medium composed as follows was used: (*a*) casein, 20.00 g. (as dried matter) + 100 cc. H_2O + 170 cc. 0.1 *N* NaOH, warmed and dissolved completely; (*b*) soluble starch, 20 g. (as dried matter) + 400 cc. H_2O, boiled and dissolved completely;

(c) 10 cc. of a 0.05 per cent solution of magnesium sulfate; 10 cc. of a 0.01 per cent solution of ferrous sulfate; 10 cc. of a 0.1 per cent solution of di-potassium phosphate. The Ingredients *a*, *b*, and *c* were mixed together and neutralized with 2 cc. 0.1 *N* HCl, using phenolphthalein as indicator, and made to 1 liter with distilled water. Fifty cc. of each were put in a 500-cc. Erlenmeyer flask with cotton plug, and sterilized 15 min. at 15 lbs. pressure. *Aspergillus* strain AOold was used for this experiment, incubated at 30° C.

Enzymes in mycelium were tested after treating with acetone, as Albert and Buchner tried with yeast, and also Dox[3] for the intracellular enzymes of *Penicillium*. This treatment has become quite popular in studies of this type. The method to test intracellular and extracellular enzymes as adapted to this particular experiment was as follows:

> Mycelium from two flasks was removed after a certain period of cultivation, washed twice with distilled water quickly, then squeezed to remove as much as possible of the water, and torn apart or teased out with the fingers. The wet mass thus obtained was immersed for 10 min. in a large volume (about 100 cc.) of acetone with constant stirring; it was then filtered off with suction through hard filter paper. It was immersed again for 2 min. in a fresh quantity of acetone and filtered off as before. It was immersed the third time in ether for 3 min., dried as much as possible with suction, spread on a watch glass and allowed to remain over night at room temperature. This dry mycelium was weighed, ground finely in a mortar, a certain quantity weighed out, and the enzymes extracted with distilled water of 100 times their quantity for 2 hrs. at room temperature. Then the extract was filtered through filter paper and tested by the author's methods for its proteolytic and amylolytic power. Extracellular enzymes were tested with the culture liquid of the same two flasks, mixed with the water used to wash the mycelium and made up to 200 cc.

The difference between the aqueous extract of acetone-treated mycelium, with and without maceration with sand, was tested, and no recognizable difference was found. The decrease of enzymic power by acetone treatment was later tested carefully, as will be described. Not much difference was noted. The enzymic powers for intracellular enzymes were estimated on the basis of weight of mycellium grown, and for extracellular enzymes on the basis of the volume of liquid culture medium (100 cc. from two flasks).

CHECKING EXPERIMENT FOR ERRORS IN METHOD

With the procedure above, AOold was grown for 115 hrs. at 30° C. Quantities of diastase in culture medium and mycelium were determined as follows:

TABLE IV

TREATMENT	Samples in Duplicate	Z. V.[1] in Filtrate	Z. V. in Mycelium
Mycelium treated with acetone	*a*	2720	454
	a'	2600	363
Mycelium ground with sand	*b*	3000	356
	b'	3000	438
Mycelium teased apart	*c*	2850	103
	c'	2850	138

[1] Total amount of disatase (Z. V.) in 100 cc. culture media.

From this experiment it may be noted that acetone treatment does not cause a great decrease in enzymic power.

CONCLUSION AND DISCUSSION

The supposition that fungi produce extracellular and intracellular enzymes is accepted provisionally. The extracellular enzymes can be obtained by percolating mature fungi with water, but the latter cannot be obtained by mere treatment with water. Some investigators have tried to get the intracellular enzyme from koji residue—i. e., a mold ferment grown on a large scale on some substratum, and the whole washed free of extracellular enzymes—by treating with many solvents, but negative results were always obtained. Experiments here show that extracellular and intracellular enzymes are the same, and after a certain period of growth all enzymes are excreted. Many investigators[2,6,12,3,13,4] have shown the same results with other fungi. In the present investigation the work was quantitative, and the ratio of exo- and endo-enzymes during the cultivation of *A. oryzae* and *A. flavus* was found.

From the foregoing experiments it is deduced that soon after spore formation almost all enzymes have been excreted into the culture media. It is also shown that the increase and decrease of enzymes in the mycelium is quite rapid but in the culture medium it is quite slow. It is doubtful whether the excretion of enzyme is due to the autolysis of the mycelium, because at the time of the most rapid excretion of enzymes the weight of mycelium is found to be increasing and the maximum amount of exo-enzyme occurs simultaneously with the maximum quantity of mycelium. Consequently, it may be concluded that in experiments intended for the study of the influence of culture media, etc., on the production of mold enzymes, the estimation of the enzymes produced in the mycelium is quite an erroneous manner of procedure, particularly when it is realized that through differences in culture media the rate of growth and the time of sporing may be varied.

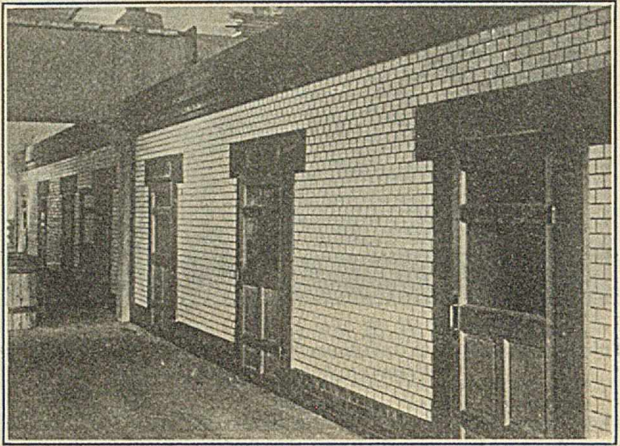

FIG. 3—A SERIES OF KOJI ROOMS FOR RIPENING WITH MOLD THE INGREDIENTS OF SOY SAUCE

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The Points of Minimum Plumping of Calf Skin[1]

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WHEN animal skin is immersed in dilute solutions of acid or alkali, the protein matter swells by absorbing some of the solution, but the effect to a casual observer is not so much one of swelling as of increased resiliency of the skin, due to its fibrous structure. The collagen fibers, in swelling, tend to fill up the interstices between them, and the full increase in volume of the protein matter is not evident from the appearance of the skin. A skin in which the fibers are not swollen may contain almost as much water as one whose fibers are swollen, as in lime water, but the bulk of the water in the first skin is held only loosely *between* the fibers and may be squeezed out by the application of slight pressure, whereas that in the second is present *within* the substance of the fibers and cannot be removed except by the application of enormous forces. During the swelling of the protein matter, the tanner observes in the skin an increasing resistance to compression, to which he has given the name "plumping," the term "falling" indicating the reverse action.

The degree of plumping of the skin at different stages is a factor of considerable importance in the manufacture of leather, affecting the yield as well as the properties of the leather. Because of the importance of this factor, the question of its quantitative determination has been receiving increased attention.

Since the degree of plumping is a function of the hydrogen-ion concentration, one should expect to find it a minimum at the isoelectric point of the skin protein. While investigating the effect of hydrogen-ion concentration upon the action of the bating process, at 40° C. Wilson and Daub[2] noted a point of minimum plumping occurring between the pH values 6.1 and 9.8, but they could not locate it more accurately because their method of observation was simply to pinch the skin, as is customary in determining the completion of the bating process. But Thomas and Kelly[3] by the use of acid and basic dyes found the isoelectric point of skin protein at a pH value of 5. Moreover, Porter,[4] while investigating the effect of hydrogen-ion concentration on the swelling of hide powder, obtained points of maximum swelling at pH values of about 2.2 and 12.9, and a rather sharp point of minimum at 4.8—agreeing very well with Thomas and Kelly's observation of the isoelectric point.

In a letter, Prof. H. R. Procter suggested that Wilson and Daub may have missed the true point of minimum plumping by not making observations at sufficiently short intervals of pH value. While the consecutive members of the series of solutions they used generally differed by less than 0.5 on the pH scale, Porter worked at intervals of 0.1 in the vicinity of the isoelectric point, which appeared to be necessary in order to show the point of minimum sharply. On the other hand, Porter made only one measurement between the pH values 6 and 9, so that he might easily have failed to locate a point of minimum occurring in this range. The possibility of finding two points of minimum plumping of calf skin seemed to warrant a more extensive investigation than had been made.

Wood, Sand, and Law[5] devised an apparatus for determining when a skin had become completely fallen during the bating process, which consisted of a sensitive thickness gage in which the pressure exerted upon 1 sq. cm. of skin could be varied by means of weights. The point of complete falling of a skin was taken as that at which no recovery in thickness of the skin took place upon removing the weights. The apparatus was also used to measure the apparent modulus of elasticity of the skin, and this was considered to be a measure of the degree of plumping. The work of Wood, Sand, and Law suggested a method more suitable for our purpose, in which the degree of plumping at a given pH value is measured by the ratio of the resistance of the skin to compression at that pH value to its resistance to compression under standard conditions.

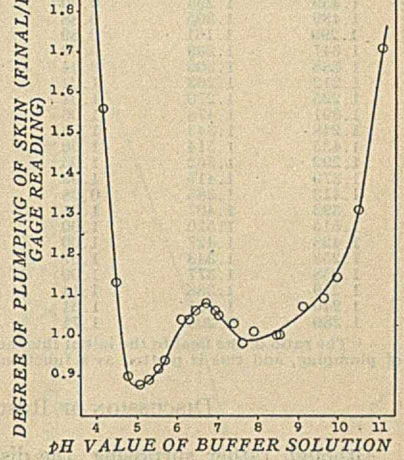

Fig. 1—Showing Two Distinct Points of Minimum Plumping of Calf Skin

Procedure

Skin for the test was cut from the butt of a calf skin in order to insure the greatest degree of uniformity of structure of the pieces, each 2 cm. square, into which the test piece was cut. The skin, previously limed and unhaired, was freed from lime by washing in a 12 per cent solution of NaCl containing a small amount of HCl, and then neutralized in cold, saturated $NaHCO_3$ solution. It was then washed and bated by keeping at 40° C. for 24 hrs., in a solution containing 0.1 g. pancreatin, 2.8 g. NaH_2PO_4, and 18 cc. *N* NaOH per liter, giving a pH value of 7.7. Microscopic observation showed that this procedure removed all the elastin fibers. The pieces were then washed in cold, running tap water having a pH value of 8, for 24 hrs., after which they were kept in distilled water in the refrigerator at 7° C. until used for the tests.

A series of 24 large reservoirs of test solutions was prepared, each having a final concentration of 0.1 *N* phosphoric acid plus the amount of NaOH required to give the desired hydrogen-ion concentration, as determined by the hydrogen electrode. The pH values ranged from 4 to 11.

The apparatus used to measure the compressibility of the skin was a thickness gage sensitive to 0.001 mm. The gage had a flat metal base, upon which the test piece of skin was placed, and a plunger, having a circular base exactly 1 sq. cm. in area, pressed upon the surface of the skin under constant pressure. The amount of compression increases with the length of time the skin is under the pressure of the plunger,

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[1] Received August 10, 1922. Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This Journal, **13** (1921), 1137.

[3] *J. Am. Chem. Soc.*, **44** (1922), 195.

[4] *J. Soc. Leather Trades' Chem.*, **5** (1921), 259; **6** (1922), 83.

[5] *J. Soc. Chem. Ind.*, **31** (1912), 210; **32** (1913), 398.

but the greatest change takes place during the first minute. It was found that reproducible results could be obtained by taking all readings exactly 5 min. after dropping the plunger onto the skin, and this rule was strictly adhered to in the taking of all measurements noted in this paper.

Into each of a series of bottles were put 200 cc. of standard buffer solution of the desired pH value, and these were kept in a thermostat refrigerator at 7° C. so as to reduce to a minimum any tendency toward putrefaction of the pieces of skin. Into each solution were placed two pieces of skin, prepared as described above, the thicknesses of which had been measured after remaining under the plunger of the gage for exactly 5 min. After 24 hrs. the solutions were replaced by fresh buffer solutions. After 4 days more, there being practically no change in the pH values of the solutions, it was assumed that equilibrium was established, and the pieces were removed and their thicknesses measured again. The results are shown in Table I.

TABLE I

Gage Readings in Mm. (Average of Duplicates)			pH Value of Solution at 20°	
Initial	Final	Ratio[1]	Initial	Final
1.421	2.729	1.92	3.96	3.97
1.205	1.885	1.56	4.14	4.17
1.269	1.431	1.13	4.47	4.49
1.439	1.296	0.90	4.78	4.79
1.489	1.305	0.88	5.08	5.07
1.299	1.161	0.89	5.29	5.27
1.347	1.239	0.92	5.57	5.57
1.388	1.306	0.94	5.78	5.72
1.212	1.263	1.04	6.04	6.08
1.225	1.270	1.04	6.29	6.29
1.391	1.478	1.06	6.48	6.42
1.248	1.343	1.08	6.69	6.68
1.435	1.514	1.06	6.96	6.88
1.292	1.362	1.05	7.08	7.00
1.379	1.415	1.03	7.41	7.41
1.413	1.385	0.98	7.68	7.62
1.393	1.407	1.01	7.97	7.89
1.515	1.520	1.00	8.42	8.44
1.428	1.427	1.00	8.56	8.50
1.253	1.343	1.07	9.03	9.13
1.258	1.377	1.09	9.59	9.64
1.219	1.388	1.14	10.00	9.98
1.240	1.621	1.31	10.47	10.51
1.289	2.206	1.71	11.06	11.08

[1] The ratio of the final to the initial thickness is a measure of the degree of plumping, and this is plotted as a function of the pH value in Fig. 1.

DISCUSSION OF RESULTS

Although rather surprising, the discovery that skin actually has two points of minimum plumping will probably assist in the elucidation of a number of very puzzling experimental data. Among other things, it brings the results of Wilson and Daub into harmony with those of Thomas and Kelly and of Porter.

In studying the effect of change of pH value upon their new method[6] of tannin analysis, Wilson and Kern[7] obtained a practically constant value for tannin with change of pH value over the range 3.6 to 7.3; but at a pH value of about 8 there was a marked falling off in the extent of combination of tannin and hide power. It seemed significant that this should occur at 8 rather than at 5. Independently, Thomas and Kelly[8] investigated the rate of tanning as a function of pH value, and found, for a great variety of tanning materials, that it decreased to a minimum at a pH value of about 5, but then increased to a maximum at a value of about 8, above which it fell off rapidly towards zero.

The discovery of two points of minimum plumping of calf skin led Wilson and Kern[9] to make a similar study of the swelling of gelatin, and they also found two points of minimum, one at pH = 4.7 and the other at 7.7. Apparently, the two points of minimum indicate the isoelectric points of two forms—possibly tautomeric—of each protein, and this view is corroborated by the work of Thomas and Kelly.

CONCLUSION

The curve representing the plumping of unhaired and purified calf skin as a function of pH value was found to have two points of minimum, the one of lower value occurring at about 5.1, the other at about 7.6. It is suggested that these two points indicate the isoelectric points of two forms of the protein of calf skin.

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[6] THIS JOURNAL, 13 (1921), 772.

[7] "Effect of Hydrogen-Ion Concentration upon the Analysis of Vegetable Tanning Materials," *Ibid.*, 14 (1922), 1128.

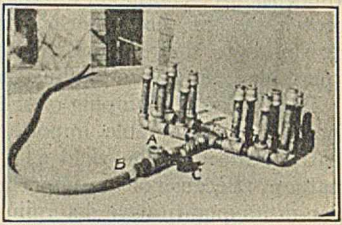
[8] Advance note.

[9] "The Two Forms of Gelatin and Their Isoelectric Points." Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

A Laboratory Multiple Burner[1]

By Frank C. Vilbrandt

UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.



The control of the rate of heating of a large number of laboratory burners under a single vessel is difficult, owing to the numerous regulating points. This difficulty was overcome in this laboratory by the construction of a burner with a single regulating part.

The burner is made from standard pipe and fittings, is inexpensive, lends itself to quick change in height and number of jets, is easy to regulate, and is efficient in gas consumption. Comparative runs with the same number of Méker burners indicated a saving of gas, more rapid heating and a considerably easier control of heating. Either a cone flame or a Méker effect can be produced by capping the jets with wire gauze.

The burner is made from three-quarter inch ells, tees, close nipples, reducers, and a cross. The jets are short pieces of piping set in tees. The regulating valve, A, is a tee in the service line, into one arm of which is attached the set of burners, into the other a glass jet, B, extending well into the burner line. Into the top arm is placed a capped nipple, C, the open end grooved with V-shaped cuts which provide for the regulation of the air introduced by screwing this up or down in the tee.

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[1] Received October 25, 1922.

Gums in Cracked Gasoline

When cracked gasoline was first placed on the market, it met with much opposition, part, at least, of which was due to lack of experience with the product. It was soon found that cracked gasoline, particularly if made carelessly, had a tendency to deposit gummy and resinous substances in storage, and in some cases in actual use in the engine. This phenomenon has usually been attributed to polymerization of the unsaturated hydrocarbons present. One theory is that the olefins themselves will not form gums, but that the latter are due to the presence of diolefins. Information has been notably lacking as to the nature, origin, and method of formation of these gummy substances. Some of the questions asked about them follow: Are the gums all of the same character? Are they similar to the coumarone resins, or are they possibly allied to the resins of commerce, which are derived from the terpenes? How should the amount of gum in a given sample of gasoline be determined? How much, if any, gum is permissible in motor gasoline; how much in aviation gasoline? The results of a general investigation of gum-forming constituents in gasoline are contained in Serial 2394 which may be obtained from the Bureau of Mines, Washington, D. C.

Estimation of the Proportions of TNT and Tetryl from the Freezing Point Curve[1,2]

By C. A. Taylor[3] and W. H. Rinkenbach[4]

Pittsburgh Experiment Station, Bureau of Mines, Pittsburgh, Pa.

In this paper data and a curve therefrom showing the equilibrium diagram of the binary system TNT–tetryl have been obtained, the existence of a new molecular complex, $2C_7H_5N_3O_6 : C_7H_5N_5O_8$, has been indicated, and practical use for the data has been outlined.

MIXTURES of TNT and tetryl are used in certain types of detonating fuses and may be found in detonators. At present there is no satisfactory method of estimating the proportions of the two substances. The method usually used is to determine the total nitrogen by the Dumas method and calculate the ratio of the ingredients using the known nitrogen content of pure TNT and tetryl as a basis. This method is tedious, and a small error in the result of the analysis causes a large error in the proportions calculated.

The binary system of TNT and tetryl was studied in order to obtain data that could be used in analytical methods and as physical constants in other work.

Materials

Trinitrotoluene—This was prepared by recrystallizing Grade I commercial TNT from hot benzene after filtering to remove any insoluble matter. The crystals were air-dried to remove mechanically held benzene. They were then recrystallized from boiling 95 per cent ethyl alcohol. The light yellow, fluffy crystals were redissolved in hot 95 per cent ethyl alcohol and then crystallized by pouring the solution into about two volumes of distilled water. The mixture was allowed to stand for several hours in a dark place to cool and complete crystallization. The crystals were then rapidly filtered on a Büchner funnel, washed several times with cold, distilled water, and given a final rinse with cold, 95 per cent alcohol in order to facilitate drying. The mass of crystals was dried on filter paper, and kept in sulfuric acid desiccators in a dark place.

The final product was a mass of very light, fluffy, white microscopic crystals. The TNT did not develop any color during 6 mo. storage in a dark room. The setting point was 80.27° C.

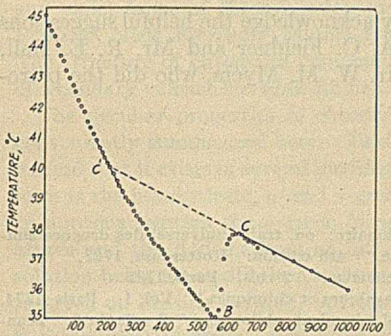

Fig. 1

Tetryl—A good grade of commercial tetryl was purified in the same manner as the TNT. Efforts to obtain colorless tetryl proved unsuccessful. The material precipitated in the water from the hot alcohol appeared colorless, but as soon as it was filtered a faint yellow color developed, even when the work was done in a dark room.

The final product of this purification was a mass of light, flaky crystals of faint yellow tint. The setting point was 128.72° C.

Method

The method of determining the equilibrium temperatures of known mixtures of TNT and tetryl was that described by Bell and Sawyer,[5] and Bell and Herty.[6] As used in this work, carefully weighed quantities of the two substances were transferred to a glass tube $^3/_4$ in. in diameter and 11 in. long. This tube also contained a carefully calibrated thermometer reading from 0° to 150° C. and a looped wire stirrer held in place by a cork. The tube and contents were heated until the substances had melted and formed a clear, homogeneous liquid. This tube was then jacketed by means of a tube 12 in. long and $1^3/_4$ in. in diameter, the mouth of the smaller tube being flush with the cork of the jacket. The jacket-tube was then immersed as far as possible in a 5-liter beaker of water or oil, maintained at a constant temperature somewhat below the crystallizing temperature of the mixture under observation, this having been roughly determined in advance.

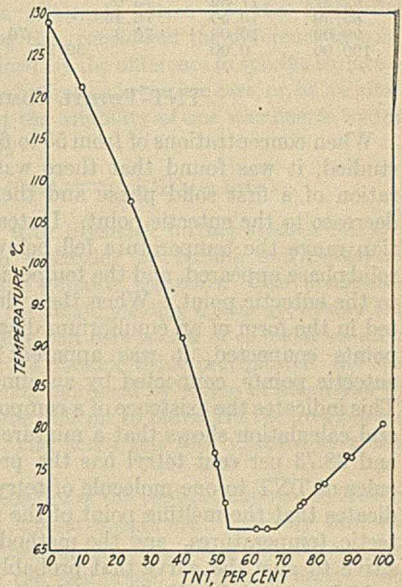

Fig. 2

Upon agitating the liquid mixture by means of the wire stirrer, the temperature fell at a uniform rate. Temperature readings were taken every minute and in some cases every half minute. After falling for some time, there would be a rise in the temperature coincident with the appearance of a solid phase. After attaining a maximum, the temperature would again fall at a time rate lower than that observed before the appearance of the solid phase. Such a typical cooling curve is shown in Fig. 1, temperatures being plotted as abscissas and time readings as ordinates.

Guia,[7] working upon the nitrotoluenes, took the point B (Fig. 1), at which crystals first appeared, as the equilibrium temperature of the mixture. Bell and Herty,[6] however, in repeating this work, showed that, although point C is nearer the true value than B, the true value, C′, may be ob-

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[1] Received July 29, 1922.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Explosives Chemist, U. S. Bureau of Mines.

[4] Assistant Explosives Chemist, U. S. Bureau of Mines.

[5] This Journal, **11** (1919), 1025.

[6] *Ibid.*, **11** (1919), 1124.

[7] *Ber.*, **47** (1914), 1718; *Gazz. chim. ital.*, [1] **45** (1915), 339.

tained by extrapolating the second and slower rate of cooling upon the initial rate of cooling.

Accordingly, this method of deriving the true equilibrium temperature was used by the writers. Upon continuing the cooling it was found possible to determine the eutectic point of the mixture with some concentrations, while with others the proportion of the solid phase was so great that after a time it was found impossible to stir and so insure equal cooling throughout.

The results obtained follow, and are shown in the form of an equilibrium diagram in Fig. 2.

TNT Per cent	Tetryl Per cent	Extrapolated Point, C′ ° C.		Eutectic Point ° C.	
0.00	100.00	128.72			
10.00	90.00	121.1	120.8		
24.89	75.11	107.5			
40.00	60.00	90.8	90.9		
44.16	55.84			67.4	67.4
49.52	50.48	76.8		67.6	
50.00	50.00	75.4	75.5	67.4	
52.08	47.92			67.6	67.6
52.50	47.50	70.8	70.8		
55.12	44.88			67.6	
61.61	38.39			67.4	67.5
65.00	35.00			67.6	67.4
75.00	25.00	70.4			
76.13	23.87	70.95			
80.40	19.60	72.7			
82.31	17.69	73.0			
89.50	10.50	76.45			
90.00	10.00	76.3	76.4		
100.00	0.00	80.27			

TNT-Tetryl Complex

When concentrations of from 55 to 65 per cent of TNT were studied, it was found that there was no preliminary separation of a first solid phase and then gradual temperature decrease to the eutectic point. Instead, over this concentration range the temperature fell below the eutectic point, a solid phase appeared, and the temperature of the mixture rose to the eutectic point. When the values obtained were plotted in the form of an equilibrium diagram (Fig. 2) and these points connected, it was apparent that there were two eutectic points, connected by an almost straight line curve. This indicates the existence of a compound of the components, and calculation shows that a mixture of 61.27 per cent TNT and 38.73 per cent tetryl has the proportions of two molecules of TNT to one molecule of tetryl. The straight line indicates that the melting point of the complex is near the eutectic temperatures, and the method is not sufficiently sensitive to give the curve that probably occurs at that point.

Melts containing 40, 60, and 80 per cent of TNT were submitted to W. M. Myers for examination under the petrographic microscope. He found that the 40 per cent TNT mixture contained tetryl and a compound other than TNT; the 60 per cent TNT mixture appeared to be almost entirely this compound; the 80 per cent TNT mixture was a mixture of free TNT and this compound.

Application of the Data

When the time rate of cooling is plotted on a large scale, the C′ point can be checked to 0.2°, and this point can be determined in the curve to 0.2 per cent. If no C′ point is found, showing the TNT content to be between 55 per cent and 65 per cent, it is still possible to determine the percentage with a fair degree of accuracy by adding a weighed portion of either TNT or tetryl to a weighed portion of the unknown mixture so as to make the TNT content less than 55 per cent or greater than 65 per cent and then determining the C′ point of this new mixture. Knowing the weights of unknown mixture and pure component, and the percentage of TNT in the new mixture as found from the curve, the proportions of the substances present in the original mixture can be calculated:

A = Wt. of sample.
B = Wt. of component added as TNT.
x = Per cent of component (TNT) which was originally present in sample.
y = Total per cent or component (TNT) present in new mixture as found from curve.

Then $x = \frac{y\,(A + B) - 100B}{A}$.

If a C′ point obtained on an unknown mixture is between 67.5° and 80.3° C., there is no means of knowing whether the point is on the tetryl or TNT side of the curve. This can be determined by changing the proportions as given above, locating another point in the curve, and noting whether the temperature is higher or lower than the original. It is usually more satisfactory to add tetryl for this purpose than TNT.

Grade I materials are usually used in the detonating fuse so that the error due to impurities as TNT is comparatively small.

Acknowledgment

The authors gratefully acknowledge the helpful suggestions and criticisms of Mr. A. C. Fieldner and Mr. R. E. Hall, and the assistance of Mr. W. M. Myers, who did the petrographic work on melts.

Rare Books

The library of the Chemists' Club, New York City, has a small collection of interesting rare books. Assuming that our readers would be interested in knowing of the existence of such a collection, Miss E. J. Fell, the librarian, has prepared the following chronological list of the most ancient of these works:

Aretino: "De metallicis libri tres." Noribergae, 1602.
Croll: "Basilica chymica." Frankfort, 1620.
Agricola: "De re metallica." Basil, 1621.
Linceo: "Discorsi dimostrazioni matematiche." Leida, 1638.
Bertereau: "La restitution de pluton." Paris, 1640.
Glauber: "Operis mineralis." 3 vols. in 1. Amsterdam, 1651–2.
Paracelsus: "Opera omnia medico, chemico, chirurgica." 3 vols. in 2. Geneva, 1658.
Boyle: "Chymista scepticus." 2nd edition. Rotterdam, 1668.
Guericke: "Experimenta nova (ut vocantur) Magdeburgica de vacuo spatio." Amsterdam, 1672.
Borrichius (Ole Borsch): "Hermetis Aegyptiorum et chemicorum sapientia." Hafniae, 1674.
Leeuwenhoek: "Arcana naturae ope microscopiorum detecta." Delphis, 1695.
Manget: "Bibliotheca chemica curiosa." 2 vols. Geneva, 1702.
Lemery, Nicolas: "Dictionaire; ou, traité universel des drogues simples; pharmacopée universelle." 4th edition. Rotterdam, 1727.
Boerhaave: "Elementa chemiae." 2 vols. Paris, 1732.
Lavoisier: "Opuscules physiques et chimiques." Vol. 1. Paris, 1774.
Dalton: "New system of chemical philosophy." 2 vols. in 3. Manchester, 1808–10.

American Academy Makes Grant

At a meeting of the Committee on the C. M. Warren Fund of the American Academy of Arts and Sciences, held on December 8, 1922, a grant of $250.00 was made to Prof. James B. Conant, of Harvard University, to be used in furthering his research in connection with the electrochemical study of the reversible reduction of organic compounds.

The next meeting of the committee for the warding of grants will be held on March 1, 1923. Applications for these grants must be in the hands of the chairman of the committee, Prof. James F. Norris, Massachusetts Institute of Technology, Cambridge, Mass., before this date.

The Colloid Chemistry of Basic Chromic Solutions[1]

By F. L. Seymour-Jones[2]

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

It is the purpose of this paper to present a review of the chemistry of chromic oxide hydrosol. In view of the large amount of research now proceeding on the chemistry of chrome liquors and on the theory of chrome tanning, such a review from a purely chemical standpoint may serve to clear the ground of some misconceptions.

EVEN to-day it is far from clear whether chrome liquors really contain basic chromic salts, or whether they are simple colloidal dispersions of chromic oxide. Postulating the existence of colloidally dispersed chromic oxide, it may exist either as a negatively or as a positively charged sol. In the first case the freshly precipitated oxide is dispersed in excess of caustic alkali, and in the second either the oxide is peptized with excess of the chromic salt or alkali is added to a solution of the normal chromic salt.

The positive sol was first prepared as such by Graham[3] in 1862, similarly to the ferric oxide sol, by peptization of the hydrogel with chromic chloride. Even before this one peculiar property of this oxide had been noted by Northcote and Church[4] in 1853. They found that chromic oxide, when mixed with certain metallic oxides, such as ferric, manganic, cobalt, and nickel oxides, which are themselves insoluble in potassium hydroxide, may render these soluble, or may itself be rendered insoluble by them, according to the proportions used.

Schiff[5] in 1862 found that chromic acetate gave no precipitate on boiling, and hence that chromium, unlike ferric iron, could not be estimated by the basic acetate method. Reinitzer[6] confirmed this and further found that the presence of chromic ion to a large extent inhibited the precipitation of iron and aluminium by sodium acetate. He also noted that chromium hydroxide, precipitated with potassium or ammonium hydroxide, etc., always contained some of the precipitating metal which could not be removed by washing, even with boiling water.

Other chemists also studied the chemistry of chromium from the analytical point of view. The equilibrium between green and violet forms of chromic salts was studied by Richards and Bonnet,[7] Niels Bjerrum,[8] Minnie Graham,[9] and many others. The structure of chromium compounds from the point of view of secondary valence has been studied by Werner and his school.

The peculiar properties of chromic salts in solution may be conveniently summarized here. Taking the chloride as typical, we find that it exists in several modifications. The most common form is the hexahydrate, α- and γ-green salts and a β-violet salt. In aqueous solution the α-green form is stable at high temperatures and the β-violet form at low temperatures, an ordinary solution being an equilibrium mixture. The change from violet to green on heating is rapid, but the reverse change on cooling is comparatively slow. The green chloride is easily soluble in water, but the violet form is practically insoluble unless a trace of chromous chloride be present. The violet solution has a greater density than the green solution.[9] In the α-salt only one chlorine, in the γ, two chlorines, and in the β, all three chlorines ionize as anions. The three chlorides can be represented by Werner's system as:

$[Cr(H_2O)_4Cl_2].Cl.2H_2O$
Green α-salt

$[Cr(H_2O)_5.Cl].Cl_2.H_2O$ $[Cr(H_2O)_6].Cl_3$
Green γ-salt Violet β-salt

HYDROUS CHROMIC OXIDE PEPTIZED WITH EXCESS ALKALI

Herz,[10] in 1901, noted that chromium hydroxide, freshly precipitated from chrome alum with alkali, was easily soluble in excess of the precipitant. After thorough washing and drying over sulfuric acid in a desiccator, the hydroxide was insoluble. These he regarded as allotropic forms of the hydroxide. Hantzsch,[11] in criticizing this, considered the difference in solubility was better explained by the difference in specific surface of the two forms, due to the hydration in the one case, or, as an alternative explanation, that the solubility of one was due to hydration on Werner's theory:

$$Cr(OH_2)_6.(OH)_3 \rightleftharpoons Cr(OH)_3 + 6H_2O$$

Herz, in conjunction with Fischer,[12] further studied the precipitation of chromium hydroxide by sodium and potassium hydroxides from chromic chloride solutions. The precipitate was soluble in excess of the alkali, yielding a clear green solution. They considered that they had here a case of colloidal solution. On long standing, hydrous chromic oxide precipitated, the stability of the solution being increased by excess of alkali and by low temperatures. It was difficult to redissolve the precipitated chromic oxide in alkali, and hence this was regarded as a case of peptization.

They examined the behavior of the peptized chromic hydroxide under dialysis with an animal membrane. In every case the external water rapidly became alkaline, while the chromic hydroxide precipitated at the membrane. In this it differs from a similar solution of alumina, where the aluminium passes through the membrane. With a similar solution of zinc hydroxide, part of the zinc passes through and part precipitates at the membrane—i. e., part exists as zincate and part is colloidally dispersed as hydroxide or hydrous oxide.

Experiments on precipitation with electrolytes gave indefinite results. They next measured the conductivity. They made the assumption that if the chromic hydroxide is a peptized colloid, the conductivity will be dependent upon the sodium hydroxide concentration alone, whereas if a compound is formed, the conductivity should alter. Just sufficient alkali was added to redissolve the precipitate first formed and then the conductivity was measured. The solution was then boiled, the precipitated chromic hydroxide filtered off, and the conductivity again measured. They found that it had not changed, and hence concluded that the chromic hydroxide is in colloidal dispersion.

Bancroft[13] remarks on this that, since it is the hydroxyl ion which peptizes the chromic hydroxide, the conductivity should be altered. When the hydroxide precipitates, it carries down with it some alkali and some water, which should change the

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] 1851 Exhibition Scholar of the University of Leeds.

[3] *Phil. Mag.*, [4] **23** (1862), 290.

[4] *J. Chem. Soc.* (*London*), **6** (1853), 54.

[5] *Ann.*, **124** (1862), 168.

[6] *Monatsh.*, **3** (1882), 249.

[7] *Proc. Am. Acad. Arts Sci.*, **39** (1903), 1, includes a bibliography of 62 references. See also *Z. physik. Chem.*, **47** (1904), 29.

[8] *Z. physik. Chem.*, **59** (1907), 336; abstracted from *Kgl. Danske Videnskab. Selskab. Skrifter naturwidenskab. math. Afdel.*, [7] **4**, 1.

[9] *Am. Chem. J.*, **48** (1912), 145, includes a bibliography of 53 references.

[10] *Z. anorg. Chem.*, **28** (1901), 342.

[11] *Ibid.*, **30** (1902), 338.

[12] *Ibid.*, **31** (1902), 352.

[13] *Trans. Am. Electrochem. Soc.*, **28** (1915), 351.

conductivity. Probably the large excess of sodium hydroxide present causes the change of conductivity to fall within the limits of experimental error.

More recently Chatterji and Dhar[14] found no appreciable change in conductivity on adding chromium hydroxide to sodium hydroxide solution. Hildebrand[15] is reported to have applied the hydrogen electrode to the measurement of the change in hydrion concentration on adding sodium hydroxide to suspensions of alumina and of chromic oxide in water. With the alumina a definite break in the curve occurs, corresponding to the formation of sodium aluminate, $NaAlO_2$. No break occurs with chromic oxide, rendering the formation of sodium chromite unlikely under the conditions of the experiment.

Wood and Black[16] in 1916 examined chromic oxide from the amphoteric standpoint. Freshly precipitated and well-washed chromic oxide was allowed to stand for two months in solutions of sodium hydroxide. At the end of that time the more concentrated solutions were becoming yellow. This did not occur when all contact with air was carefully excluded. They conclude that minute traces of chromic oxide dissolve to form sodium chromite, which is slowly oxidized by the atmospheric oxygen to form chromate. The acidic dissociation constant of chromium hydroxide was too small to measure, but the results led to the conclusion that it functions as a polybasic acid.

The conclusions reached by Herz and Fischer[12] were criticized by Kremann,[17] who pointed out that Nernst, in the electrolysis of chromium solutions, found that the colored boundary shifted towards the anode. Kremann concluded that it was probably not a case of colloidal electrophoresis, but rather that chromites of the type $Na_2Cr_2O_2$ were formed, where the colored chromite ion migrated anodically. With some justice he pointed out that Fischer and Herz dialyzed against water, and hence that chromite, if present, might be sufficiently unstable to hydrolyze, and a precipitate of the hydroxide would naturally form at the membrane. He dialyzed an alkaline solution of chromium hydroxide against dilute alkali, and, after some hours, found that chromite ion had dialyzed through.

Fischer[18] replied to these criticisms. Any anodic migration was explained by Bredig's results, which showed that colloids were able to migrate with the current. Further, in the dialysis experiments Kremann made up his solutions from chrome alum. Fischer and Herz[12] had previously shown that chrome alum gave very peculiar and indefinite results, which they attributed to the formation of chromium-sulfuric acids, capable of dialysis. Fischer also argued that chrome alum is a salt of the violet variety, while the chloride he used was the green one. He dialyzed green chromium chloride against sodium hydroxide solution for thirty-six hours, and no chromium passed through the membrane. Traces coming through later were due to the destructive action of the alkali on the membrane.

Nagel[19] ultrafiltered a dispersion of hydrous chromic oxide in alkali through collodion filters. The oxide was completely filtered out, the liquid coming through colorless. Bancroft found on shaking precipitated chromic oxide with water and benzene that the oxide went to the dineric interface. Nagel therefore tried to shake out the peptized chromic oxide with benzene or kerosene, but this was useless in alkaline solutions.

We can, therefore, conclude that chromic oxide can be colloidally dispersed in alkali solutions, from which on long standing it precipitates out. If these solutions are exposed to the air, some oxidation to chromite and chromate occurs. The nature of the peptizing electrolyte is uncertain. It may be the alkali itself—the hydroxyl ion, as some would say—or quite possibly a trace of alkali chromite.

HYDROUS CHROMIC OXIDE PEPTIZED WITH CHROMIC CHLORIDE

Fischer[12] studied the solubility of freshly precipitated and washed chromium hydroxide in violet chromic chloride solutions. The results showed that the solubility of the hydroxide was not directly proportional to the chloride concentration. He could not precipitate the chromium hydroxide from solution, either with electrolytes or by heating for eight days on the water bath. He concluded that a basic chloride was probably formed by hydrolysis, and that chromium hydroxide was also present as a colloid. However, he abandoned the study of chromium salts, owing to their color and general complexity, and turned to aluminium as providing a simpler system.

Neidle and Barab[20] studied the dialysis of colloidal solutions of hydrous chromic oxide in chromic chloride, using parchment paper membranes. The results are somewhat confusing, as at first the colloidal particles diffused through the membrane. This ceased later, which they attributed to the growth of the particles. They also studied the diffusion at high temperatures (around 80° C.), and as a result discovered the more rapid preparation of purer sols. The examination of these sols showed that the reputed stability of chromium hydroxide sols to electrolytes was in reality due to insufficient dialysis. This is shown by the following table:

Hydrous Cr_2O_3 Sol	—G. Eq./Liter— Cr_2O_3	HCl	Cc. 0.1 *N* KCl Required to Precipitate 10 Cc. of Sol
1	0.0693	Trace	0.37
2	0.0984	0.0020	3.00
3	0.0888	0.0058	30.00 did not precipitate

They conclude that (*a*) the higher the temperature, the less electrolyte is necessary for the stability of a sol, and (*b*) the concentration of electrolyte necessary for stability at a given temperature increases with the concentration of the colloid. The green chromic chloride readily yields sols on dialysis, while only traces are obtained on dialyzing the violet salt.

Niels Bjerrum[8] applied conductivity and hydrogen-ion measurements to the study of the hydrolysis of violet chromic chloride, and these tend to throw some light on the colloidal aspect. His results in adding sodium hydroxide to chromic chloride solution show decreased conductivity until one mol of NaOH per mol $CrCl_3$ was added; then the conductivity very slowly increased until three mols NaOH per mol $CrCl_3$ were added, after which the conductivity rapidly increased. This indicates the formation of a definite basic salt, $CrOHCl_2$. His results were corroborated by Denham,[21] using the electrometric method. Nagel[19] tried the ultrafiltration of a "basic" chromic chloride solution, and found that the peptized chromic oxide was filtered out, a normal solution of chromic chloride passing through. He therefore concluded that no appreciable amount of basic salt was formed, which is strange in view of Bjerrum's results. If Nagel's chloride solution was more basic than $CrOHCl_2$, he may very possibly have had hydrous chromic oxide peptized in a solution of $CrOHCl_2$. But this does not explain why *normal* $CrCl_3$ solution passed through the filter.

HYDROUS CHROMIC OXIDE PEPTIZED WITH CHROMIC SULFATE

T. W. Richards and F. Bonnet[7] in 1903 studied "the changeable hydrolytic equilibrium of dissolved chromic sulfate." An attempt was made to determine whether any definite basic salt was formed. Shaking out the green solution with an alcohol-ether mixture, they finally obtained a solution in which the salt appeared to be $CrOHSO_4$. A similar result was obtained by

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[14] "The Physics and Chemistry of Colloids" (Faraday and Physical Societies' Discussion), **1921**, 122.

[15] Discussion following paper by Bancroft. See footnote 13.

[16] *J. Chem. Soc.* (*London*), **109** (1916), 164.

[17] *Z. anorg. Chem.*, **33** (1903), 87. The reference to Nernst given by Kremann appears to be incorrect.

[18] *Ibid.*, **40** (1904), 39.

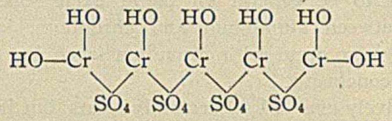
[19] Nagel, *J. Phys. Chem.*, **19** (1915), 331, 569; Bancroft, *Ibid.*, **19** (1915), 275.

[20] *J. Am. Chem. Soc.*, **38** (1916), 1961; **39** (1917), 71.

[21] *J. Chem. Soc.* (*London*), **93** (1908), 41.

digesting the green solution with the hydroxide on the steam bath for several hours. But this is not the limit of basicity in the cold. By shaking for several days a violet solution with chromium hydroxide, whereby it is rapidly converted into green, they finally obtained $Cr_5(OH)_7(SO_4)_4$.

Of course there is no limit to the theoretical number of basic salts. The last one named can be written



and obviously the process of formula building can be extended ad lib., though practical justification may not be forthcoming.

Another test for the existence of a basic salt was applied. When the sulfate ion in chromium sulfate is precipitated as $BaSO_4$, the precipitate contains some of the green salt occluded, since the green salt is highly hydrolyzed, but does not occlude any of the violet salt. Richards[22] had previously shown that such occlusion, which is quite a general phenomenon, is probably due to the distribution of a definite molecular species between the solvent and the precipitate at the moment of formation of the latter. Consequently, he hoped in this way to get at the formula of the basic salt. Solutions of sodium sulfate and chromic chloride were mixed, allowed to stand, and then precipitated with barium chloride. The amount of salt occluded increased with the delay in precipitation, showing that time was necessary for the formation of the more complex sulfates. The salt occluded was a basic chromium sulfate and not a chloride.

They also examined the migration on electrolysis of a basic sulfate solution. The migration was entirely cathodic, and there were 19.3 g. Cr per 96,580 coulombs, a surprisingly large figure. They argue that, since the atomic weight of chromium is 52, each atom of chromium cannot be associated with more than two charges and probably with not more than one. Assuming that the sulfate ion alone migrates anodically with a mobility of 70, the mobility of the chromium group, if with one charge, is 41, if with two charges, is 243. The latter figure is improbable, while the former resembles those for zinc and magnesium. They regard it as possible that the cation may be CrO^+ or $Cr(OH)_2^+$, which Siewert[23] and Whitney[24] showed to be the most probable cation in boiled (green) solutions of chromic chloride or nitrate, or the cation may be yet more complex, with basic groups attached.

In general, Richards and Bonnet concluded that a green basic salt existed, but they were not prepared to assign any definite formula to it, since hydrolysis might very possibly proceed in steps. Further work as to the existence of a colloidal substance in the hydrolyzed solution was promised, but does not appear to have been published.

In view of the foregoing and Bjerrum's results with the chloride, I carried out the ultrafiltration of a basic chromic sulfate solution. This was prepared by reduction of a sodium dichromate solution with sulfur dioxide, the excess sulfur dioxide being removed by boiling. The dark green, concentrated solution contained 269.9 g. Cr_2O_3 per liter. This was ultrafiltered through hard filter papers impregnated with 1 and 5 per cent gelatin dispersions, the papers being subsequently hardened in 4 per cent aqueous formaldehyde solution, and through a collodion disk. In every case the solution passed through unchanged, no colloidal particles being retained by the filter. The same result was obtained when the solution, diluted with three volumes of water, was allowed to remain in a collodion bag suspended in air. The concentrated solution and one diluted to ten volumes with water were dialyzed in collodion bags against water, the water being changed frequently. In less then eighteen hours even the concentrated solution had completely dialyzed through the membrane, the liquid remaining in the bag being colorless.

Such a solution as that described above should have a basicity equivalent to $CrOHSO_4$, or, according to Bassett,[25] would contain a mixture of 95 to 96 per cent chromic sulfate and 4 to 5 per cent chromium dithionate.

Conductivity titrations of chromic sulfate solutions with barium hydroxide have been carried out by A. W. Thomas and S. B. Foster,[26] and by W. R. Atkin and D. Burton.[27] These, however, were for the purpose of determining when all three sulfate ions had been precipitated, and the readings are insufficient to determine definitely whether there is a break in the curve corresponding to the formation of a definite basic salt. In the former's curves there is evidence of such a salt being formed. I intend to investigate this point by this and other methods as time permits.

It seems probable that there may exist a basic salt, $CrOHSO_4$, analogous to the chloride. The question is complicated by the fact that in *certain* basic chromic sulfate solutions part of the chromium is found in a complex anion. It is quite possible that such basic solutions and colloidal dispersions of hydrous chromic oxide may exist together. The whole question is certainly a most complicated one, and the pure chemistry of "basic" chromic solutions must be cleared up before any definitive theory of chrome tanning can be elaborated.[28]

OTHER SOLS

Biltz,[29] in 1902, arguing that in the series of precipitating anions NO_3^- was the least powerful, proceeded to study the formation of colloidal hydroxides of polyvalent metals by dialysis of their nitrates. Chromium hydroxide hydrosol was prepared by an eight-day dialysis through parchment of a fairly concentrated solution of commercial chromic nitrate, changing the external water three times a day, until it finally gave no test for NO_3^-. The sol so prepared was dark green by both transmitted and reflected light. It had a neutral reaction, and contained NO_3^-. Like other chromium sols, it was apparently resistant to electrolytes. Sodium and barium chloride solutions gave no turbidity, nor did a few drops of hydrochloric acid. Sulfuric acid or saturated sodium chloride solution gave decided turbidity and precipitation.

Woudstra,[30] in 1909, prepared a "red" colloidal sol of chromic hydroxide from chromic acetate solution, both by dialysis and by distilling off the acid in steam. The sol was brownish red by transmitted and a dirty green by reflected light. The sol was electropositive and very resistant to electrolytes. Twenty per cent solutions of $MgSO_4$, $BaCl_2$, Na_2CO_3, KCN, KSCN, $KMnO_4$, and concentrated solutions of H_2SO_4, HCl, HNO_3, NaOH, $(NH_4)_2CO_3$, and $(NH_4)_2(COO)_2$ gave no coagulation. The acids dissolved the chromic oxide and gave green solutions.

CHROMIC OXIDE JELLIES

Bunce and Finch[31] studied the formation of chromic oxide jellies. If sufficient sodium acetate is added to a chromic sulfate solution, and then an alkali, the solution sets to a jelly which is not completely reversible. The concentrations of reactants employed can vary within wide limits, and both violet and green jellies formed, according to whether ammonia and slight or large excess of alkali be employed. Nagel[19] also studied this

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[22] *Proc. Am. Acad. Arts Sci.*, **35** (1900), 377; *Z. anorg. Chem.*, **23** (1900), 383.

[23] *Ann. Chem. Pharm.*, **126** (1863), 86.

[24] *Z. physik. Chem.*, **20** (1896), 40.

[25] *J. Chem. Soc.* (*London*), **83** (1903), 692.

[26] *J. Am. Leather Chem. Assoc.*, **15** (1920), 510.

[27] *J. Soc. Leather Trades' Chem.*, **6** (1922), 14.

[28] Thompson and Atkin, *Ibid.*, **6** (1922), 207.

[29] *Ber.*, **35** (1902), 4431.

[30] *Kolloid Z.*, **5** (1909), 33.

[31] *J. Phys. Chem.*, **17** (1913), 769.

jelly formation. Recently Weiser[32] reviewed the literature on hydrous chromic oxide, and also showed that jellies of both the positive and negative colloid could be formed.

CONCLUSION

It will be seen that the question of whether chrome liquors contain basic salts or positively charged chromic oxide sol or both, is as yet undecided. Possibly an explanation may be found in the work of Pauli and Adolf,[33] in their research on alumina hydrosols. They find that the usual aluminium hydroxide hydrosol, as prepared from aluminium acetate, proves to be a basic acetate, or aluminium monoacetate [$Al(OH)_2.CH_3COO$], which is largely hydrolyzed and in which the complex ions $3Al(OH)_3.Al(OH)_2^+$ and CH_3COO^- have grouped themselves into colloidal particles. They were able to prepare from aluminium chloride the following transitions to aluminium hydroxide sol: $Al(OH)Cl_2$; $Al(OH)_2Cl$; $2Al(OH)_3Al(OH)_2Cl$. Further, with increasing proportions of alumina, the aluminium hydroxy salts incline to the formation of negative aluminate complexes, in addition to positive ones, a tendency which increases with dilution. These exist for zirconium hydroxide and probably also for dilute ferric hydroxide sol, and this may, according to Pauli, prove to be general for metal oxide sols. From the similarity between aluminium and chromium, something of this sort may also occur with chromium sols,[28] but the evidence so far is not conclusive.

The negatively charged sol certainly exists, but is of no application in tanning practice. The concentration of alkali necessary to peptize the chromic oxide is such that it would rapidly dissolve any hide put into it, apart from the sol being precipitated by the salts or acid in the hide. I tried such a sol on hide powder and the latter was very rapidly hydrolyzed. The positive sol probably exists, but its investigation is complicated by the possibility of basic salts and negative chromium complexes.

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[32] *J. Phys. Chem.*, **26** (1922), 401.

[33] "The Physics and Chemistry of Colloids" (Faraday and Physical Societies' Discussion), **1921**, 14.

Earning Power of Research as Demonstrated by the Experience of the American Rolling Mill Company[1]

By D. M. Strickland

THE AMERICAN ROLLING MILL CO., MIDDLETOWN, OHIO

The experience of many business men is that to make research pay it is only necessary to adequately support a sufficient number of studies on worthy projects under competent direction. One and often more than one problem is sure to be successfully solved, and this more than repays the entire expense.

IT HAS BEEN SAID with much truth that many research programs are not undertaken in this country until some pressure is brought to bear upon the corporation financing it. This pressure may be economic, or it may be the strong arm of the law, which insists that earth, air, or water be no longer polluted. A much brighter picture is that presented by corporations which set out to attain a definite objective, and who from the beginning ally themselves with science in the confident knowledge that with its assistance its ideals can always be realized.

The American Rolling Mill Company was founded by men who foresaw the trend of the times and who recognized the possibilities of organized research. In addition to the research staff there are many executives and directors of operating activities who are keenly appreciative of research development and who coöperate whole-heartedly with the men in the research laboratories. In any plant the greatest earnings are produced by research when there is this close coöperation between the men responsible for productive manufacture and the theoretical investigators of the research organization. Mutual confidence among the technologists and the men who work out in practice the laboratory recommendations insures research accomplishment and better commercial products.

HIGH-GRADE STEEL OBTAINED

Years ago the need for high-grade steel for electrical requirements was recognized. Electrical engineers insisted that the cost of electrical equipment be reduced and its efficiency increased. Here was a problem calling for team work on the part of the chemists, the metallurgists, and the electrical engineers. It was not sufficient that the analytical composition of this steel be satisfactory; it was also imperative that the most efficient productive methods, rolling procedure, and all manufacturing steps be determined scientifically. Conscientious endeavor along these lines resulted in sheet steel for electrical equipment of such perfection that to-day it is used throughout the land. The peculiar qualities of this steel are such that in transformers alone it is responsible for a reduction in the cost of electric current wherever it is used at the present time. This saving—one of the dividends on the research undertaking—can be reckoned in millions of dollars annually.

RUST-RESISTING METAL

Having accomplished this primary result, research was then directed toward another commercial need—the production of a rust-resisting sheet metal. The rust problem was scientifically studied and it was found that governmental investigators and testing engineers had already reached the conclusion that the purer the iron the more enduring it is when exposed to corrosive conditions. The research organization proceeded at once to the study of producing commercially pure iron. Raw materials had to be chosen with exacting care; purification processes, rolling practices, annealing procedures, and other necessitated manufacturing steps were changed before the requirements of commercially pure iron were met. In the end a rust-resisting iron was developed which has been produced with great uniformity year after year. The sum of such impurities as sulfur, phosphorus, carbon, manganese, copper, silicon, hydrogen, nitrogen, and oxygen is always less than sixteen-hundredths of one per cent.

In the production of sound metal the occluded gas is a major problem. Research investigation proves that the service life of finished metal sheets was shortened when they were contaminated with appreciable amounts of occluded gases. It was

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[1] Received June 24, 1922.

necessary to devise new methods of chemical analysis so that gaseous impurities could be quantitatively determined. It was found, too, that occluded gases play a part on corrosion resistance, interfere with galvanizing, and are detrimental to paint-holding and enameling qualities.

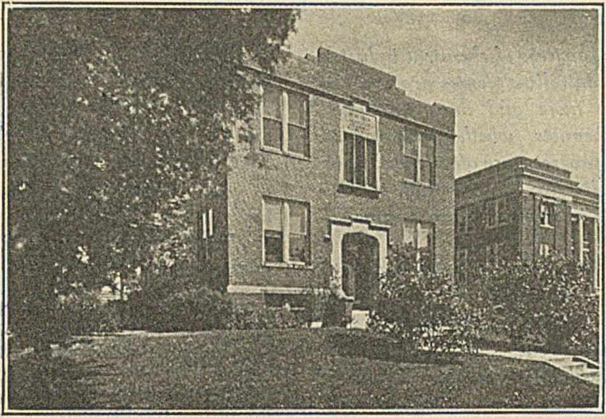

FIG. 1—RESEARCH LABORATORY OF AMERICAN ROLLING MILL COMPANY

COMMERCIALLY PURE IRON

Research pointed the way to the perfection of degasification practices, and the illustration indicates great improvement in the soundness of ingots and compares the sound commercially pure iron with the gaseous steel product (Fig. 2). This commercially pure iron has been used with great success for galvanizing, and experience has shown that the purer the spelter coating can be applied the more corrosion-resistant and long-lasting such coating will be. The research organization has determined that coating purity is a measure of the service life of every galvanized installation. It has further shown that commercially pure iron, being a properly degasified metal, possesses to a high degree the valuable characteristic of tenaciously holding a coat of paint. Such iron has a further advantage of resisting the rusting action of any moisture which may penetrate the paint film. For vitreous enameling purposes this same metal has a homogeneity, chemical purity, ductility, and degasification which play an important part in successful enameling. The most satisfactory welding is done with pure metals free from occluded gases (Fig. 3). Commercially pure iron has been found to surpass the Swedish and Norway irons formerly thought necessary for such work.

DREDGE PIPE AND OTHER SPECIAL STEELS

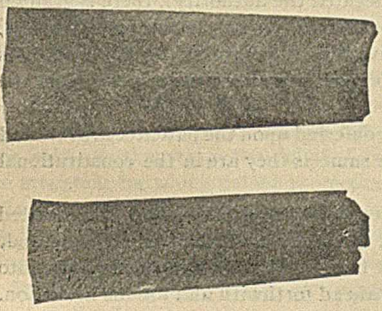

FIG. 2

Another accomplishment of this research to be measured in dollars and cents is the production of a dredge pipe. This involves the production of a special analysis steel, an improved design of pipe, and perfection in welding. Owing to special lipped joints which add to the worth of this research accomplishment, the pipe line can be laid straight or in a form of a circular arc.

The provision of special sheet metal for deep drawing and spinning is also to be credited to research. To produce such products it was necessary to develop special finishes, scientific cold-rolling, heat-treating, and pickling methods.

IMPORTANCE OF COLLABORATION

The research department of the American Rolling Mill Company realizes the mutual advantage to be gained by collaboration with experimental departments of kindred organizations. Its research investigators and service engineers confer with representatives of customers, visit their plants, examine their peculiar conditions, and utilize their science in an effort to adapt the products to the customer's needs, or to adapt the customer's fabrication methods to the needs of the iron specialty. The organization finds it imperative to continually study and try out developments perfected by scientific societies, university research laboratories, and many individuals. During the development of commercially pure iron it was necessary that chemical control be studied in its entirety. New methods of analysis were studied so that minute quantities of impurities could be accurately determined.

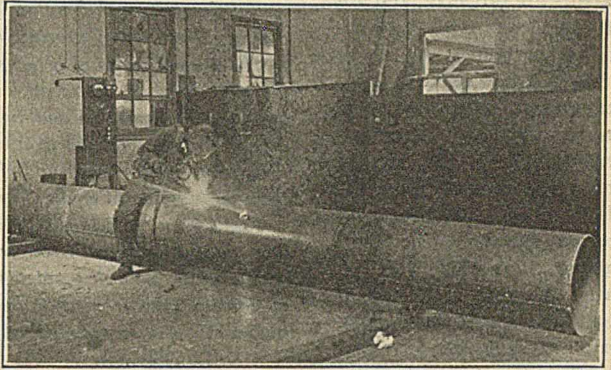

FIG. 3

"RESEARCH AND METHODS OF ANALYSIS"

In 1911, the first edition of "Research and Methods of Analysis" was published, and contained various analytical procedures which had been found satisfactory. To meet an increasing demand, a second edition appeared in 1920. The 1920 edition is a comprehensive book containing the very latest information on iron and steel analysis. The methods outlined are of greatest use to the chemist seeking traces of impurities that may be present in commercially pure iron. Chemical, metallurgical, and electrical testing methods are given, together with an interesting study of old irons. It contains many methods of analysis perfected by members of the United States Bureau of Standards, Westinghouse Research Laboratory, Institute of Industrial Research, eminent college men, and other scientific experts.

DOES RESEARCH PAY?

It is noteworthy that during the recent business depression, when research organizations of many industrial enterprises were dismissed in their entirety—even when all business experiments were curtailed and appropriation for "productive" departments reduced to a minimum—the activities of the research department of the American Rolling Mill Company continued unabated, and new iron and steel specialties, new manufacturing methods, and new commercial uses for ferrous metal products were developed and perfected.

The following Industrial Fellowships have been established at Mellon Institute since July 1, 1922: food container, corrosion, gelatin, ester, oil, metallic oxides, slag, gas, liquid carbonic, and perfumes.

A committee of ten members of the American Zinc Institute has been appointed to act with the Bureau of Mines in an effort to promote research on behalf of the zinc industry and to consider the problems from a national viewpoint.

Patent Law of Interest to Chemists. I—Patent Rights[1]

By Frank E. Barrows[2]

165 Broadway, New York, N. Y.

The new inventions which mark the progress of chemical industry are to an important and often to a controlling degree protected by patents. Such progress is becoming more and more dependent on organized chemical research. Chemists, whether engaged in research or otherwise interested in such progress, are often called upon to deal with patent questions, and must give consideration to such questions if they would safeguard their interests and avoid unnecessary litigation.

Most chemists must acquire their knowledge of patents and of patent law by experience or by individual study. In only a very few of the colleges and universities do the courses in chemistry and chemical engineering provide instruction in patent law.

The present series of articles will include a discussion of some of the principles of the patent law, as well as some of the practical questions that arise in dealing with patents and inventions. The articles are not intended as a treatise on patent law, but rather as a discussion of the law, and of questions of practical importance, from the standpoint of the chemist and chemical engineer.

The present article will deal with the nature of patent rights; later articles will deal with the subject of patentable inventions, the procedure in obtaining patents, the construction and interpretation of patents, patent searches, foreign patents, and other questions of patent law and its practical application.

MEANING OF "PATENT"

In its limited or legal sense the term "patent" is an abbreviation of "letters patent" and refers to the grant by the Government to the patentee of certain exclusive rights in the invention patented. In this sense patents are property, and are often referred to as "intellectual property."

In a more general sense patents are referred to without regard to any rights protected thereby. Patents, in this more general sense, include both domestic and foreign patents. The term "patent," as thus used, is rather a means of identification or a descriptive term than a term having any legal significance. In this broader sense patents constitute a part of the technical literature and stand on much the same footing as other publications. Thus, we may consider patents merely for the information they contain, just as we consider the periodical literature as a source of published information. From this standpoint it is immaterial whether the patents are domestic or foreign, and, in the case of domestic patents, whether the patents have expired or are still in force.

It is important to keep these different meanings of the term "patent" in mind, because in considering patents from their legal aspect we are concerned with the rights which they secure to the patentee, while in considering patents from the more general aspect we may not be at all concerned with these rights.

It is with the more limited aspect of patents as property, and the nature of such property, that we are primarily concerned in the following discussion. In some respects property rights in patents are similar to other property rights; in other respects they are governed by rules peculiar to themselves.

THE STATUTORY BASIS OF PATENTS

Patents are creatures of statute. There is no natural right to a patent. The only natural right which an inventor has in an invention is the right to keep it secret. As long as he may be able to keep his invention secret, and as long as others do not independently make the same invention, he will be protected, but his rights are subject always to the peril of independent discovery of the same invention by another, as well as to possible treachery on the part of confidants. If another should independently make the same invention, the first inventor could not prevent him from using it if his invention could not be protected by patent.

Since patents are thus creatures of statute, we must look to the patent statutes, and the constitutional provision on which they are based, to find out what inventions are patentable, how they may be protected, and the nature of the protection obtainable. The basis of our patent system was laid in the Constitution as originally adopted in 1787, which provided that:

> The Congress shall have the power * * * * to promote the progress of science and useful arts, by securing for limited times to authors and inventors the exclusive right to their respective writings and discoveries.

The power to grant patents is thus delegated to Congress, and it has been in pursuance of this power that the patent statutes have been enacted. Their object, as stated in the Constitution, is "to promote the progress of science and useful arts;" and while this object has sometimes been lost sight of, yet it has been repeatedly emphasized by the Courts as the guiding principle of our patent system.

The progress of science and of the useful arts is promoted by the early disclosure of inventions and by the stimulation of invention. In order to accomplish this result the inventor is rewarded or compensated by the grant of patent protection.

A patent is therefore a reward or compensation to the inventor for disclosing his invention. It is also in the nature of a contract between the inventor and the public, whereby the inventor is accorded patent protection for his invention for a limited period of time, and whereby the public secures an early disclosure of the invention and the right to use it after the patent expires.

THE EXCLUSIVE NATURE OF PATENT RIGHTS

When a patent is issued by the United States Patent Office (to which Congress has delegated the authority), there is granted to the inventor, his heirs or assigns, "the exclusive right to make, use, and vend the said invention throughout the United States and territories thereof," for the term of seventeen years from the date of grant.

In this grant the rights conferred upon the patentee are referred to as "exclusive rights" the same as they are in the constitutional provision above quoted.

It is natural for a patentee to assume that the right thus granted him is an affirmative right to make use of the invention patented, and many a patentee has been misled by this assumption into believing that he could go ahead forthwith and use his invention. In fact, however, the grant of a patent does not give to the patentee any right whatever to use his invention.

The exclusive right granted by a patent is exclusive only in the sense of a right of exclusion. The exclusive right granted is the right to exclude others from making use of the invention patented—i. e., the invention claimed. Whether or not the patentee is himself free to make use of his invention is a separate and distinct question governed by considerations independent of those which govern the grant of his own patent.

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[1] Received December 2, 1922.

[2] Member of the firm of Pennie, Davis, Marvin & Edmonds, Counselors-at-Law.

A proper understanding of the "exclusive" nature of patent rights is of fundamental importance. Unless it is clearly understood it will be difficult to understand many of the practical questions that arise in dealing with patents. As pointed out above, the granting of a patent does not give the patentee any right to use his invention; it merely gives him the right to exclude others from using it. The measure of this right of exclusion is determined by the claims of his patent.

Let us consider how a misunderstanding of the nature of patent rights may lead to serious loss or litigation. If the patentee assumes that the grant of his patent gives him the affirmative right to use his invention, he may go ahead with a sense of false security and disregard the rights of other patentees whose patents may dominate his own invention, that is, whose patents may contain broad and dominating claims that give a superior right of exclusion. The inventor who thus proceeds may find later that he has incurred a substantial liability for the infringement of patent rights of others, and he may thus be exposed to litigation, which, if successful, may involve substantial damages or may even result in the entire loss of the investment made in exploiting his own invention.

Had such a patentee clearly understood the "exclusive" nature of patent rights, he would have appreciated that the grant of his own patent gave him no affirmative right to use his invention. He would have appreciated, moreover, that other patentees might perhaps have exclusive rights which would dominate his own. It is common experience in dealing with patents to find that an early patentee has secured a broad and dominating patent giving him rights of exclusion which will prevent later patentees from using the particular improvements which they have patented.

An appreciation of this possibility of litigation naturally suggests that an investigation be made of the rights of other patentees before going ahead with the commercial exploitation of a new invention. Such an investigation will disclose whether or not other patentees have a superior right of exclusion which will dominate the invention in question. If such an investigation shows that there are no such dominating patents, the patentee may then proceed with a reasonable sense of security, although it is impossible to investigate applications for patents still pending in the Patent Office and which may mature into patents at a later date.

If such a preliminary investigation discloses a patent or patents of others that are infringed, the later patentee may govern his actions accordingly.

The questions of infringement and patentability are two separate and distinct questions. The question of infringement depends upon whether there are patents which secure to other patentees a superior right of exclusion which will prevent the later patentee from using his invention. The question of patentability depends upon whether the invention is itself a patentable invention or improvement. The Patent Office in granting patents is not at all concerned with the question of infringement. The only question which the Patent Office determines is whether the invention for which patent protection is sought is patentable. A large number of patents are granted for improvements upon the inventions of earlier patents, and often an earlier patent or patents may dominate the later improvements. The inventions of the later improvement patents cannot in this case be used without liability for infringement of the earlier dominating patents.

It will be helpful to keep in mind that the first inventor in a new field may obtain a broad and dominating patent with comprehensive claims which will exclude others from that particular field, but that later inventors may invent improvements which will be patentable as improvements. The patentee of an improvement may prevent others, including the dominating patentee, from using his patented improvement; while the dominating patentee, because of his dominating patent, may exclude the improver from using his patented improvement. When the dominating patent expires, the patentees of the improvements will be no longer excluded by the dominating patent.

The Right to Make, Use, and Vend

The exclusive right granted to a patentee is defined in the patent grant as "the exclusive right to make, use, and vend" the invention. The exclusive rights to make, to use, and to vend are three distinct rights. They are "exclusive" rights in the sense that the patentee can exclude others from making, using, or vending the thing which is patented. In the case of patents covering chemical processes, the right is essentially an exclusive right to use or to practice the process, and does not extend to the product made thereby. In other words, the patentee of a process patent has the right to prevent others from using his process, but he cannot prevent others from making the same product by other processes, or from importing the same product made in some other country. In the case of new chemical products or compositions or new articles of manufacture, and in the case of new apparatus or machines, the right granted to the patentee is a right to exclude others from making, as well as from using and from selling, the patented invention. The patentee in such cases can enforce his rights, not only against the manufacturer or the one who makes the invention, but also against the importer and against others who use it and who sell it.

The Territory Covered by a Patent

The territory covered by a United States patent is the United States and its territories. A United States patent has no force and effect in foreign countries, and, if the invention is not patented in such foreign countries, the patentee of the U. S. patent cannot prevent the citizens or subjects of such countries from making use of the invention in their respective countries.

Similarly, foreign patents have no excluding force and effect in the United States. If there is no United States patent for an invention patented abroad, such invention becomes public property in this country. Accordingly, unless some patentee in this country has a dominating patent which will be infringed by the practice of an invention disclosed in such a foreign patent, any one in this country is free to use such invention.

The question of foreign patents will be later dealt with in greater detail, but in considering the territory covered by a United States patent it should be kept in mind that these rights do not extend to foreign countries, and that foreign patents have no excluding force and effect in the United States.

The Term of a United States Patent

A United States patent is granted for a term of seventeen years from the date of grant. Upon the expiration of this term the invention becomes public property—that is, the patentee can no longer exclude others from using his patented invention.

It is important to keep in mind that the term of a United States patent is from the date of grant and not from the date of application. In this respect a United States patent differs from patents of many other countries where the term of the patent begins to run from the date of application.

United States patents cannot be renewed or extended except by act of Congress, and for practical purposes the right may be considered not to exist.

There are no taxes or renewal fees for the maintenance of a patent after it has been granted, nor are there any requirements for the compulsory working of the invention in this country. The granting of the patent secures to the inventor protection for the full term of seventeen years, without further expense for fees or taxes and without any obligation on his part to use his invention or permit others to use it. In these respects our patent laws are much more liberal than those of most foreign countries.

Method in Research[1]

By D. B. Keyes

U. S. Industrial Alcohol Co., 27 William St., New York, N. Y.

Research methods as applied to the everyday problems of the chemical plant are somewhat different from those followed in the college laboratory—as the differences between the two types of problems dictate. This article presents an outline of the steps that must be followed if the worker is to have reasonable assurance of success. Its value lies rather in the expression of a tried and trusty method than in the presentation of revolutionary ideas. It is hoped that the younger generation of chemists going into research laboratories will find food for substantial thought in the scheme presented.

YOUNG men beginning the study of research methods have a right to know those general principles that will help them in the solution of any research problem; yet, few are given this opportunity. Educational men and research chemists have rarely brought forward clearly defined and workable plans of attack for research problems in general. Most research chemists at the beginning of their training are either left strictly alone and allowed to flounder as best they may, or they are told explicitly what to do and how to do it by someone else, without being allowed to develop their own ideas. Ultimately, each investigator devises some plan of his own which is usually more dependent on "hunches" that cannot be explained than upon any definite scheme of procedure.

A few definite principles similar to those developed in patent practice form the basis of every successful plan. Research men familiar with patent procedure generally show a remarkable degree of accomplishment compared with those who do not have the advantages of such experience. It is our purpose to present a plan developed from experience with commercial and industrial research which has resulted in successful, practical operation and the issue of broad basic patents.

SEARCH OF LITERATURE

The collection of all available information bearing either directly or indirectly on the problem in hand is recognized as the first step in any research. The importance of indirect bearings on the problem cannot be over-estimated, for analogy is a powerful weapon when properly applied. Let us suppose, by way of illustration, that a new and more efficient process for the oxidation of acetaldehyde to acetic acid is desired in order to dispose of a plentiful supply of the former and to fill an existing demand for the latter. The literature search should cover, not only the particular oxidation in question, but also the oxidation of related compounds to their corresponding acids. Ketones, alcohols, hydrocarbons, and other aldehydes might conceivably act similarly under similar circumstances. As the problem begins to take more definite shape in the mind of the worker, leads along this line will be developed and should be carried through.

ELIMINATION OF UNSUITABLE PROCESSES

From the mass of information thus collected, some more or less definitely applicable processes must next be selected with a view to their commercial possibilities. To continue the hypothetical case, let us suppose that the methods found for carrying out the oxidation were, among others:

1—In aqueous solution using nitric acid, hypochlorous acid, potassium permanganate, or potassium bichromate.

2—In the vapor phase using air as the oxidizing agent in the presence of a catalyst such as platinum black or vanadium pentoxide.

Others may be found in this case, but the examples given may be considered typical. The elimination of those unsuited to the present case may be done without experimentation. Oxidizing agents that are too costly, such as potassium permanganate, nitric acid, and potassium dichromate, need not be considered unless the yields obtained are unusually good. Processes involving chlorine point to a high equipment cost and upkeep, and therefore can be eliminated. Catalyzers such as platinum need not be considered if the yields are poor or if the catalyzer is delicate and easily poisoned, because the cost of the material would make the cost of the process prohibitive. We have left the oxidation of acetaldehyde with air in the presence of vanadium pentoxide. The result of this elimination is not the only one possible, because many factors will influence the researcher's opinion but the existing economics of the question will play the leading role.

CONSIDERATION OF CHANGES IN METHOD SELECTED

Having the nucleus for the research work, we must now see where changes can be made, or, in other words, what are the factors involved in the process chosen. By *factors* are meant not only the chemical and physical characteristics of the constituents of the reaction, but all such conditions as are variable. The principal factors involved in our hypothetical example can be considered as follows:

Catalyzer:	Physical characteristics
	Chemical characteristics
Oxidizer:	Physical characteristics
	Chemical characteristics
Acetaldehyde:	Physical characteristics
	Chemical characteristics
Temperature	
Pressure	
Concentration	
Velocity	

It is of great importance to consider every factor possible because actual laboratory work is still not necessary and no "good bets" should be overlooked. The preparation of this list of variables is one of the most difficult, as well as important, parts of the problem.

When these changes are actually to be made, we must limit the number of variable factors and also the number of variations to those for which we have the time and money available. We must also remember that no change shall be made for which there is no sound and substantial reason. Our variations must be based upon logical principles rather than upon guesswork.

Let us first consider a change in the physical character of the catalyzer. It is well known that the greater the catalyzer surface the greater its activity. Evidently, if vanadium pentoxide is more finely divided it will have more surface and more activity. The same result can be obtained by placing the catalyzer on a porous body such as pumice stone, but the physical properties of the foundation material in any catalysis are of extreme importance. Pumice stone is a poor heat conductor, and this will prevent a fine temperature control. The reaction is exothermic and large quantities of heat must be conducted away rapidly. If this were not done the temperature would rise, and complete oxidation to carbon dioxide would result. A foundation material having both high porosity and high heat conductivity is needed.

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[1] Received June 24, 1922.

In recent years methods have been described in the literature for making metals, such as copper and aluminium, very porous.

Vanadium pentoxide can be replaced for trial purposes by other oxides in the same periodic group or by any other oxide catalyzer that might act similarly. Combinations using two or more compounds as a catalyzer work better than any one alone. Energy in the forms of light and electricity work well in many cases. Enzymes act as catalyzers in fermentation processes. All such principles should be considered, even though time permit only a few changes based on such principles.

Though we have picked out of the literature as the most feasible process the oxidation of acetaldehyde in the vapor phase by means of air, it is not necessary to limit experiments to this oxidizer. If experience or the literature has shown that other oxidizers have worked unusually well in other instances, it might be worth while to try them. Compounds liberating oxygen are not the only oxidizing agents. Oxidation is an electrical phenomenon, therefore an electric current and also the halogens may be considered. The physical character of the oxidizing agent is very important. Oxygen in the atomic state is much more reactive than in the molecular state.

The research man may discover that the base material acetaldehyde may be replaced by acetylene, ethylene, or ethyl alcohol, and a distinct economic advantage be gained thereby. Though such a change is not within the scope of his problem, this line of investigation should be followed if time permits.

The highest yields along with a practical velocity occur within a definite temperature, pressure, and concentration range. The control of the temperature is especially important in catalytic work. The literature is full of methods that have been used to control accurately the temperature of gaseous, exothermic, catalytic reactions. It must be admitted that most of the methods so far devised are poor, but good pointers may be obtained by reading about these failures. Boiling liquid jackets, elimination of dead air space, metallic supports for the catalyzer, and dilution of reacting gases, are a few of the means described to overcome this difficulty. Changing pressure and concentration in order to take advantage of a possible equilibrium is a common means for increasing the conversion factor. The rapid removal of the finished product is especially advantageous.

A factor which influences the temperature, and indirectly the yield, is the time of contact of the reacting gases with the catalyzer, or, in other words, the velocity with which the gases are passed across the catalyzer. In this connection yield and not conversion factor is the important thing. That is to say, a conversion of 70 per cent with 30 per cent waste of raw material by passing the catalyzer once is far less advantageous than a conversion of 10 per cent which results in practically no loss through complete oxidation to carbon dioxide and water. It is conceivable that the same gases may be passed over the catalyzer many times and still maintain an economical advantage provided the over-all yield is materially increased.

Experiments on Semicommercial Scale

After the process has been pronounced a success upon a laboratory scale, the research chemist's work has not been completed—oftentimes it is really just begun. He must now collaborate with the mechanical engineer and work out the process on a semicommercial scale. Large-scale apparatus is a "bird of another color," and new troubles arise. The research chemist should never be allowed to turn over his laboratory process to others. He must be held responsible to the very end, because it is only with this experience well in mind that he can develop in the laboratory the nucleus of a commercial process. He will soon learn that laboratory processes are usually only successful when standard pieces of equipment are needed for industrial scale work. The time necessary to produce special plant equipment may be longer than can be allowed. It is easier to change the laboratory process to fit the standard plant equipment than to experiment with new and unique plant design. Standard chemical engineering operations give enough trouble without borrowing troubles from the unknown. The real experimenting should be done in the laboratory, not in the plant. A full-sized unit should not be made at first, but rather a semicommercial unit. These points cannot be over-emphasized.

Selling the Product

The research man's work carries him into at least one more field. If he has developed a new product he must go with the salesman and help overcome the difficulties experienced by the customer. The research man can remedy the troubles more quickly than anyone else, and, furthermore, he will learn economic principles that are essential in his work. The customer's requirements, the shipping requisites, and the sales field should be thoroughly appreciated by the research man. The customer is, after all, the person who supplies the money for research work, and his wishes should be carefully considered. Business principles and production methods have never injured the highly scientific research chemist, but rather have broadened his viewpoint and increased his productive ability.

The plan of research outlined is not one that is offered as a tentative scheme, but it is one that has proved its value in the cold gray dawn of industry. It is recognized that the ideas expressed are not in themselves new, but an attempt has been made to crystallize these ideas so that all may benefit by them.

Lexington Section Officers

The election of officers of the Lexington Section resulted as follows:

President: John A. Gunton, Transylvania College, Lexington, Ky.
1st Vice President: L. A. Brown, Experiment Station, University of Kentucky, Lexington, Ky.
2nd Vice President: J. R. Mitchell, University of Kentucky.
Councilor: H. P. Newton, Georgetown College, Georgetown, Ky.
Secretary-Treasurer: E. L. Jackson, Experiment Station, University of Kentucky.

South Jersey Section Officers

The following officers of the South Jersey Section have been elected for the coming year:

Chairman: H. W. Mahr
Vice Chairman: A. F. Odell
Secretary-Treasurer: W. Fletcher Twombly, care of E. I. du Pont de Nemours & Co., Box 525, Wilmington, Del.
Councilor: W. S. Calcott

Officers of New York Section

At the meeting of the New York Section at Rumford Hall, New York City, on December 8, 1922, the following officers for 1923 were elected:

Chairman: C. A. Browne, New York Sugar Trade Laboratory.
Vice Chairman: C. E. Davis, National Biscuit Company.
Secretary-Treasurer: B. T. Brooks, The Mathieson Alkali Works, Inc.
Executive Committee: M. H. Ittner, Colgate Co.; James Kendall, Columbia University; H. C. Parmelee, *Chemical and Metallurgical Engineering;* and H. G. Sidebottom, Jayne & Sidebottom, Inc.
Councilors: C. A. Browne, C. E. Davis, B. T. Brooks, James Kendall, H. C. Parmelee, H. G. Sidebottom, R. G. Wright, F. H. Getman, Ellwood Hendrick, K. G. McKenzie, David Wesson, H. R. Moody, M. H. Ittner, A. C. Langmuir, D. W. Jayne, B. R. Tunison, A. W. Thomas, Williams Haynes, Lois M. Woodford, Mary E. Pennington, and F. M. Turner.

Length of Work Periods on Continuous-Process Work in the Chemical Industries[1]

By Horace B. Drury[2]

INSTITUTE OF ECONOMICS, WASHINGTON, D. C.

During the past two years the writer has been engaged in an investigation of the labor shift systems employed in the various continuous industries.[3] Everyone has heard of the twelve-hour day in the steel industry; but it has not been generally realized that this same problem is to be found to a greater or less degree in many other lines. There are about forty important American industries which at some stage of their work require the services of men for twenty-four hours a day. In these industries it is usually inconvenient, if not impossible, to employ labor on the familiar ten-hour or nine-hour day basis. The practical choice lies between having two groups of men work twelve hours each or three groups of men work eight hours each. Until about a decade ago, not only the steel industry, but most of the other continuous industries, were on twelve-hour shifts. More recently there has been a widespread tendency toward three shifts. To-day there are few continuous industries where some plants do not operate on three shifts; but, on the other hand, there are few in which there are not some plants still on two shifts. The purpose of this article is to sketch the general situation with respect to shifts, particularly in the chemical industries, and to discuss the results which have followed where plants have changed from two to three shifts.

IN CONSIDERING the chemical industries, nothing will be said concerning steel or the other metal industries. These are, of course, chemical, especially in ore reduction and refining. But the importance of the metal industries, and the special character of the equipment and processes employed, has set these industries apart as a field to themselves. Of the chemical industries that lie outside the field of metallurgy, the number involving continuous work is large. The manufacture of glass, cement, lime, brick, pottery, heavy chemicals, fertilizers, explosives, dyes, soap, corn products, industrial alcohol, distilled wood products, electrochemical products, drugs, sugar, salt, petroleum products, cottonseed oil; paper, rubber, and gas—all involve a larger or smaller proportion of continuous work. They represent every stage of shift practice from industries wholly on twelve-hour shifts—in some cases even with day workers on twelve hours—to industries that are wholly on eight-hour shifts.

INDUSTRIES ON TWO AND THREE SHIFTS

Among the chemical industries that are practically without exception on twelve-hour shifts are the acid plants in fertilizer works, the cottonseed crushing industry, and the refining of Louisiana cane sugar. On the other hand, the refining of petroleum and continuous-process work in the rubber industry seem to be universally on three shifts. The manufacture of heavy chemicals is in most cases on three shifts; the twelve-hour shift in the manufacture of gas has practically disappeared. In many parts of the country the burning of brick is altogether on twelve-hour shifts, but elsewhere, particularly in Illinois, three eight-hour shifts have been introduced with great success. A somewhat similar situation prevails with respect to burning pottery and terra cotta. In most parts of the country the burning of lime is wholly or almost wholly on two shifts, but near Philadelphia some exceptional results have been obtained with three shifts. Likewise, beet sugar is generally refined on two shifts, but one important company has made an outstanding success of three shifts. The most important company refining imported sugar, with plants in many seaport cities, is successfully operating on three shifts. The cement industry is divided between two-shift and three-shift operation. The twelve-hour plants are still in a majority, but an important portion of the industry, including two of the largest companies as well as many of the smaller companies, is on three shifts. A few cement plants are on a mixed system of part two shifts, part three shifts. The manufacture of table salt would seem to be mostly, but it is not altogether, on three shifts. Paper was one of the earlier industries to move toward three shifts, or "tours," as they are called; but there are still a considerable number of paper mills on two tours, especially in the manufacture of certain types of paper, as tissue paper, and in certain localities which lie apart from the larger paper manufacturing districts.

The manufacture of plate glass and window glass is mainly on three shifts, though with exceptions in the case of a few plants or a few occupations. Twelve-hour shifts are worked to a limited extent in other branches of the glass industry, mainly about the furnaces. The main plants manufacturing industrial alcohol are on three shifts, but there is a considerable amount of twelve-hour work in plants engaged in wood distillation. The largest company manufacturing corn products is on three shifts. The largest manufacturer of explosives and allied chemicals has most of its shift work on three shifts; in this industry, however, the volume of shift work is small. The manufacture of dyes and soap requires little continuous work. In some cases this is on twelve-hour shifts, but the volume of such work amounts to very little in the aggregate. The electrochemical industry is on three shifts in the North, but in the South on two shifts.

EFFECT ON PLANTS OF CHANGE TO THREE-SHIFT OPERATION

In view of the great variety of the chemical industries, the diversity of their processes and equipment, and the diversity in their practice regarding two-shift and three-shift operation, it is difficult to draw conclusions which will be generally applicable regarding the policies that have been pursued in the matter of shifts or the results that have followed; nor is it possible within the limits of an article to give a full account of the situation which has developed in each industry taken by itself. The general statement may be made, however, that whereas a few years ago three eight-hour shifts were unknown in most of the industries mentioned, at present three shifts have displaced two shifts in some plants in all of the chemical industries, with the exception of two or three. With but very few exceptions, plants which have once gone to three shifts have remained on that system, or at least have not returned to twelve-hour shifts. This was shown very clearly during the depression which began in 1920–21. At that time many plants which had put their day workers on eight hours during the war went back to nine or ten hours, but the plants which had gone from two to three shifts during the war did not, except in rare instances, go back to two shifts. This was so although in most of the continuous

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[1] Received November 1, 1922.

[2] Member of the staff.

[3] Investigation carried on under the auspices of the Cabot Fund and of the Federated American Engineering Societies.

industries the three-shift plants were competing with plants which had remained on two shifts.

One reason why plants have been able to go from two shifts to three shifts and remain on that system in competition with other plants which have not made the change is that the labor cost for shift work is usually not a decisive factor. The shift workers are usually in a minority, sometimes very much in a minority. When allowance is made for these facts: first, that labor cost is only a part of total cost; second, that shift labor is only a part of total labor; third, that the employment of an extra shift involves an enlarged payroll only to the extent that hourly wage rates are increased or new salaried men taken on; and fourth, that such expense is offset to the extent that it is possible to increase efficiency—in short, when the threatened increase in cost is carefully sifted, it is invariably found that the percentage of increased cost necessitated by three-shift operation is much smaller than it would at first thought appear. Hence, the greater cost of three-shift operation is smaller than the differences in cost between plants because of differences in location, equipment, management, etc. Much or all of it may be recoverable through increased efficiency or better spirit. In any case, the issue of continuing or abolishing twelve-hour work becomes one which a management can afford to settle on the basis of its own feeling on the matter, the sentiment of the men, and the attitude toward twelve-hour work assumed by the general public.

Attitude of Labor

There can be no question but that labor as a whole is better satisfied on eight-hour than on twelve-hour shifts. There can be no better test of this than the statistics of labor turnover and those of absenteeism. One thing on which the evidence is practically unanimous is the fact that the three-shift system has in practically all cases reduced labor turnover and absenteeism, usually to a striking degree. This is so even although the men may earn considerably less per week on eight hours than on twelve hours. The general spirit of the men as evidenced by willingness to coöperate with the management is also better on eight-hour shifts.

Not all the men welcome the reduction in weekly earnings which ordinarily accompanies a reduction in hours from twelve to eight. Not always are they anxious to work a little harder for eight than for twelve hours so as to avoid a reduction in earnings. Sometimes managers have striven for years to induce their men to go to three shifts on the basis of the first or the second of these adjustments. This applies especially to the older men and to that element of the foreign born who have not yet become Americanized. But the seriousness of this resistance has been greatly exaggerated. Usually it lasts only until the men have adjusted themselves in mind and habits to the new system. The men who object to three shifts, after a brief experience with it, almost always prefer it and would not want to return to two shifts. The few exceptions to this rule are usually unimportant. Among American workmen there is often a passion for eight-hour as contrasted with twelve-hour shifts. On the whole, if the initial disinclination of the workmen to change of any sort is tactfully dealt with, and the change is made in a spirit of fairness and mutual accommodation, it will be found that the weight of opinion among the men is overwhelmingly in favor of three shifts.

Problem of Wage Adjustments

In the matter of increases in wage rates in going to three shifts there has been great diversity in practice. Sometimes as much is paid for eight hours' work as for twelve hours' work—that is, the hourly wage rates are advanced fifty per cent. Sometimes no change is made in hourly wage rates—that is, the men receive one-third less weekly pay. The policy which has been followed in this matter has been influenced a great deal by the general tendencies in respect to wages and employment at the time the change from two to three shifts is made. When wages were going up rapidly, as during the war, it was not uncommon for companies to pay men almost as much for eight as for twelve hours' work. But this should be considered as being in lieu of an actual increase in weekly wages which would otherwise have occurred. During periods of widespread depression and unemployment, hourly wages have often been kept about stationary, the decrease in hours taking the place of a laying off of a greater or smaller proportion of the force. Usually there is some increase in hourly wages on changing from two to three shifts, but not enough to make the daily earnings as great for eight as for twelve hours' work. A plan by which the cost of shortening the day is divided between employer and employee is usually acceptable to both parties.

From the fact that there is no uniformity regarding adjustments in wage rates, it is obvious that there can be no uniformity in the matter of increase or decrease in costs in going to three shifts. If the men receive no higher hourly wage rates than before, there is obviously no occasion for increase in labor cost even if fifty per cent more shift men should be employed. If hourly wage rates are advanced, there need be no increased cost if the efficiency of the plant can be increased in an equal measure by a reduction in the number of men required at any one time, by an increase in output, or by savings in materials or in the cost of maintaining equipment. In most continuous industries it is not an easy matter to increase efficiency to such an extent as to make up for any considerable increase in hourly wage rates. Hence, many plants that have made substantial increases in wage rates in going to three shifts have found that their labor costs have risen. In fact, this is usually the case. Nearly always, however, such plants have indirectly received some benefit through lessened labor turnover and a more satisfied feeling on the part of the men, including a willingness to work under conditions and at times (as for instance during hot weather) under which they would have refused to work had they continued on twelve-hour shifts.

Examples of Positive Gain from Three-Shift System

It is an interesting and encouraging fact, however, that in many of the continuous industries, including the chemical industries, there have been instances of plants which have made a positive success of going to three shifts, not only neutralizing their losses but realizing tangible gains. This has been notably true of certain plants in the cement industry, the lime industry, the brick industry, the refining of beet sugar, the refining of imported cane sugar, the manufacture of sulfuric acid, and the manufacture of paper. Excellent results, though not marking quite so definite a gain, have been obtained in the manufacture of terra cotta, in processes preliminary to the manufacture of soap, and in the electrochemical industries. Satisfactory results have also been reported for the various branches of the glass industry, for petroleum refining, and for miscellaneous chemical industries.

The School of Chemical Engineering Practice of the Massachusetts Institute of Technology has this year an enrollment of 65 men, representing the following educational institutions:

Armour Institute of Technology
Bates College
California Institute of Technology
Case School of Applied Science
Cornell University
Harvard University
Imperial College of Science and Technology (England)
Indiana University
Iowa State University
Massachusetts Institute of Technology
Middlebury College
Northeastern College
Oberlin College
Princeton University
Pritchett College
Rhode Island State College
Richmond College
Stanford University
Tulane University of Louisiana
University of Chicago
University of Detroit
University of Minnesota
University of North Dakota
University of Pennsylvania
University of Rochester
University of Wisconsin
Washington University
Wesleyan University
Western Reserve University
Williams College
Yale University

Trend of Modern Fertilizer Plant Construction[1]

By Peter S. Gilchrist

CHARLOTTE, N. C.

There is a great tendency to get away from the time-honored fertilizer buildings, brought about by the difficulty of getting sufficient labor for short seasons, high-wage schedule, and heavy insurance, and the fact that manufacturers are beginning to realize that they will have to operate on a closer margin of profit. In this paper we have pointed out the requirements for construction of a modern fertilizer plant, together with a description of present practice in manipulation of equipment and handling of materials.

A MODERN factory should meet the following principal requirements:

1—Be a substantial structure and of such materials and construction as to entail the minimum upkeep and obtain the lowest rate of insurance.

2—Be so designed that the minimum amount of labor shall be required for operation, and that the fertilizers are produced in the best chemical and mechanical conditions.

3—Have printing press for bags.

4—Have ample trackage.

5—Make provision for condensing noxious vapors.

6—Locate office and bag shed convenient to factory.

7—Provide ample fire protection.

8—Be equipped with mechanical labor-saving devices when they can show a definite return upon the investment after deducting wear, tear, and depreciation.

9—Be so designed that the materials are handled as little as possible, and the manufacture may be as nearly continuous as practicable.

10—The grinding material should be carefully selected so that the rock is of correct fineness to obtain the best mechanical reactions with sulfuric acid, thereby producing a high available with low insoluble and with a negligible percentage of free acid.

11—Acid phosphate, when cured, should be of the lowest moisture content and in good mechanical condition.

12—Sufficient equipment should be installed so that all fertilizer materials are ground to sufficient fineness before manipulating, and the manipulating should take place considerably in advance of the shipping, as the fertilizer should be shipped as dry as possible so that it will be in good mechanical condition for drilling. Furthermore, it should be of sufficient dryness so that the weights will be accurate.

13—Provisions for filling and weighing the bags and moving them to the cars with the least possible delay in handling.

LOCATION OF PLANT

Care should be taken to get the local advantages of the site with relation to wharf, railroad connections, and contour, as well as the receiving of the various raw materials and shipping of the finished fertilizer.

BUILDINGS

The buildings should be of concrete base with steel frame and hollow tile walls with noncombustible roof of tile, cement, or gypsum, the idea being to make the structure as near fireproof as possible, and to reduce the upkeep and repairs to the minimum.

Light and ventilation are now considered absolutely essential to economical operation, as it means less waste of materials, and labor gives a higher efficiency when operating in a well-lighted and ventilated building.

The loading platform should be housed in, with continuous sliding doors for protection from the rain and severe cold weather. The floors for this platform and for the main buildings should be of hard-surfaced concrete.

ROCK STORAGE

There should be one or two concrete or steel silos of ample capacity, located conveniently so that cars can discharge the phosphate rock into silo elevator, or be unloaded from cars by automatic shovel into elevator, as the case may be. If rock is coarse a crusher is used through which the rock passes on its way to the elevator, so that the greater part of the rock can run from the silos directly into the grinding mill, arrangements being made so that the balance of the rock in the silos can be transferred mechanically to the mills.

GRINDING AND ACIDULATING

Many different mills are used for grinding the rock, the type being determined by capacity, repairs, and depreciation and power consumed. Some mills give a finished product, but it is generally advantageous to use air separators through which the partially ground rock is passed, or to maintain a strong suction on the mill and pass the air and finely ground rock through air separators. Considerable difference exists as to how fine the rock should be ground. Many superintendents look upon capacity as the goal, and are content with 96 per cent through 60 mesh in place of thinking in units of available P_2O_5 in the acid phosphate. Modern plants require a 98 per cent product through 80 mesh as a minimum, while some aim for 96 per cent through 100 mesh.

Fine grinding enables a minimum amount of sulfuric acid to be used, the reaction is quicker and more intense, with the result that the greater heat dries off more of the moisture, all of which tends to dryer acid phosphate and low insoluble.

Acid phosphate dens are of various designs, the great essentials being solidity, ease of discharging, and a product as dry as possible and in a fine mechanical condition. Hand labor in dens is very objectionable and difficult to handle, apart from the cost of same. There have been developed other devices for discharging the dens—an electric shovel is used in some instances where a clam-shell or orange-peel bucket operated by an overhead crane is used. Mechanical discharging dens are used, such as the Svenska and the Forbis. Several of each are in operation in this country.

The mechanical discharging den is receiving the most consideration to-day. The grab-bucket operation, while giving a large tonnage, does not have the acid phosphate in as good mechanical condition as it might be, and the compression the phosphate receives is apt to be detrimental to the P_2O_5 solubility. In mechanical discharging dens it is most important that as little machinery be used as possible, for the free phosphoric acid and the corrosive action of the gases act rapidly on iron, and this naturally entails a heavy upkeep.

The Forbis den, in the writer's opinion, comes nearer giving an ideal equipment. It consists of a circular concrete den, hollow in the center, operated on a single circular track, making a complete revolution in about 12 hrs. and requiring not over 3 h. p. to revolve it when loaded. Above the den is a solid stationary platform with a cover for the den suspended from it.

On the platform is the mixer with weighing hopper and acid boots, the excavator for the acid phosphate, the fume pipe,

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[1] Presented before the Division of Fertilizer Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

etc. The measuring and weighing devices for the raw materials are such as to get very accurate results, this being a very important part of the manufacture. The mixing of the acid phosphate and excavating the acid phosphate go on simultaneously. The acid phosphate remains in the den 24 hrs. before it reaches the excavator. Since the construction of the den is such that it is not opened up, the phosphate retains the heat until it is cut. The cuts are about $^1/_8$ in. thick when the steam is liberated and drawn off by an exhauster.

The thin layer of phosphate, as it is cut, falls onto angle-iron trays where it is discharged to any convenient point, its condition resembling sand. The excavator is simply a two-strand elevator with links capable of withstanding the free phosphoric acid present, with angle-iron trays in place of buckets.

The capacity of the den is from 100 to 150 tons per day, but if operating continuously it is approximately 400 tons per 24 hrs. The den only revolves while the mixing is being done; when completed the den is stopped.

The finished product as it leaves the den is very light and contains usually about 11 per cent moisture, with about 1 to $1^1/_4$ per cent insoluble P_2O_5, which in a short time rapidly reduces. It is equivalent to acid phosphate made three to four weeks by the other methods. There is only one man operating it—namely, the mixer—and either a crane man or car man to take it to storage from the den.

HANDLING ACID PHOSPHATE

This is done most economically by the electrically operated grab-bucket crane of from 2- or 4-cu. yd. capacity. One crane man at one of the factories handles 6000 tons per 10 hrs. with a $2^1/_2$-cu. yd. bucket. No hand labor or any other mechanical device has been able to come anywhere near this when labor and equipment upkeep are taken into consideration, as it not only handles the material but digs it at the same time.

MANIPULATION OF COMPLETE FERTILIZER

Accurate weighing is absolutely essential to success. The inaccurate weighing of ingredients with consequent overages is one of the chief sources of loss to manufacturers.

Usually, a series of hoppers is elevated so as to admit of a wide belt being installed to carry the materials to the manipulating or bagging machines, as the materials are discharged from the scale hoppers and located underneath the storage hopper.

The crane or other mechanical device puts the various ingredients into the hoppers, which have close cut-off gates. The scales have large dials so that the operator sees the weight all the time the material is on the scale and can shut off instantly when the desired weight is attained. The scale hoppers are discharged at a given signal, and refilled for the next batch. The hopper system calls for fewer men than are generally needed. The manipulated goods are taken by the crane to storage and are finally passed through bagging machines.

The manipulating and bagging machines are of various types. The vibrating screens are receiving much attention. Good work has been done with the hexagonal revolving screens with suitable tapping devices. Rapid operation is necessary to get tonnage; hence, a batch mixer has to be used that will fill, mix, and empty in a very short time. Automatic weighing machines are being extensively used, and little difficulty is experienced when the goods are dry.

Instead of weighing the bags on the ground floor, this is being done on an elevated platform, with an endless slat conveyor located so that as the weigher drops the bag it falls onto the slat conveyor where the bag sewer gets it. The bag travels till it is discharged at the end, down a chute, where the chute man directs it onto a truck—three 200-lb. bags or five 135-lb. or six 100-lb. bags being dropped onto a hand truck. The truck man has no difficulty in handling 600 lbs. to a load on a good floor, and discharging it in the car stacked, obviating stackers unless the car is to be heavily loaded. This method gives a clean bag with accurate weight. Test bags should be taken at intervals to see that the weight is correct.

The complete fertilizers are delivered to a hopper in front of the bagging machine, requiring one man at the elevator, one on the machine, one weigher, two sewers, one chute man, two or three tuckers, one tag boy, and, if stackers are used, two additional men. These easily do 200 to 225 tons per 10 hrs.

A modern factory can put out fertilizer in good mechanical condition without harm to the bags, maintaining a uniform output with a very small labor charge; the overhead expenses are not excessive and the upkeep of a well-designed and well-built factory is low, enabling the manufacturer to produce his goods at the lowest possible cost and make a profit when others fail to do so.

In days of close competition the old-type factories are at a great advantage as compared with the modern factory.

Hotel Accommodations for the Spring Meeting of the A. C. S.

It is very apparent that the coming spring meeting of our SOCIETY will be very largely attended, and it is recommended that all who desire hotel accommodations make their reservations as early as possible—at least thirty days in advance of the meeting. The hotel headquarters will be at the Hotel Taft, and the management of this hostelry advises that reservations for this hotel be made, if possible, ninety days in advance. In case there is an overflow which cannot be provided for with accommodations in New Haven, arrangements have been made whereby guests may obtain suitable reservations in hotels of neighboring cities—namely, Hotel Stratfield in Bridgeport, Conn., Hotel Winthrop in Meriden, Conn., and Hotel Elton in Waterbury, Conn.

The committee on hotels and transportation have canvassed very carefully the hotel and apartment house situation and desire to announce the following list of hotels, arranging them as nearly as possible in the order of convenient location.

NEW HAVEN HOTELS

	CAPACITY	RATES	
		Single Room	Double Room
Taft	400	$3 to $3.50	$5 to $6
Garde	100	$2.50 up	$5 to $6
Duncan	100	$2 to $3	$4 to $6
Bishop	50	$3	$5
Strand	40	$1.50 to $3	$3 to $5
Liberty Baths	150	$2 (flat rate and for men only)	
Royal	75	$1.50 (men only)	$2 to $3

OUTSIDE HOTELS

	CAPACITY	RATES	
		Single Room	Double Room
Stratfield, Bridgeport	100	$3.50	$5 to $6
Winthrop, Meriden	50	$2 to $3	
Elton, Waterbury	100	$2.50 up	$5 to $8

The Hotel Taft offers a special arrangement on the American plan:

Double room, bath, meals (3) $13.00 per day
Double room, bath, meals (2) $11.00 per day

It is too early for the committee to make any announcement regarding possible accommodations in university dormitories. It can be stated, however, that the Yale dining hall will be in operation during the week of the convention. The members of the hotel committee will be glad to assist in every way possible in the making of early reservations.

HOTEL AND TRANSPORTATION COMMITTEE

DR. RALPH W. LANGLEY, *Chairman*, 84 McKinley Ave., New Haven, Conn.
PROF. H. W. FOOTE, Sterling Chemistry Laboratory, New Haven, Conn.
DR. E. MUNROE BAILEY, 621 Elm St., New Haven, Conn.

AMERICAN CONTEMPORARIES

Harvey Washington Wiley

THERE is a large fraternity, unorganized and unofficered, of "Men Who Worked under Dr. Wiley." When chance brings two or three of them together, some one invariably asks, "What do you hear of the old man?" and someone always remarks, "Isn't he a wonder?"

Certain characteristics stand out as the basis of this loyalty. First of all, everything about Dr. Wiley is big—his body, his mind, his policies, and his philosophy of life. He never "passes the buck," but assumes full responsibility for the work of his assistants. Once, when directed by the President to discharge a subordinate, he replied, "He was acting under my general directions. If his action was at fault I am responsible."

Dr. Wiley has always radiated vitality. He has never crystallized in opinions or habits. At seventy-eight he directs his farm, writes magazine articles, gives extensive courses of lectures, and devotes more time than the average father to his two small boys. He also takes an active part in movements that relate to public welfare, especially public health. A walk to and from his office—a total distance of four miles—is his minimum daily exercise. His interest in athletics has not abated and he takes especially keen pleasure in matters pertaining to baseball and football. He has always been known for his great physical and mental vigor, quick wit, and ready anecdotes. As a lecturer he has few equals. He humors his audience, recognizes its different elements, wins its attention, and, finally, does with that audience anything he desires.

Harvey W. Wiley

His associates in the Bureau of Chemistry used to marvel at his concentration. His mind focused like a lens on each successive undertaking. He thought rapidly, formed his opinion, and then dismissed the subject from his mind. After a day of the most intensive work, even in the midst of his greatest controversies, he always closed the office door on the problem, and when he reached the street was discussing other matters. Work, worry, excitement, or controversy have never interfered with his sleep.

Incessant work and tireless application mark every period of Dr. Wiley's life. As a child he worked on his father's farm in Indiana. During his college life he cooked for himself the food that he brought from his father's farm, and burned wood that he himself had cut. As a medical student he supported himself by teaching Latin and Greek—his fondness for the classics has in no wise diminished.

While a student in Berlin he became acquainted with the polariscope, an instrument then unknown in this country. This was the real starting point of the activities that won for Dr. Wiley the newspaper title of "Father of the Pure Food Law." Returning to Purdue, he persuaded the university to purchase a polariscope and secured an appropriation of fifty dollars from the State Board of Health to defray the cost of samples of sugar, sirup, and honey.

In 1883, when he was thirty-eight years of age, Dr. Wiley was appointed chief chemist of the United States Department of Agriculture—a position which he held for nearly thirty years. Under his direction substantial contribution was made to agricultural chemistry, especially to the chemistry of cereals and soils. He was a potent factor in the development of the beet-sugar industry and introduced chemical control into the cane-sugar industry—resulting in extensive and fundamental changes therein. His office early became the headquarters of the Association of Official Agricultural Chemists. Shortly after he became chief of the Bureau, Dr. Wiley was made secretary of that association, and remained secretary and editor of its proceedings throughout his official life, and since then has been its honorary president.

But it is because of his work in connection with the control of the manufacture of foods that Dr. Wiley is best known. In addition to epoch-making contributions to the laboratory phases of the question, he early took the lead in the nation-wide movement for legislation to control the purity of foods sold on the market. Undoubtedly, his own personality was a great factor in creating the public interest that led in 1906 to the adoption of the Pure Food Law of which he was the author. He is always convincing, arresting, and at times spectacular. He won national popularity through the same buoyant friendliness that made it necessary for him somewhat earlier in life to answer to charges that he had so far violated professorial dignity as to ride a bicycle and play ball with the boys. He pays scant attention to precedent and convention, and does not hesitate to establish precedents when occasion demands.

In the conduct of the affairs of the Bureau of Chemistry, however, he insisted upon the strictest possible compliance with every law and every regulation. Under no circumstances would he permit evasion or circumvention of the Civil Service law or regulations. In the purchase of supplies he insisted on strict obedience to the laws governing such transactions and to the interpretation of the comptroller. On one occasion, when it was pointed out to him that his attitude was neither in his personal interest nor that of the Bureau of Chemistry—that it did not make for efficiency or economy—he replied, "That is the law. Some day there will probably be an investigation of this bureau, and our affairs will be found in order."

Sterling integrity of mind and purpose, rugged straightforwardness, and imperturbable good humor characterize all his actions and make the name of Harvey W. Wiley a household word that links science with humanity.

W. D. Bigelow

Indigo Investigations

Indigo is one of the most important dyes manufactured in the United States. The process at present in use in this country has been not altogether satisfactory, and an investigation has been undertaken by the Bureau of Chemistry with a view of substituting an alternative method for the preparation of this dye. A survey of the entire process has been made, and the results obtained indicate that indigo of good quality can be obtained at a somewhat lower price than is possible by the method now in vogue.

A new dye similar in dyeing properties to indigo has been made from cymene; a waste product obtained in the preparation of paper pulp from certain resinous wood.

Louis Pasteur—His Contribution to Science

By I. K. Russell

1133 Fullerton Ave., Chicago, Ill.

ONE OF THE remarkable facts about the life of Louis Pasteur is that the 100th anniversary of the date of his birth finds him more alive in the hearts of humanity than he was at any time during his unusual thrust into the events of modern life.

The French government drew perhaps as strong a reaction from peasants and artisans as it did from the world's foremost scientists to its proposal to celebrate the 100th anniversary of Pasteur's birth on December 27, 1922. The scientific world can claim Pasteur the scientist, for its own, but Pasteur the world hero, it must share with the cattle raisers of France, whose herds Pasteur saved through finding the nature of the anthrax plague; with the silkworm breeders, whose industry he saved by stopping a contagious disease among the silkworms; with brewers, to whom he explained the cause of bitter beer; with milk producers, whom he gave control of putrefactive bacteria and bacteria which too speedily soured the milk; and even with bakers, for to the baking industry Pasteur introduced the modern science of baking with all that is accomplished through the complete control of fermentation and the leavening process.

Chemists the world over can take special pride in this 100th anniversary of the birth of Pasteur, for he seemed to make his life a living personification of the spirit of research. Acute observations of things other men have seen since the beginning of time gave him the key to some of the most consequential facts of modern life.

For instance, he observed early in life that dough would turn sour in bread batch, while baked bread would not turn sour. He asked himself the question of what happened in the oven to change the nature of the dough so that it would no longer turn sour. He worked with microscope and culture media to find out, and succeeded in discovering the nature of yeasts. He found they were living self-reproducing cells, and that in feeding upon the dough they ultimately were responsible both for fermentation and for the souring of the dough that resulted when they worked too long within its midst.

Inconspicuous as he was—a laboratory research man when he made this discovery—it brought the French government to him with the problem that, perhaps, set him upon the major trails of his long and useful life.

"If yeasts are separate living organisms within dough that sour it," he argued, when the government asked him what he could do with soured wine, of which the French fleet's sailors were bitterly complaining, "perhaps we can save the wine by heating it until its yeasts are killed. Perhaps the same treatment given bread when baked will make it possible for the French war fleets to put to sea with good wine, and still have good wine in what casks are unconsumed when the fleet returns."

Pasteur was a devotee of applied science. He found out at what temperature wine yeasts and acetic acid bacteria could be killed in wine, so that if it was kept free from access of air it would remain permanently sweet. The French sailors then went to sea with a cheer for their wine supply, and Pasteur applied himself to other problems just as practical as this.

We may almost say that modern medicine, in its power to control contagion, is a by-product of Pasteur's experiments in the nature of fermentation. At that time throughout the world of medicine it was believed that putrefactions and degeneration of human tissue occurred spontaneously from elements within the human body.

While he was working as a chemist he happened by accident to see litters being carried into a building adjacent to his laboratory. Later he saw coffins being carried out. Upon inquiry he found that the building was an annex to a maternity hospital. It set him to thinking and he wished to try out the theory that was already beginning to form in his mind—that there were air-borne bacteria which leavened bread if they fell upon dough from the air and spoiled wine if they fell into it from the air. He went to the hospital—and on the very first visit of his life to a hospital he qualified as the father of antiseptic medicine and the father of modern sanitation. He noticed the way the surgeons used their instruments and the nurses their bandages, made out of old, unsterilized sheets. He took the instruments from a surgeon's hands and passed them through a flame. He took the bandages from a reluctant nurse and baked them, as he had the wine and the dough in his previous experiments. The death rate was lowered almost immediately. Before this time those who entered the hospital expected to die; after this they expected to live.

Perhaps laboratory and clinic were never joined in a common cause out of which so much good for humanity flowed as at the clinical meeting at which Pasteur came from his laboratory to the Academy of Medicine and demonstrated to the world by means of sick hens suffering from splenic fever or anthrax, the tremendous importance of temperature in the control of bacterial growth. He had noticed in a barnyard where the cows and the pigs died of splenic fever during an epidemic that the hens were immune. He experimented and found he could give anthrax to all farm animals but the poultry.

He found that the bacteria-producing anthrax would not live in the blood of a hen, which is four degrees warmer than the blood of mammals. With one of those brilliant inspirations which come to born scientists, Pasteur conceived the idea that if he could reduce a hen's temperature through chilling her, until her blood was at the temperature normal for mammals, her immunity to anthrax infection would disappear.

He promised the Academy of Medicine that he would bring its members some dead and dying hens in whose bodies he would ask them to find, through clinical operation, samples of anthrax germs. Since he had just been insisting that such a thing was impossible, both the Academy of Science and the Academy of Medicine sent its ablest representatives to the test. Pasteur kept his promise and appeared at the Academy of Medicine with the hens. He threw a dead hen down before the master physicians, and stated that it had died twenty-nine hours after inoculation. He told of keeping the hen in an ice bath for some time previous to inoculation.

"Ah," said some of the Academicians, "death might have resulted from the chill."

"Then" said Pasteur, as Vallery-Radot, his biographer, records the great meeting, "I will show you this gray hen. She was in the bath as long as the other one which died, but she was not thereafter inoculated." The gray hen was lively, happy, and normal.

Thus Pasteur has awakened the world to the importance of the infinitely small. He was now on the track of finding important controls for this bacterial life, and in noticing the tremendous consequences of a difference of four degrees he had struck at the heart of one of the most important methods of control even yet discovered.

There were still some flings at Pasteur, even as an accepted Academician. With great passion Pasteur turned upon his detractors in the Academy. He cried out:

> I say it with no sham modesty, I have considered that my only right to a seat in this place is that given me by your great kindness, for I have no medical knowledge. I, therefore, consider that I must be more scrupulously exact than anyone else in the presentations which I have the honor to make to you. I should promptly lose all credit if I brought you erroneous or merely doubtful facts. If ever I am mistaken—a thing which may happen to the most scrupulous—it is because my good faith has been greatly surprised. I have come among you with a program to follow which demands accuracy at every step. I can tell you my program in two words. I have sought for twenty years, and I am still seeking "spontaneous generation," properly so called.
>
> If God permit I shall seek for twenty years and more the spontaneous generation of transmissible diseases. In these difficult researches, while sternly depreciating frivolous contradictions, I only feel esteem and gratitude towards those who may warn me if I should be in error.

Thus Pasteur laid down the platform of every research chemist, as he stood at the threshold of his career as a medical Academician.

The hospital from now on claimed him more than did his physiological laboratory. He attacked the problem of bubonic plague; in the humble farmyards he found hens dead on their nests from chicken cholera. He had a heart for poor farmers, for his ancestors had been serfs. He isolated the chicken cholera germ and observed "the prodigious faculty of multiplication of microörganisms" when grown in a suitable culture medium. He noticed that the smallest drop of the infected culture medium on a crumb of bread caused the death of a hen. He noticed that the bacteria grew in the hen's intestinal canal and in the excreta spread infection to other hens. He was now on the trail of the method of the spread of typhoid, and yet many physicians had sneered at his ideas by declaring that "such mad gossip would one day lead to the notion that even typhoid was a germ disease."

Pasteur's genius for observation now brought out into the light one of the most important of medical discoveries. It marks the passing of his interests from the laboratory to the clinic, and marks the initiation of an entirely new field of medical technic.

Pasteur accidentally inoculated a hen with chicken cholera microbes that had stood in the laboratory for several weeks. He saw her become ill and then recover. It was a new experience, and he immediately reinoculated the hen with fresh virus. Fresh virus had never before failed to kill a hen, but this time it did fail. What could have attenuated the activity of the microbe?

Looking backward, we can easily see that here Pasteur first picked up the trail of discovering the nature of vaccine. Inoculation of the attenuated germs made it impossible for the fresh-culture germs to kill the vaccinated hens although all others speedily died. In a spirit of incomparable enthusiasm and happiness he set to work to apply what he had found in a farmyard to the contagious ills of mankind.

Mankind has always feared death by a mad dog's bite. In Mexico overseers of brush cutters go into the brush and simulate the cry of a mad coyote to make their workmen leap to tasks that must be accomplished before they can quit that neighborhood. What a glad day for the world, then, was it for fond parents to lead the victim of a mad dog's bite to Pasteur and have him cured! The method had already been discovered in the case of chicken cholera and had been applied in the case of a splenic fever plague.

For his work on carrying the theory on over into the case of rabies, Pasteur won himself a place as a world-wide hero. No wonder Huxley declared in a lecture at the London Royal Society: "Pasteur's discoveries alone suffice to cover the war indemnity of five milliards paid by France to Germany in 1870."

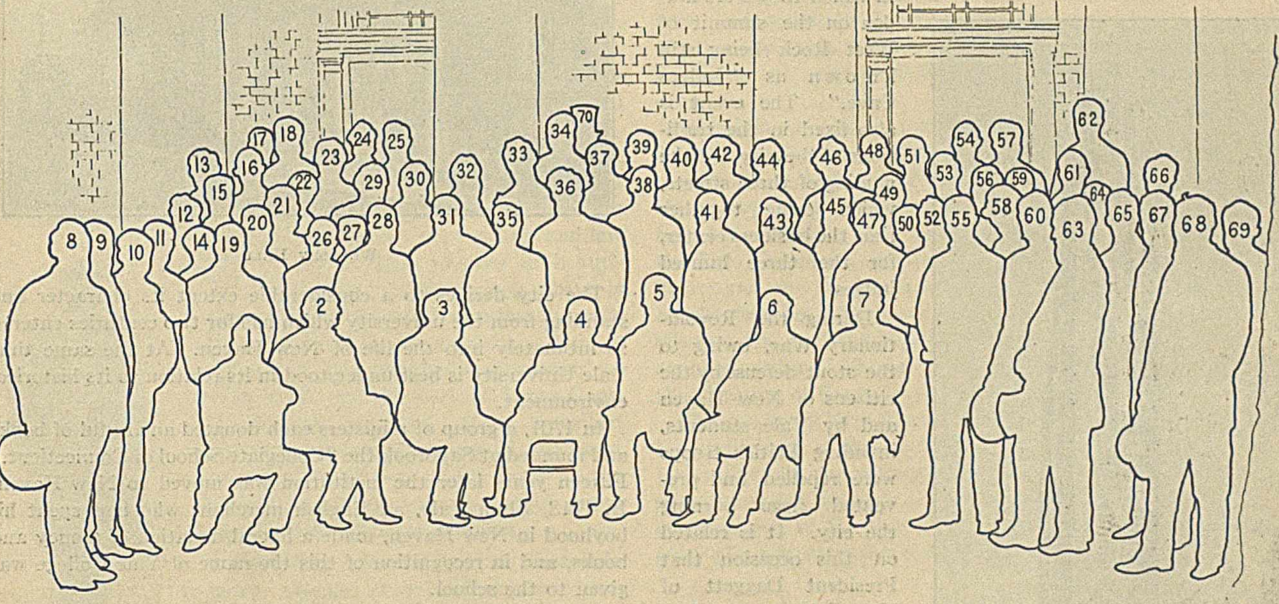
Priestley Centennial, Northumberland, Pa., July 31 to August 1, 1874

Among the most prized of the historical relics in the Chandler Chemical Museum of Columbia University are seven photograph negatives (6 × 8 in.) taken by Prof. Louis H. Laudy, of Columbia College, at the Priestley Centennial at Northumberland, Pa., in 1874. These negatives, which are the earliest photographic reminiscences of any meeting of American chemists, are the remainder and the more valuable of the original twelve plates described on page 465 of Vol. V of the *American Chemist* (1874–1875). They comprise (1) a large group of 70 attending chemists and visitors (see opposite page), (2) a small Columbia College group of 19 chemists and visitors, (3) a photograph of two tables of chemical apparatus that belonged to Dr. Joseph Priestley, the discoverer of oxygen, (4) a photograph of a table of Priestley's electrical apparatus, (5) a photograph of a table of miscellaneous apparatus (telescope, magic lantern, orrery, etc.) that belonged to Priestley, (6) a photograph of manuscripts, books, and other Priestley relics, with the Stewart portrait of Priestley, (7) a smaller (5 × 6 in.) photograph of an old print showing the destruction of Priestley's house and laboratory during the Birmingham riots of July 14, 1791.

The Chandler Museum has arranged that members and friends of the American Chemical Society may obtain unmounted mat prints from these interesting old but clear negatives at a nominal cost of 35 cents apiece, including first-class postage and packing. The two group photographs make excellent enlargements for a laboratory, office, or lecture room; they can be obtained for the 14 × 17 in. size at $1.50 a piece, including postage and packing.

Of the chemists and visitors in the large group, about 55 of the 70 have been identified. Among those identified are T. S. Hunt, J. L. Smith, F. W. Clarke, C. F. Chandler (all of these former presidents of the American Chemical Society), E. N. Horsford, B. Silliman, Jr., H. C. Bolton, E. Waller, E. L. Youman, C. A. Joy, S. P. Sharples, R. C. Kedzie, T. M. Drowne, P. W. Bedford, A. A. Breneman, W. H. Chandler, J. P. Remington, and many others. Owing to the fact that all the attending chemists were not in the group and that several unknown visitors were included in the picture, the identification of all the faces has not been possible. It is hoped that with the distribution of the picture among American chemists, other identifications may be made. Of the Columbia group, 18 of the 19 have been identified. A key to each of the group photographs ordered will be included along with the print.

Applications with remittances for the photographs should be addressed to T. L. Schultze, 297 Fulton St., Brooklyn, N. Y. In ordering photographs, the number of the negative according to the foregoing list should be indicated. These negatives will be left in the hands of the photographer only until March 1 next. Orders to be filled by him must be received before that date. [C. A. Browne and Ralph H. McKee.]



1—B. S. Hedrick
2—E. N. Horsford
3—T. S. Hunt
4—J. L. Smith
5—B. Silliman
6—H. Coppeè
7—Rev. T. R. Pynchon
8—Thos. Lyon
9—Conyers Button
10—
11—
12—W. M. Iles
13—
14—E. J. Hallock
15—W. H. S. Thorburn
16—John A. Church
17—
18—S. St. John
19—H. C. Bolton
20—C. F. Chandler
21—E. Waller
22—Arthur Macy
23—H. G. Torrey
24—E. L. Youmans
25—W. K. Kedzie
26—C. A. Joy
27—M. S. Thompson
28—S. P. Sharples
29—
30—
31—J. Priestley
32—S. H. Douglass
33—J. M. Maisch
34—R. C. Kedzie
35—M. B. Priestley
36—David Taggart
37—F. Hoffman
38—E. T. Cox
39—C. G. Wheeler
40—
41—
42—
43—P. W. Bedford
44—W. W. Daniels
45—H. B. Nason
46—A. P. S. Stewart
47—T. G. Wormley
48—F. W. Clarke
49—A. A. Breneman
50—C. S. Allen
51—
52—
53—H. Endeman
54—
55—P. Frazer, Jr.
56—A. H. Gallatin
57—C. H. Chandler
58—Traill Green
59—
60—W. H. Chandler
61—
62—J P. Remington
63—
64—E. W. Hilgard
65—A. R. Leeds
66—
67—T. M. Drowne
68—P. H. Vander-Weyde
69—
70—

SCIENTIFIC SOCIETIES

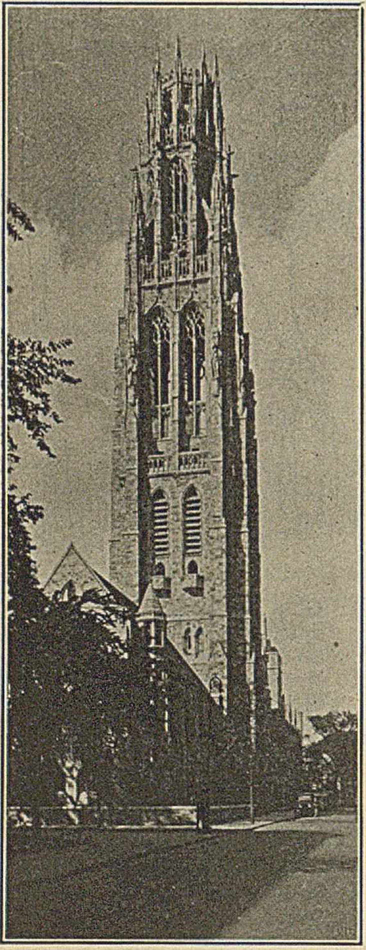
New Haven, Yale, and the A. C. S. Spring Meeting

(This material has been furnished by the New Haven Section and by the Yale Secretary's Office)

When the AMERICAN CHEMICAL SOCIETY meets in New Haven next April, its members will find not only the usual functions of such a meeting, but also many things of interest to see in the historic city of New Haven. At that time Yale University will open her beautiful buildings and grounds and all the famous collections of the university. The program will be arranged so that time and leisure will be afforded the visitor for the enjoyment of these things.

New Haven was founded in 1638 by a company of English Puritans, who landed at Quinnipiack, the Indian name meaning "Long River Place," and laid out a settlement. Of the nine equal squares into which the settlement was divided, the central square remains in its original dimensions as the "Green." Occupied by three churches which preserve colonial architecture at its best, this open space in the heart of the business district adds a distinctive charm to the city.

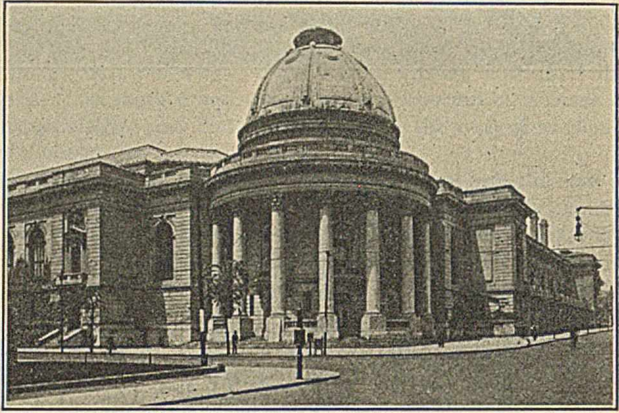
Upon the accession of Charles II to the English throne, the lives of the judges who had condemned Charles I to death were demanded. Three regicides, Whalley, Goffe, and Dixwell, were harbored and protected by the Puritans of New Haven, the cave in which they were hidden on the summit of West Rock being still known as "Judges Cave." The event is also fixed in the traditions of the city by the naming of three streets, which come together near the business center, for the three hunted judges.



ENTRANCE TO HARKNESS QUADRANGLE

During the Revolutionary War, owing to the stout defense by the citizens of New Haven and by Yale students, invading British troops were repelled and prevented from burning the city. It is related on this occasion that President Daggett of Yale College, who had been captured and forced to act as a guide, was compelled by the British forces to offer prayer for the King. He said "Oh, Lord, bless Thy servant, King George, and grant him wisdom, for Thou knowest, Oh, Lord, he needs it."

For many years New Haven was a shipping center, but after the War of 1812 its activities became largely manufacturing. To-day it possesses some eight hundred industries, employing over thirty thousand workmen. The products which come from its factories are varied, finished metal products all the way from steam boilers to machine tools and insulated wire being represented. The first rubber shoe factory that ever operated in the United States is located in New Haven and has grown into a large institution. The most extensive single industry is that of firearms, ammunition, and hardware made by the Winchester Repeating Arms Company. The population of New Haven, including outlying suburbs and villages, is nearly 200,000, this being the largest city in the state of Connecticut.



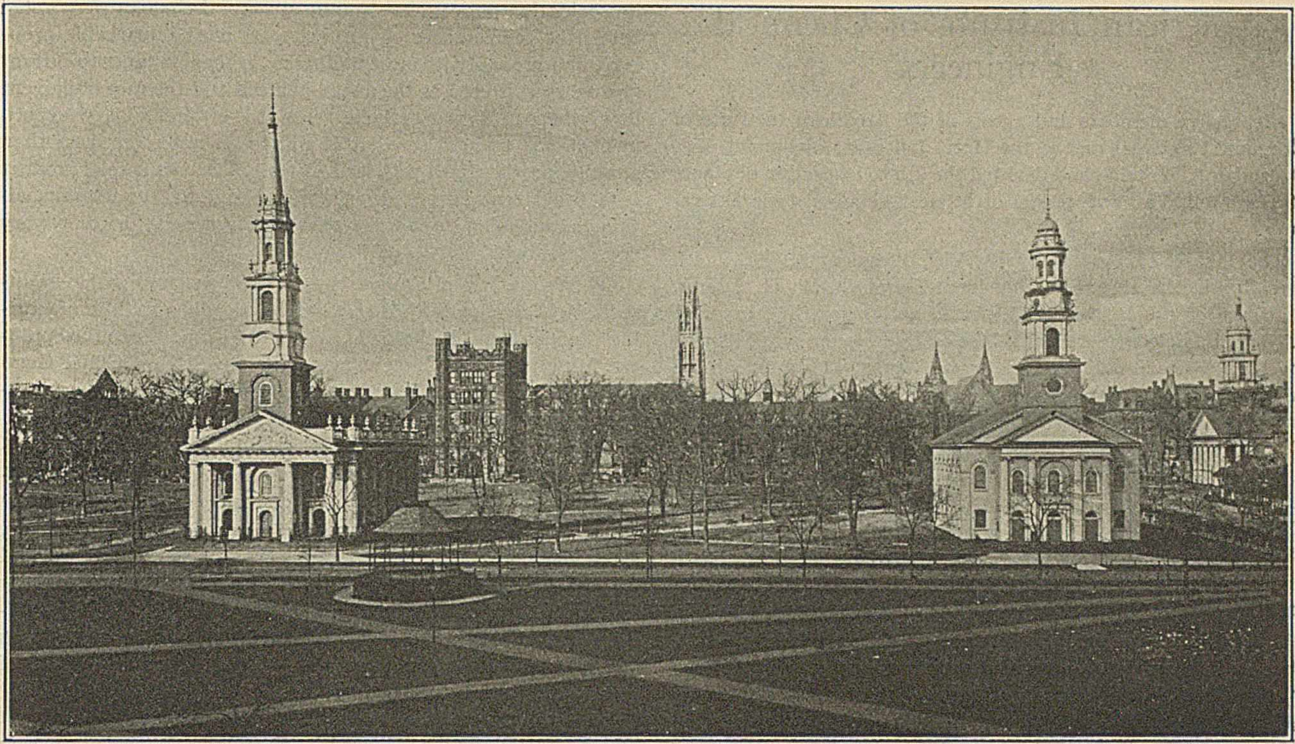
WOOLSEY HALL

The city derives to a considerable extent its character and standing from the university which has for two centuries entered so intimately into the life of New Haven. At the same time Yale University is best understood in its relation to its historical environment.

In 1701, a group of ministers each donated an armful of books and founded at Saybrook the "Collegiate School of Connecticut." Fifteen years later the institution was moved to New Haven. In 1718, Elihu Yale, an English merchant who had spent his boyhood in New Haven, made a liberal donation of money and books, and in recognition of this the name of Yale College was given to the school.

In 1759, a dormitory bearing the name of Connecticut Hall was added, up to that time all the college activities being centered in one building. Connecticut Hall, restored to its original form, still stands and is in daily use. In this building Nathan Hale lived as a student, and just outside the room he once occupied stands a statue of the young patriot and martyr.

Yale University, now well into the third century of its history, has an endowment of nearly $33,000,000. In addition to this there is a fund of $20,000,000, a bequest of the late John W. Sterling, a graduate of Yale College. This fund is being used for memorial buildings, the founding of lectureships and scholarships, and for endowment of professorships. The great Sterling Chemistry Laboratory, now just completed at a cost of $2,000,000, is the first building to be erected from this fund. The Sterling Hall of Medicine is now being built.



New Haven Green

Notable in the equipment of Yale are the Artillery Armory, the Gymnasium, the Carnegie Swimming Pool, the extensive athletic fields, and the great Yale Bowl, where nearly eighty thousand people can be gathered to witness the traditional Yale-Harvard and Yale-Princeton football games.

Further equipment of Yale includes great laboratories for the sciences, engineering and medicine, a library of a million and a quarter books, a handsome auditorium and commons, buildings used by the art, music, forestry, and law schools, and a large number of beautiful dormitories. Chief among these is the famous Memorial Quadrangle with its courts and its great tower. This is the gift of Mrs. Stephen V. Harkness, of New York, and the work of James Gamble Rogers, architect. It is described by competent critics as one of the finest examples of Gothic architecture in the world, and is the most beautiful group of college buildings in America.

Statue of Nathan Hale

Following the war period, thoroughgoing changes were made in the educational organization of Yale University. The freshman classes of the college and the scientific school were joined into a common freshman class, in charge of a separate dean and faculty. The course of the scientific school was extended to four years. All graduate work was centered in the graduate school. The development of graduate instruction has been especially noteworthy, and it is particularly gratifying to those interested in chemistry to note the prominent place which this science plays in the graduate school. The enrollment of graduate students in chemistry, physiological chemistry, and metallurgy is over eighty, or twenty per cent of the total enrollment in the Graduate School. This is in addition to a number of research fellows and associates with doctorate degrees.

The spring meeting of the American Chemical Society is the week of April 2 to 7. This is just at the close of the Easter recess at Yale, and the visitor will have an opportunity of seeing the university in full running order. The public meetings will be held in Woolsey Hall, which has a seating capacity of 3000; the Yale Commons, seating 2500, will be used for entertainment; and the Section meetings will be in the lecture rooms of the Sterling Chemistry Laboratory and those of nearby laboratories. All the buildings and collections of Yale will be open to visitors. Special guide service will be provided under the direction of the Yale chapter of Alpha Chi Sigma.

The people of New Haven, the New Haven and Connecticut Valley Sections of the American Chemical Society, and Yale University, all are making extensive plans for carrying on the spring meeting in such a way that all who attend will enjoy every minute of the time they spend at the meeting and take away pleasant memories of New Haven and Yale.

W. T. Read, *Chairman,*
Publicity Committee

New Haven, Conn.

Calendar of Meetings

American Ceramic Society—Annual Meeting, Pittsburgh, Pa., February 12 to 17, 1923.

American Institute of Mining and Metallurgical Engineers—Annual Meeting, New York City, February 19 to 24, 1923.

American Chemical Society—65th Meeting, New Haven, Conn., April 2 to 7, 1923.

American Electrochemical Society—43rd Semiannual Meeting, New York City, May 3 to 5, 1923.

American Institute of Chemical Engineers

Eighty-five members and guests of the American Institute of Chemical Engineers met at the Hotel Jefferson, Richmond, Va., December 6, 7, and 8, and devoted the 9th to inspection of plants at Hopewell, Va., and points of interest about historic Petersburg.

The first session opened with Vice President A. W. Smith presiding in the absence of President Howard. W. H. Adams, chairman of the Board of Aldermen, acting for the Mayor of Richmond, welcomed the members and guests; he was followed by Allen J. Saville, director of Public Works, who spoke on the advantages Richmond offers to chemical industries. He described the development of the present city with a population of 170,000 from the utter waste which was left by the Civil War, and emphasized the active services offered by the city to those contemplating the establishment of new industries. T. M. Carrington, president of the Tobacco Association of the United States, followed with an address on the tobacco industry, treating first the cultivation of the plant and continuing with a comprehensive survey of the economic features of the industry.

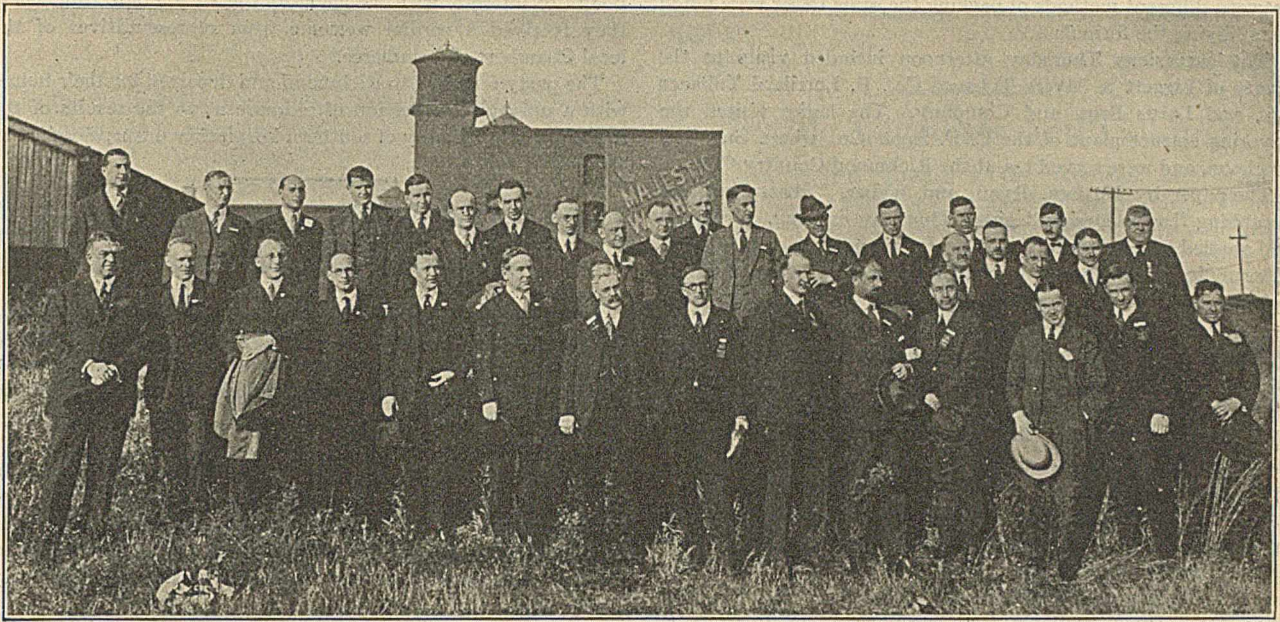
P. C. Kingsbury, chief engineer of the General Ceramics Co., gave an interesting and well-illustrated paper on the application of stoneware to the chemical industry. The first pieces of chemical stoneware in this country were made in 1816 by potters who were not specialists, but actual production for chemical purposes was started in 1836. Prior to 1915, 80 per cent of the clays required were imported from Cilicia, but since the World War domestic sources for all needed clays, with the exception of less than 5 per cent of English ball clay, have been utilized. The necessity for aging some clays as long as five years for the making of stoneware coils and most clay for at least two years for other shapes, was mentioned, but thus far no satisfactory explanation has been offered for the increase in plasticity which is secured. The old time- and fuel-consuming periodic kiln probably will be replaced by regenerative continuous kilns, recently demonstrated and now in successful operation. It is believed that these kilns will not only reduce the time cycle of kiln operation, which is now three to four weeks, but will also reduce breakage. Many problems of a purely physical nature remain to be solved. Glazing is applied for finish only, for ordinarily glazers are less resistant to corrosive action than is the body of the vessel. Expansion troubles are largely overcome by rounding corners, etc. Thus far, efforts to increase thermoconductivity to approach that of metal have been unsuccessful. Accomplishments, both in regard to form and size, are illustrated by the present manufacture of filter presses, tanks of large capacity, pipe coils, cooling pipe units up to fourteen feet in length, pump parts, etc.

Dr. Clarence W. Balke, chemical director of the Fansteel Products Co., Inc., spoke on "Ductile Tantalum." Ductile tantalum can be obtained only by separation from columbium as the fluoride and reduction from the fluoride or a double fluoride with an alkali metal by a private process. Reduction from the oxide gives a brittle product with any reducing medium. The ductile product is remarkably resistant to hydrochloric and nitric acids separately or as aqua regia. Hydrofluoric acid attacks it slowly, but rapidly when mixed with nitric acid. The metal readily absorbs hydrogen, nitrogen, or oxygen, but must be completely melted to expel them. It is very brittle when containing absorbed gases. The wrought metal has a density of 16.6 and melts at 2850° C. It may be drawn from $^3/_8$ in. to filament size without annealing between, although some strain hardening was noted. It has a very high tensile strength, low coefficient of expansion, a thermal conductivity of 0.13, and can be spot-welded to itself and possibly other metals, although these experiments are not complete. It has a comparatively low oxidation temperature and no structural changes were noted below the temperature of burning. Its most remarkable property, and probably its most useful one, is the resistance to current flow when it is used as the anode in a cell and the ease of current flow when it is the cathode. Results of preliminary experiments seem to indicate that it will form better rectifiers than aluminium when used with lead plates. The commercial product is 99.5 per cent pure and costs now about $1.00 per gram, although widening use will probably decrease this cost very considerably.

On Wednesday afternoon three excursions were held—sightseeing in Richmond, a visit to the Standard Paper Manufacturing Company and Richmond Car Works, and a visit to the Southern Manufacturing Company and the Cheek-Neal Coffee Company plants. The ladies were entertained on Wednesday afternoon at a musical and tea given by the Woman's Club. On Wednesday evening a reception was given at the Hotel Jefferson, where the guests were entertained by a negro double quartet singing old negro melodies.

On Thursday morning J. V. N. Dorr, in discussing wood, presented a number of special uses to which wood has been placed in the chemical industry. In addition to tanks protected by various methods of coating, general construction, and the ordinary uses of wood, he mentioned wood linings for centrifugals and pumps. Reference was made to the difference in rate of attack upon various woods by different acids and alkalies, and it was stated that cypress and redwood had been found best where weak inorganic acids were concerned. Redwood appears to resist organic acids satisfactorily. The use of sheet metals, such as lead, for the lining of wood containers, and the use of concrete and of para rubber were also discussed. Largely because of the cracks which develop in bakelite with a change in volume of wood and the absence of elasticity, it has been found unsatisfactory as a protective coating for wood. In some equipment containers must withstand, not only the corrosive action of liquids but abrasion as well, and recently constructed alum tanks were cited as an example where lead lining and lead coating for agitator plates had been found necessary. H. K. Moore pointed out the advantage of wood in connection with electrical circuits, and the use of wood pipes, wood spigots, and other parts of the system used to convey brine solutions. He also mentioned the use of maple in cylinders working in bleach solutions, the fibers having sufficient felting properties to pick up bleach fibers from the solution. Crosby Field, in his discussion of the paper, developed the desirability of providing satisfactory treatment to render wood at least slow burning, and pointed out that in chemical plants wood is frequently used advantageously as compared with metal because of its resistance to corrosion. Henry Howard called attention to established practice in ship-building, which if applied by inland carpenters in the installation of wooden equipment could obviate the use of metal fastenings, etc., and be a decided advantage.

Max Y. Seaton, in discussing magnesia and Sorel cement, referred to the initiation of the use of magnesium oxychloride cements by Sorel in 1867, and the various attempts to use the material for artificial stone, floors, stucco, etc., before the material had been really understood. The work of the last ten years has cleared up many questions and led to a widely extended use of plastic calcined magnesium oxide for this purpose. The low volume changes, the early development of strength, and the ability to bind materials to wood fibers are among the advantages of this material. Mr. Seaton's paper stressed the control of time and temperature necessary in burning magnesite where the carefully sized ore is heated to 1100° C. in a rotary kiln. The quality of the ore is controlled by chemical analysis where special attention is given to iron, alumina, and silica. The calcined material is ground in ring roll mills, using air separation, but the best results are obtained with the old style Burr mill. The



principal source of magnesium chloride is the salt wells of Michigan. The selection of aggregate, which must be dry, was stressed, and present-day applications of the magnesium oxychloride cements indicated.

F. C. Zeisberg, in his paper on "Glass Rings—a New Filling Material for Towers," described the use of small glass rings ranging 12 mm. and less in diameter for packing rectifying columns. These were found to give satisfactory results on account of large surface exposed per cubic foot, low heat conductivity, and cleanliness. Two thousand pounds of 90 per cent alcohol were distilled from a column 9 in. in diameter and 13 ft. high filled with such rings 11 mm. in diameter without undue crowding.

The paper on "Glass" by A. E. Marshall, which followed, will be printed in full in the February number of THIS JOURNAL.

At the first business session a hearty vote of thanks was extended to the local committee for its efforts in contributing to the success of the meeting. During the year the following committees have been appointed: patent, educational, on appeal of New York engineers on registration law. The action of the Council in authorizing student branches and the organization of the first branch at the University of Michigan were announced. The treasurer's report showed a surplus over previous years, and in view of the improved financial condition it was announced that the dues for 1923 would be reduced to $18 for active members and $12 for junior members. The Council announced favorable action on the request for financial support for the Annual Tables of Constants and Numerical Data. The secretary reported 451 active members, 113 junior members, and 2 honorary members of the Institute. It was voted to continue membership in the Federated American Engineering Societies, with H. E. Howe as representative and A. E. Marshall as alternate. Brief reports were made by the membership and educational committees, and at a later business meeting the recommendations of the publication committee, of which F. C. Zeisberg was made chairman, were adopted. To raise the standard of the papers to be presented before the Institute and to facilitate the publication, it was voted that hereafter manuscripts in duplicate must be in the hands of the secretary two months prior to the meeting, that at the discretion of the publication committee preprints of the papers or extended abstracts of them are to be circulated before the meeting. At the meeting, papers are to be presented in general in abstract, to allow time for extended discussion, and further regulations provided for prompt handling of notes of the meeting and galleys of the proceedings to insure prompt publication. The Institute voted to withdraw from the Metric Association, and the following resolution was passed with respect to the licensing of chemical engineers:

> *Resolved*, that the American Institute of Chemical Engineers reiterates its opposition in principle to the licensing of chemical engineers and to the activities of those agencies that are fostering this movement.
>
> *Be it further resolved*, that the American Institute of Chemical Engineers encourage and lend its moral support to all legitimate efforts to the defeat or repeal of such legislation as far as chemical engineers are concerned.

It was also moved that in the future the secretary shall ascertain in advance whether manufacturers are willing to have guests of the Institute visit their plants, and if not, due notice shall be printed in the program.

The following officers were elected for 1923:

President: HENRY HOWARD.
Secretary: JOHN C. OLSEN.
Treasurer: F. W. FRERICH.
Auditor: CHARLES F. MCKENNA.
Directors (for three years): EDWARD BARTOW, J. V. N. DORR, and R. H. MCKEE.

The Council voted to hold the June 1923 meeting in Wilmington, Del., and the June 1924 meeting in Denver, Col.

In his paper on "An Extension of the Theory of Gas Absorption Towers" immediately after the business session, Wallace B. Van Arsdel, of the Brown Co., developed formulas on the basis of the absorption of sulfur dioxide in a liquid, considering temperature and gas velocity as the chief variables, which proved out in experimental towers. Several other factors were introduced which made the formulas highly complicated in most cases, depending on whether the heat of solution was positive, negative, or negligible.

F. C. Blake, in his paper on "Resistance of Packing to Fluid Flow," applied the accepted formulas for fluid flow in pipes to flow of gases and liquids through packed towers by the introduction of a viscosity factor. These formulas were found to give fairly accurate results with air, water, and carbon dioxide in an experimental tower. The variation between different towers and between different methods of packing the same tower were noted as nullifying the formulas.

The excursions Thursday afternoon included visits to the plants of Liggett & Myers Tobacco Co., P. Lorrilard Tobacco Co., and Larus Bros. and Company. The ladies visited the flavoring extract plant of the C. F. Sauer Co., where they had luncheon, and were served tea at the Richmond Country Club.

The paper by Haslam, Ryan, and Weber, "Absorption and Scrubbing Tower Design," given Thursday evening, developed and applied to practice formulas for the calculation of the design of scrubbing towers based on plant experiments. Gerard Osterhof and James R. Withrow followed with a paper on "The Density of Lime as a Function of Burning Conditions." Burning of lime at high temperatures does not always give the densest product, although ordinarily considered so. Small amounts of impurities, especially alumina, iron oxide, silica, and magnesium, have marked influence. This paper was in the nature of report on work still in progress.

The third paper, on "The Use of Propane for Refrigeration," was given by H. D. Edwards. Propane offers decided advantages in producing cold at temperatures below those obtainable with carbon dioxide, ammonia, and other agents now used. The cost of it is too great to warrant its application, except in special cases. It is now available from casinghead gas in extreme purity.

The fourth paper, "Asbestos-Protected Metal; Its Development, Manufacture, and Use," by J. H. Young, described the development of the commercial product from experimental beginnings to its present form, the detailed method of manufacture, and illustrations of its use. A. C. Irwin's paper, on "The Use of Concrete in Chemical Works," detailed the preparation of concrete mixes and the use of "gunite" as a dense coating.

The papers by A. H. White, on "Integral Waterproofing of Concrete," and by W. B. Pratt, on "Oil Sulfur Substitution Compounds," which were presented on Friday morning, will be printed in full in the February issue of This Journal, as will also the paper on "The Importance of Impurities" by Jerome Alexander.

In his paper on "Some Engine Experiments with Oxidized Oils," J. H. James outlined experiments with partially oxidized gasoline and kerosene in an automobile, which gave superior results to unoxidized fuels. Test runs of ninety miles were made. J. C. Wood, E. R. Whittemore, and W. L. Badger, in their paper, "A Method of Analysis of Stirrer Performance and Its Application to a Common Type of Paddle Stirrer," outlined experiments for the measurement of stirrer performance based on simultaneous readings of electrolytic cells in various parts of a vessel in which salt was being dissolved. A series of curves derived from the experimental data gathered was presented. The efficiency of a simple paddle type stirrer was found to be surprisingly high, even at slow speeds.

Edward Bartow, in his paper "Purification of Sewage by Aeration in the Presence of Activated Sludge—IV," discussed developments during the last two years in this field, with illustrations of typical installations.

On Friday afternoon, trips were taken to the Virginia-Carolina Chemical Company's Richmond Chemical Works and the Richmond Cedar Works, and the ladies, husbands, and the Council were entertained at luncheon at the Valentine Museum.

The banquet was held Friday evening at the Hotel Jefferson, during which President Howard announced the election of Wm. H. Nichols to honorary membership in the Institute. Speeches were made by Arthur Glascow, a consulting engineer from London, Hugh K. Moore, of the Brown Co., Vice President Smith, and Chas. L. Reese.

On Saturday those of the party who remained were taken by automobile to Hopewell and Petersburg, where they visited the plant of the Hummel-Ross Fiber Corporation and various other points of interest, with luncheon at the City Point Inn, where they received a cordial welcome from representatives of the local Chambers of Commerce.

The party returned to Richmond and departed for their homes with a universal expression of pleasure as to the results of the meeting and a memory of southern hospitality unsurpassed.

Symposium on Materials of Chemical Equipment Construction

Many prominent chemists have suggested from time to time that a symposium should be held upon the subject relating to materials as applied to construction and equipment in the industry. Therefore, at the spring meeting it has been decided to hold a symposium entitled "Materials of Chemical Equipment Construction."

The literature upon this subject is widely scattered and published in many journals inaccessible to the average chemist, so that in many cases much time must be spent in duplicating work which has already been done. The symposium will tend to bring together such matter for which chemists are constantly in search.

The officers of the Industrial Division have secured Philip A. Singer, a consulting engineer of the Singer-Perlstein Co., Chicago, Ill., to act as chairman of this symposium. This choice is especially fortunate in view of Mr. Singer's experience in the design, construction, and operation of chemical plants.

The subject matter of the symposium will cover woods, metals, vitreous materials, coatings, rubber, fabrics, etc., and will deal with the resisting properties of these materials to acids and alkalies, their resistance to temperature, oxidation characteristics, cost, chemical composition, etc.

It is hoped that industrial chemists and university professors will coöperate in every possible way with Mr. Singer by writing to him directly, stating on what phase of the subject they would like to present papers at the New Haven meeting.

Western New York Section Program

The program for the remaining meetings of the season of the Western New York Section of the American Chemical Society is as follows:

January 2: At Niagara Falls. Convivial Night. F. A. Lidbury.

February 6: At Canisius College, Buffalo. G. L. Coyle, on "Reorganization of the A. C. S."

March 6: At Niagara Falls. W. D. Bancroft, on "The Chemistry of Certain Colors."

April 19: At Technical High School, Buffalo. H. C. Parmelee. Subject open.

May 1: Probably at Grosvenor Library Auditorium, Buffalo. Chas. H. Herty may be the speaker.

(The Niagara Falls meetings are usually held at the Chamber of Commerce.)

Two other speakers of the season will be E. C. Franklin, of Leland Stanford University, and Thomas Midgley, Jr., of the General Motors Research Corporation.

Rochester Section Program

The Rochester Section of the American Chemical Society has announced the following speakers for its meetings for the remainder of the year 1922–1923:

January 22: Professor Chambers, University of Rochester.
February 5: Mr. Ferguson, Jell-O Company.
February 19: Dr. Wright, Geophysical Laboratory.
March 6: Open.
March 19: Dr. Skinner, Bureau of Chemisty.
April 2: Professor Taylor, Princeton University.
April (16?): Professor Franklin, Leland Stanford University.
May 7: Mr. Burrows, Eastman Kodak Company.
May 21: Open.

Division of Physical and Inorganic Chemistry

At the Pittsburgh meeting of the AMERICAN CHEMICAL SOCIETY, September 4 to 8, 1922, the Division of Physical and Inorganic Chemistry passed a resolution instructing its executive committee to arrange for the printing of edited abstracts of all papers to be presented at its meetings, and the distribution of such abstracts to all members before the meetings. To cover the cost of these abstracts it is necessary to charge a fee of \$1.50 to each member of the Division, which will entitle him to receive abstracts of papers for both of the 1923 meetings.

Since the present membership list of the Division of Physical and Inorganic Chemistry is very fragmentary, a letter is being mailed to all old members, and to many others not previously affiliated with the Division, in order to give them the opportunity of receiving abstracts of all papers presented at the divisional meeting. The mailing list, however, is most incomplete, and the present notice is to request all members of the SOCIETY who may desire to be enrolled in this Division, and to receive abstracts of papers, to send their names, with check for \$1.50, to the secretary of the Division.

In order that sufficient time be allowed for the distribution of these abstracts, it is essential that an abstract of each paper to be presented at the New Haven meeting be sent to the secretary with the title, and that such abstract be in his hands not later than March 10, 1923.

UNIVERSITY, VA. GRAHAM EDGAR, *Secretary*

Textile Chemists and Colorists

The 2nd annual meeting of the American Association of Textile Chemists and Colorists was held at the Hotel Pennsylvania, New York City, December 2, 1922. There were 160 in attendance. The amendments to the constitution which had previously been proposed were adopted as drafted, with the single exception that the section pertaining to the duties of local secretaries was changed to provide that the annual reports of local secretaries shall be submitted to the secretary of the Association each year, before February 1 of the same year in place of before February 1 of the succeeding year, as originally recommended.

The following officers were reëlected for another year:

President: LOUIS A. OLNEY.
Vice Presidents: WILLIAM D. LIVERMORE and WILLIAM H. CADY.
Secretary: WALTER E. HADLEY.
Treasurer: WINTHROP C. DURFEE.
Councilors: ELMER C. BERTOLET, ARTHUR E. HIRST, GEORGE A. MORAN, WILLIAM K. ROBBINS, and WALTER M. SCOTT.

W. R. Morehouse was elected an additional councilor for a period of three years.

NOTES AND CORRESPONDENCE

Comment on America's Part in the International Congress of Combustible Liquids

Editor of Industrial and Engineering Chemistry:

* * * * * I am sorry that our people in the United States did not feel enough interest in the affair to take a more active part in it. It is a shame that we do not at least do as much in the matter of coöperating in these affairs as is done by other countries. Mr. Gérard knew of the presence in Paris of Prof. John Frazer, of the University of Pennsylvania, exchange professor to France this year, and myself, and sent us invitations to be present. The only other Americans who were here were three representatives of the Standard Oil Co., headed by a Mr. Cobb, and Dr. Gray, of the Texas Oil Co., who was sent over by his company especially for the meeting; the Standard Oil men were here on other matters. I should think that as a general principle the United States should be as much interested in developing the better utilization of liquid fuels, and, as the French express it, of a "Carburant National," as the other nations of the world; in fact, more so since we are the principal producers, and it should be our business to improve the methods of utilization, and extend the application of these fuels.

* * * * *

At the banquet Dr. Gray responded for America, and was the only representative of about fifteen countries called who did not speak in French. I do not say that I could have done so, but I certainly hope that some day I may be able to make a better showing for my country than I have seen made so far during my sojourn here.

ATHERTON SEIDELL

PARIS
October 15, 1922

Say "Diatomaceous Earth"

Editor of Industrial and Engineering Chemistry:

I would like to call your attention to the confusion often arising in technical and scientific literature through the use of trade names in place of "Diatomaceous Earth," the correct descriptive name for the material in question.

This valuable heat-insulating material and filter aid, aside from bearing the burden of numerous trade names, has been described in the literature by such names as Celite, Kieselguhr, Infusorial Earth, Diatomite, Fossil Meal, Fossil Flour, Desmid Earth, Molera, White Peat, Tellurine, Randanite, Ceyssatite, Tripoli, English Rotten Stone, Bergmehl, etc. Many of these names are correctly applied to other materials, and their use in place of "Diatomaceous Earth" is both confusing and misleading.

Diatomaceous Earth, as it appears on the American market, is composed almost entirely of the fossilized remains of diatoms, either fresh water or marine, or a mixture of the two types. Radiolarian remains and sponge spicules may be present in minor proportions.

When the use of trade names is essential to the clarity of a technical article, much confusion can be eliminated if the true nature of the material also be indicated by the use of the proper descriptive name, "Diatomaceous Earth."

NORRIS GOODWIN

FEATHER-STONE INSULATION COMPANY
LOS ANGELES, CALIF., November 23, 1922

Photo-Engravers Coöperate

The following resolution was recently adopted by the Photo-Engravers' Board of Trade of New York, Inc.:

Resolved, that the Photo-Engravers' Board of Trade of New York, Inc., endorse and approve the action taken by the American Chemical Society in their endeavor to bring about a simpler and more workable administration of the provisions of the Volstead Act as affecting industries requiring alcohol for manufacturing purposes.

Needs of the Library of the Chemists' Club

The accompanying list shows some of the more important vacancies in the files of journal literature available to the chemists of the country through the library of the Chemists' Club, New York City. It is earnestly requested that you look through your own library and offer such duplicates as may help fill these gaps to the librarian, 52 East 41st St., New York City, for it is only in this way that these volumes may be made available to the profession as a whole.

American Food Journal. New York.
Vols. 1–3 (1906–1908)
American Journal of Science. New Haven, Conn.
Ser. 1, Vol. 2 (1820)
Vols. 5–7 (1822–1824)
Vols. 10–11 (1826)
Vols. 14–15 (1828–1829)
Vol. 49 (1845)
Ser. 2, Vols. 20–21 (1855–1856)
Vols. 23–24 (1857)
American Mineralogist. Philadelphia, Pa.
Vols. 1–4 (1916–1919)
American Perfumer and Essential Oil Review. New York.
Vols. 1–4 (1906–1909)
Vol. 13 (1918–1919), index only
Vol. 14 (1919–1920), index only
Vol. 15 (1920), to date
Anales de la sociedad quimica Argentina (now *Anales de la asociacion quimica Argentina*). Buenos Aires.
Vol. 8 (1920), to date
Analyst. London.
Vols. 46–47 (1921–1922)
General index, Vols. 21–30 (1896–1905). 1906
Annalen der Physik und Chemie, ed. by Poggendorff. Leipzig.
Vols. 9–160 (1826–1876)
Annales de chimie analytique appliquée a l'industrie. Paris.
Vols. 3–12 (1898–1907)
Annales des falsifications. Paris.
Vols. 1–3 (1908–1910)
Vol. 8 (1915), to date
Arbeiten aus dem kaiserlichen Gesundheitsamte (now *Arbeiten aus dem Reichsgesundheitsamte*).
Vols. 17–31 (1900–1907)
Vol. 49 (1916), to date
Archief voor de Suikerindustrie in Nederlandsch-Indië. Soerabaja, Java.
Vols. 1–17 (1893–1909)
Vols. 27–28 (1919–1920)
Archiv für Chemie und Mikroskopie. Wien.
Vols. 1–2 (1908–1909)
Vol. 8 (1915), to date when publication ceased.
Asphalt und Teerindustrie. Berlin.
Vol. 3 (1903)
Vol. 10 (1910), date of latest volume unknown
Beiblätter zu den Annalen der Physik. Braunschweig.
Vols. 41–43 (1917–1919)
Biedermann's Zentralblatt für Agriculturchemie. Leipzig.
Vols. 1–30 (1872–1901)
Vol. 41 (1912) to date
Biochemical Bulletin. New York.
Vol. 4 (1915) to date
Biochemische Zeitschrift (formerly *Beiträge zur chemischen Physiologie und Pathologie*). Berlin.
Vol. 4 (1904) } *Beitrage*
Vol. 7 (1905) }
Vols. 49–58 (1913)
Vols. 72–77 (1915–1916)
Vols. 79–84 (1917)
Vols. 93–100 (1918–1919)
Brennstoff-Chemie. Essen.
Vols. 1–2 (1920–21)
Bulletin of the Imperial Institute. London.
Vols. 1–7 (1903–1909)
Bulletin of the Philosophical Society of Washington. Washington.
Vol. 15 (1906)
Bulletin de la société industrielle de Mulhouse. Mulhouse, France.
Vols. 1–33 (1826–1863)
Vol. 36 (1866, March) } or
Vol. 74 (1904, September) } complete
Vol. 77 (1907, April-May) } volumes
Vols. 83–85 (1913–1919) }
Le Caoutchouc & la gutta-percha. Paris.
Vols. 1–5 (1904–1908)
Vol. 15 (1918), index only
Vol. 16 (1918)
Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten, II Abt. Jena.
Vols. 1–22 (1895–1909)
Vols. 25–50 (1910–1920)
Chemical Trade Journal. London.
Vols. 1–44 (1887–1909)
Vol. 47 (1910)
Chemiker-Zeitung. Cöthen.
Vols. 1–2 (1877–1878)
Chemische Industrie, Die. Berlin.
Vols. 37–42 (1914–1919)
Chemische Revue über die Fett- und Harz-Industrie (now *Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze*). Stuttgart.
Vols. 1–3 (1894–1896)
Vol. 5 (1898), index only
Vols. 6–8 (1899–1901)
Vol. 9 (1902), index only
Vol. 11 (1904)
Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze formerly *Chemische Revue. . .*). Stuttgart.
Vols. 26–27 (1919–1920)
Chemisches Zentralblatt. Berlin.
Vol. 86, No. 23 (1915), or complete vol.
General Register (1902–1906). 1907
Deutsche Färber-Zeitung. Leipzig.
Vols. 1–56 (1865–1920)
Note: Vols. 1–4 (1865–1868) *called Thüringer Musterzeitung für Färberei*
Dinglers polytechnisches Journal. Berlin.
Vol. 325 (1910)
Elektrochemische Zeitschrift. Berlin.
Vol. 22 (1915)
Vols. 25–26 (1918–1919)
Engineering and Mining Journal. New York.
Vols. 1–14 (1866–1872)
Vols. 17–18 (1874)
Vol. 23 (1877)
Vol. 25 (1878)
Vol. 41 (1886), index only
Vol. 45 (1888)
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Vol. 13 (1910), date of latest volume unknown
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Vol. 39 (1909), date of latest volume unknown

Research on the Corrosion of Steel Pipe

The National Tube Co., of Pittsburgh, Pa., has announced the establishment of an Industrial Fellowship in the Mellon Institute of Industrial Research of the University of Pittsburgh, Pittsburgh, Pa.

The purpose of this fellowship is a systematic study of practical methods for the prevention of corrosion in hot-water supply systems. It is also giving attention to the classification of waters of various chemical composition with respect to their relative corrosive action upon iron and steel, particularly in the form of pipe lines, boiler economizers, tubes, etc.

The present incumbent of this fellowship is Clifford R. Texter, who for the past several years has been carrying out research on the corrosion of iron and steel, where not exposed directly to the atmosphere. Mr. Texter will be glad to correspond with engineers and manufacturers interested in the field to which his fellowship relates.

An Aid to Petroleum Chemists

Editor of Industrial and Engineering Chemistry:

May I have a little space in your journal to emphasize one of the points made by Dr. Dean in his recent review of Brooks's "Chemistry of the Non-benzenoid Hydrocarbons?"

The fact was mentioned that the author has brought together the literature of his subject from a large number of journals, some of which are not easily accessible. This painstaking work required a great amount of effort, which was justified by the importance of the subject. The recent activity in the study of the chemistry of petroleum is leading to uses of these hydrocarbons in the preparation of substances of importance in industrial organic chemistry, and I am of the opinion that further work will eventually place petroleum in a position similar to that of coal tar as an industrial raw material.

The appearance of Dr. Brooks's book at this time serves to facilitate markedly research in this field, and will, no doubt, inspire investigations which would never be undertaken if such an admirable review of past work were not available.

The book has been of great service to both my students and myself.

JAMES F. NORRIS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
November 29, 1922

The Classification of Coal

Editor of Industrial and Engineering Chemistry:

In the October issue of the journal, Prof. S. W. Parr has brought up again this most interesting subject and has made a valuable contribution to it. There is now a widespread interest in the classification of coal, since it is being appreciated that the high prices paid for coal are in part at least due to poor marketing and that this in turn depends in part on poor classification. A satisfactory use of classification of coals properly applied would cut down the nation's fuel bill materially. Bridging the gap from a scientific to a market grouping of any category of goods is a long step, but no step can be taken save from a starting point and a rational scientific classification; one which places the various coals according to natural groupings and at the same time is easily and quickly applied would afford such a point.

As Professor Parr shows in his brief historical introduction, the subject is not new. Horace C. Porter in 1915[1] gave a more detailed review of the development of ideas along this line, and following that, in the same paper, O. C. Ralston illustrated on trilinear diagrams the groupings developed by recalculation of 3000 analyses of coals made in the government laboratories. He showed that when ultimate analyses of coals are reduced to moisture- and ash-free basis (less nitrogen and sulfur), the various ranks fall in definite areas of a trilinear diagram on which carbon, hydrogen, and oxygen contents have been plotted. He also developed "isovolatile" and "isocalorific" lines running in divergent directions across the diagram, but with such relations that the position of the coal could be predicted either from the ultimate analysis or the calorific value and volatile content. The latter is the basis used by Professor Parr, and the difference in appearance of the diagrams is incident mainly to the use in the trilinear of lines crossing at an obtuse angle as against those at right angles to each other in Professor Parr's figures. Any student of the subject will want to have both before him. The Parr diagrams are admirably clear and simple and with the coals he has plotted show good definition of groups, except between eastern and western bituminous where too much is not to be expected. Possibly, if all the analyses used by Ralston had been plotted, the shading of one group into another might be more pronounced.

Professor Parr and his associates have given us much to think of on the classification of coals. Now can some one tie their work with uses of coal and so furnish a basis for a market classification?

H. FOSTER BAIN

BUREAU OF MINES
WASHINGTON, D. C.
November 28, 1922

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[1] *Bur. Mines, Tech. Paper* **93**.

Admissions to U. S. Pharmacopeia

A list of additional admissions to the U. S. Pharmacopeia (10th Revision), and an additional list of U. S. P. (9th Revision) titles which it is recommended not to admit to the U. S. P. X., has recently been issued. These represent reports from the Subcommittee on Scope submitted since the first lists were made public, some months ago.

Comments are invited on these recommendations and careful consideration will be given to all communications by the Special Referee Committee on Scope, which consists of the twenty-one physicians of the General Committee of Revision.

Where the recommendations of the subcommittee do not meet with approval, and a protest is submitted, this should be accompanied by evidence and facts to substantiate the claim, that the referees may have all evidence before them.

There are a few questions of admission and deletion not yet announced by the Subcommittee on Scope.

Information concerning these lists may be obtained from, and comments should be sent to E. Fullerton Cook, Chairman, 636 So. Franklin Square, Philadelphia, Pa.

Heat Transfer by Conduction and Convection. II—Liquids Flowing through Pipes—Correction

In the article under the above title [THIS JOURNAL, **14** (1922), 1101] the following errors should be noted:

Page 1102, 2nd col., Eq. 7, the term (ρu^n) should be $(\rho u)^n$.

Page 1102, 2nd col., Eq. 7*b*, the term $(\rho \mu)^{0.83}$ should read $(\rho u)^{0.83}$.

Page 1103, 2nd col., first line after Eq. 10*a*, change "which" to "Eq. 10."

Pages 1103 and 1104, Equations 9*b* and 9*c*, *b* should read B.

Page 1104, Col. 1, the line preceding the table should read "The range of the values for *water* is as follows:"

Page 1104, Nomenclature Table:
B = Constant.
Change *first* ρ to p = Intensity of absolute pressure, etc.
y = Exponent.
μ = Absolute viscosity of liquid *at average film temperature*, as lbs. per sec. per ft. = 0.0672 times film viscosity as poises.

W. H. MCADAMS
T. H. FROST

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
December 13, 1922

Report of the Viscosity Committee of the Cellulose Division—Correction

In this report, published in THIS JOURNAL, **14** (1922), 1164, in the list of specifications, the eighth item should read:

Temperature of solution to be maintained by a water jacket within..........25° C. ± 5°.

G. J. ESSELEN, JR.,
Chairman

BOSTON, MASS.
December 13, 1922

WASHINGTON NOTES

Distinguished Service Awards

The men listed below, formerly connected with or assigned to the Chemical Warfare Service, have been awarded Distinguished Service Medals for exceptionally meritorious and distinguished service in the following particulars:

Raymond F. Bacon, Colonel, C. W. S., Chief of Technical Division, A. E. F. Untiring energy, marked scientific attainment, and comprehensive technical knowledge in the organization and operation of laboratory units and proving-ground tests.

Karl Connell, Major, Medical Corps. Exposed himself unhesitatingly to highest concentrations of deadly gases while working with experimental models and masks. Invented, tested out, and perfected a new type of gas mask superior to any then in existence.

Harry L. Gilchrist, Lieutenant Colonel, Chief of the Medical Section, C. W. S., A. E. F. Not only performed services of the utmost value, both to the Medical Department and the Chemical Warfare Service, but developed a degassing unit for treating men exposed to mustard gas which proved so successful that it was adopted for the entire American Expeditionary Forces.

Byron C. Goss, Lieutenant Colonel, C. W. S., chemical adviser, Office of Chief, C. W. S., later as Chief Gas Officer of 1st Corps, and finally, of 2nd Army. Exceptional ability and wide knowledge of gases; connected with practically every battle in which American troops were engaged.

Joel H. Hildebrand, Lieutenant Colonel, C. W. S., Commandant, C. W. S., Experimental Field, A. E. F. Profound knowledge of chemistry, coupled with rapid grasp of military problems, enabled him to render services of value in determining the best means of using gas and gas materials in the field.

Edward N. Johnston, Colonel, Corps of Engineers, Assistant to Chief, C. W. S., in France from June to December 1918. Ability of high order in supervision of operations of all gas troops. Later also, to June, 1919, as Acting Chief of C. W. S. abroad, showed keen business ability and sound judgment in closing the chemical warfare activities of the American Expeditionary Forces.

Gilbert N. Lewis, Lieutenant Colonel, C. W. S. Secured first-hand data in uses and effects of gas and submitted reports of such value that they became fundamentals upon gas warfare policies of the American Expeditionary Forces. As Chief of the Defense Division, he was instrumental in securing more effective gas production, especially mustard gas.

Augustin M. Prentiss, Major, General Staff Corps, then Major, C. W. S. Knowledge of supplies and material, especially in proper choice of gases, gas shells, and other materials used by gas troops and artillery.

John W. N. Schulz, Colonel, Corps of Engineers, representative, C. W. S., at General Headquarters. Service in the solution of many problems relating to the offensive use of gas and also in planning more effective method for issuance of equipment and training in gas warfare. Later, as Chief Gas Officer of 1st Army, had entire responsibility of gas warfare in that army during St. Mihiel and Meuse-Argonne offensives.

Richmond Mayo-Smith, Lieutenant Colonel, C. W. S., Chief of Supply Section. Built and administered supply organization consisting of twelve seaport, intermediate, and front-line depots, which fully met at all times the demands of chemical warfare supplies which active operations brought upon the service.

Joaquin E. Zanetti, Lieutenant Colonel, C. W. S., Chief Liaison Officer, C. W. S., with French forces. Familiarity with French language and methods and superior technical ability enabled him to gather an enormous amount of detailed information concerning the manufacture, handling, and use of gases.

Calcium Arsenate Situation

Government officials and manufacturers of white arsenic and calcium arsenate held a conference at the Hotel Astor, New York, N. Y., on December 13, to discuss the prospects of increasing the supply of calcium arsenate to check the ravages of the boll weevil. The sentiment of those attending the conference seemed to be that the shortage is not so acute as some reports indicated and is the result of inactivity in the lead and copper smelting industry. Apparently, consumers are doing everything possible to increase domestic production, but appreciable results from these efforts can hardly be expected for about six months. B. R. Coad, of the Department of Agriculture, in outlining the probable calcium arsenate needs for the coming year, said that whereas some 3200 tons had been used during the past year, the estimated requirements for 1923 would be three times that amount. These figures are exclusive of the quantities for other products in which arsenic is needed.

The following committee was appointed to investigate and submit a report on the situation: B. R. Coad, Department of Agriculture, chairman; G. F. Loughlin, Geological Survey; Hamilton Bush, American Smelting and Refining Company; F. Y. Robinson, United Smelting Company; Frank Hemingway, Sherwin-Williams Company; R. N. Chipman, Chipman Manufacturing Company; W. O. Tuck, Pittsburgh Plate Glass Company; and O. A. Hasse, Glidden Company.

Industry and Government Coöperate in Wool Research

As a result of a conference between representatives of the National Association of Wool Manufacturers, the American Association of Woolen and Worsted Manufacturers, and the Bureau of Standards, arrangements have been made by which the Textile Division of that bureau will conduct special scientific investigations with the textile industry. An elaborate program of work is planned and seven specific investigations have been authorized, which have to do with the setting of standard nomenclature in wools; the filling quantities of wool; oils used for the emulsion of wools in the manufacture of yarns; the effect of scouring raw wools and finished fabrics, and standardization of methods of testing scouring processes; wearing qualities of woolens; determination of the value of reworked wools and fibers and the construction of fabrics; determination of the relative fastness of various textile materials; and the establishment of standards of moisture and oils in yarns and fabrics. Meetings will be held from time to time to consider progress on the surveys under way and to formulate plans for future investigations which may be of practical aid to the industry.

Leather Investigations

The Bureau of Chemistry has completed some of its coöperative work with the War Department on shoe leathers which was started during the war. A report in which the following general conclusions are drawn has been filed with the War Department, and will also be published as a bulletin of the Department of Agriculture:

> Under the conditions of these tests, bark-tanned upper leather was not as satisfactory as were the other types of upper leather; fiber soles, while showing a very high resistance to wear, were not suitable, mainly because of development of physical failures during service; oak, chestnut, and hemlock sole leather tannages showed practically the same average wear resistance, while belting leather indicated a slightly greater serviceability; chrome sole leathers outwore the vegetable tannages, with unwaxed chrome showing the highest wear resistance. There was practically no difference in the wear of loaded and unloaded leathers; well-rolled leathers showed about 16 per cent more wear than unrolled ones. Soles from the shoulder end of the bend did not show an average wear equal to those from the butt end. Extensive data on the comparative chemical composition of the original leathers and parts of the worn soles are given.

Joint Meetings of Sections

On November 24, the Washington and Maryland Sections of the American Chemical Society held a joint meeting in Baltimore. The Washington chemists arrived in Baltimore at 2 P.M., and were taken in automobiles to the new plant of the American Sugar Refining Company. The remainder of the afternoon was spent in inspecting this plant, which is said to be the largest and most up-to-date sugar refining unit in the world. Few, if any, questioned the truth of this statement after making the round of inspection.

Dinner was served at the Engineers' Club, following which addresses were made by R. C. Wells, chairman of the Washington Section, and H. E. Howe. The address of the evening was delivered by C. L. Huttlinger, superintendent of the sugar plant, who gave an interesting review of the history of sugar growing and refining.

About fifty members of the Washington Section, twenty-five students from College Park, thirty students from Johns Hopkins University, and between forty and fifty members of the Maryland Section attended the dinner.

Dye Advisory Committee Meets

The Dye Advisory Committee, consisting of G. W. Knight and Peter Feiberger of the Customs Service, New York, N. Y., W. N. Watson of the Tariff Commission, and W. D. Appel of the Bureau of Standards, held a meeting in the Appraisers' Stores, in New York, on December 19, 1922, to consider certain features of the dye standardization work.

December 19, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

International Conference on Refrigeration

The International Conference on Refrigeration has just met in Paris. Of the 45 countries represented 24 ratified the creation of the International Institute of Refrigeration. J. F. Nickerson, general director of the American Association of Ice and Refrigeration, was appointed a member of the administrative council.

Government Soda and Ammonia Works

During the war the topographic situation of soda factories in France was greatly criticized. These factories are, indeed, situated in the northeast of France, in the Lorraine region, and their proximity to the war zone slackened their production. These soda works belong to the Solvay Society, which has a monopoly on soda in France.

The French government, in order to escape from this monopoly, considered establishing a soda factory which should be the property of the government, under the direction of the Powder Service. This project has been abandoned and the government has favored the establishment of a soda factory in the southwest of France, in the vicinity of Bayonne. This is the factory of Mouguerre where Briscous sodium chloride waters are treated. These waters were analyzed during the war to see if there was any possibility of extracting in notable quantities the bromine which it contains.

The State has advanced to the society for the construction of this factory a capital of 8 million francs. In this factory sodium carbonate will be manufactured by the ammonia process. The yield will be 100 tons per day of sodium carbonate capable of being converted into 75 tons of caustic soda.

The participation of the State in the installation of this factory is an indication that the French government intends to have control of factories useful in case of war. That which has just been done in the case of soda has also been done in the case of ammonia.

The Finance Committee of the House has approved the project on the manufacture of synthetic ammonia. The contract of 1919 between the Ministry of Industrial Reconstruction and the Badische Anilin und Soda Fabrik has just been carried out—that is, the ancient powder mill of Toulouse has been equipped to produce nitrogen by the Haber process.

The society is formed with a capital of 50 million francs, which has been subscribed by the syndicates, corporations, and agricultural associations, by the Chambers of Commerce, the syndicates of chemical products and the workmen's syndicates, of 20 million; the other 30 million were furnished by the State. The society will be governed by a council of administration formed of technicians and representatives of consumers of nitrogenous fertilizer.

This form of constitution of the society is evidently a compromise between a monopoly pure and simple, such as exists over the Powder Service, and administration by a private society. In France, at the present time, monopolies are being strongly opposed; those of powders and matches, for example, are being severely attacked, and it has been demanded that these monopolies be leased to the commercial societies. The ammonia project is a compromise between the two systems until absolute control of the State is admitted in the society; but it appeals to the capital coming from the consumers' societies, and especially from coöperative societies where only the small capitalists are represented. This project will probably be opposed by a certain portion of Parliament, who consider it too much of an undertaking for the State.

The scarcity of nitrogen in France is great, since Germany imports some of it by right of the reparations. The wheat crop having been deficient this year, during the discussion of the budget of the Ministry of Agriculture the deputies insisted on the necessity of obtaining a new source of fertilizer supply. The calcium phosphates from the region of the Bourgogne have been recommended as a substitute for superphosphates, which, used in a very finely powdered condition, would give results analogous to the superphosphates, but the cost of pulverization of this calcium phosphate is such that the superphosphates seem at the present time to be less objectionable.

In connection with this superphosphate industry, it is known that one of the great inconveniences of this industry is in the use of sacks of cloth or jute, which because of the acidity of the superphosphate cannot be used for any length of time. Mr. Bruno, general inspector of the laboratory of the Ministry of Agriculture, has perfected a process for treating these sacks using a sizing of algae or seaweed; the sacks thus treated can be put in contact with the acid superphosphates without being destroyed, and are used a great number of times. This process is now used on a large scale by the factory at St. Gobain.

Alsatian Potash

In regard to Alsatian potash also the government project has just been settled. It provides for the formation of a society composed of the professional syndicates of consumers of potash which will be the property of the mines under the control of the State. The agricultural syndicates will have 50 per cent of the proprietary rights of the mines; 10 per cent will be given to the French chemical industries; 20 per cent to the departments of the Chambers of Commerce of Haut-Rhin, Bas-Rhin, and Moselle; 15 per cent to the particular holders of the parts or "kuxes" possessed previously by them; and finally, 5 per cent of the property will be given to the personnel operating the mine. The selling price will be fixed by the State, and exportation will only be authorized after the needs of our own country are assured.

International Foodstuffs Laboratory

The French government, in carrying out the international conventions passed in 1913, is going to establish the international laboratory for the purpose of standardizing the methods of analysis of foodstuffs used in the different countries.

The chemists of all nations will work at this laboratory. Although America has not yet agreed to this convention, it would be desirable that American chemists having worked in the laboratories of Washington (Bureau of Chemistry) be assigned to this laboratory. There has also been installed in the Service of the Institute of Agronomic Research, someone in charge of studying the rational utilization of foods for men and animals. The calorimetric methods of Atwarter and all the American studies on the chemistry of nutrition will be largely investigated in these new services.

Institute of Cellulose

The establishment of an Institute of Cellulose is being considered in France. The large quantities of wood which we have in our colonies ought to make it possible for us to obtain cellulose in abundant quantities. Heim, Rorick, and Maheu have just been studying the oaks of Indo-China. The cellulose content of these oaks varies between 30 and 40 per cent.

The studies on cellulose will be centralized in the region of Grenoble where the Institute of Cellulose will be situated. This Institute will include an office of documentation for the cellulose industry, a laboratory for the preparation of the cellulose with models illustrating the processes of electrolytic bleaching, by sulfite, etc. This laboratory will study also the manufacture of viscose and of artificial silks, as well as the nitrocelluloses, cellulose acetates, and celluloid. The moving picture industry ought to contribute in large part to the establishment of this Institute.

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Mr. Lemoine, dean of the Section of Chemistry of the Academy of Science, has recently died. A mining engineer and professor at the Polytechnic School, Mr. Lemoin has published several books on the allotropy of phosphorus and its sulfide. To him also we owe excellent studies on chemical equilibrium and dissociation.

December 1, 1922

The American Paper and Pulp Association has voted to raise $10,000 to finance a study of the relation of the degree of decay to the pulping value of wood, with special reference to improving present methods of grading pulp wood. The investigation is to be carried out in coöperation with the Forest Products Laboratory. The action was taken at a recent meeting of the woodlands section and was based on a tentative outline for the proposed investigation which had been prepared by the laboratory.

Personals

Mr. M. G. Donk has reported for duty with the Chemical Division of the Tariff Commission and probably will be assigned to special work on heavy chemicals.

Dr. W. Grenville Horsch has resigned as research associate in the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, to accept a responsible research position in the laboratory of the Chile Exploration Company in New York City.

Dr. Peter Feiberger, a color specialist, has been appointed chief of the Dye Investigation Laboratory of the Customs Division of the Treasury Department in New York. He will be in charge of the comparative tests on coal-tar products, which are necessary under the new Tariff Act, and will also assist in the tariff standardization work. Three assistant chemists will be appointed to assist him in his work.

Mr. F. W. McSperron, of Wilmington, Del., has been appointed specialist in chemical cost accounting in the Chemical Division of the Tariff Commission.

Prof. Robert T. Haslam, director of the School of Chemical Engineering Practice, has been appointed director of the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, to succeed Dr. R. E. Wilson who recently resigned.

Dr. J. E. Teeple will sail for Europe on January 2 on a business trip and will be gone about four weeks.

Mr. J. M. Weiss, director of development of The Barrett Co., and **Mr. Charles R. Downs**, at one time chief chemist of The Barrett Company and more recently research group head of the National Aniline and Chemical Co., have formed a partnership, effective January 1, with offices in New York. They will specialize in coal-tar manufacture and utilization, and in general catalytic processes. Chemical engineering will be a feature of their activities.

Mr. Jerome Alexander has opened an office in the Chemists' Building, New York City, as consulting chemist and chemical engineer, with special experience in colloid chemistry and its application.

Prof. Walter G. Whitman, formerly assistant professor of chemical engineering, has been appointed assistant director of the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology.

Mr. A. A. Heller has taken over the management of the International Oxygen Company. He succeeds Mr. L. W. Hench, secretary and general manager, who has resigned.

Mrs. Florence Burlingame, formerly research assistant with the War Trade Board, has joined the Chemical Division of the Tariff Commission. Mrs. Burlingame specialized in the chemical dye statistical work in the War Trade Board, and her work at the Tariff Commission will be along similar lines.

Mr. Gaston Du Bois, president of the Monsanto Chemical Works, sailed from New York for Europe on November 7 for a six weeks' business trip.

Mr. C. S. Gwynne has resigned as chemist in the Forest Products Laboratory to become chief chemist for the Arrowhead Mills, Inc., Fulton, N. Y.

Dr. Victor Yngve has resigned his position with the Hydrol Co., Niagara Falls, N. Y., to accept a research fellowship in Cryogenic Engineering at Harvard University.

Dr. Minnie A. Graham, who has been acting professor of chemistry at Wells College during the past year has been appointed associate professor of chemistry at Mills College in California.

Prof. L. A. Fitz has resigned his position at the Kansas State Milling Department to accept a position with The Fleischmann Co., New York, N. Y., where he will be in charge of wheat, flour, and bread research work.

Mr. William C. McIndoe has joined the technical staff of the Portland Gas & Coke Company. He is also acting as assistant to the professor of mechanics and testing materials at Oregon Agricultural College.

Dr. Frank C. Gephart, analytical and consulting chemist, has established a laboratory and office at 23 East 31st St., New York, N. Y.

Dr. Calvin Adam Buehler, of the Ohio State University, has been appointed assistant professor of chemistry in the University of Tennessee, Knoxville, Tenn.

Industrials

The Board of Governors of the Synthetic Organic Chemical Manufacturers Association of the United States has elected H. F. Wilmot technical advisor to the association in matters involving administration of Customs Duties under the present Tariff Act. Mr. Wilmot was president and a director of the Tinc Tura Laboratories, Brooklyn, N. Y., and has severed his connections with that organization in order to devote his entire time to his new duties with the association. His office will be Room 1648, Equitable Building, 120 Broadway, New York City.

The Supreme Court of North Carolina has rendered a decision of interest to all fertilizer concerns doing business in that state. The statutes of North Carolina provide that no claim for damage to a crop by commercial fertilizers can be maintained unless a sample of the fertilizer was properly drawn and analyzed by the state chemist. A farmer who had failed to have such an analysis made refused to pay his fertilizer note and brought a counterclaim against the fertilizer company for damage to his crop supposed to have been caused by the presence of borax in the fertilizer. The court decided in favor of the fertilizer company, and the decision has now been confirmed by the Supreme Court.

It is reported that Arghan, the new textile fiber discovered by Sir Henry Weckham, the pioneer of the plantation-rubber industry, has qualities unsurpassed by any other textile, being as strong as steel, bulk for bulk. Its tensile power is recorded as 50 per cent superior to that of the best flax and hemp. The cloth is very firm and takes dyes well.

A German corporation has been organized, with the participation of the Badische Anilin und Soda Fabrik and a number of German textile producers of the lines which are interested in the production of high-grade substitute fabrics, to exploit in Germany and surrounding countries the textile inventions of Dr. Wilhelm Schweitzer. It is stated that an English company has been formed to exploit the processes in China and Japan. One process relates to the manufacture of a fabric similar to raw silk from vegetable substitutes claimed to be immune to water baths. The second process is intended to enable the manufacture of high-grade yarns out of all sorts of the low-grade wool and wool waste. The product is claimed to have appearance and texture of pure silk, and to have warming qualities higher than ordinary wool. The third process relates to the manufacture of artificial silk from cheap and medium-priced wool and animal fibers in combination with waste products of the artificial silk and pure silk industry. The fourth process enables manufacturers of artificial silk to give it the luster, feel, and appearance of high-quality silk. By the fifth process, flax fibers are to be made into artificial raw silk.

Agronomists of five midwestern states—Ohio, Indiana, Michigan, Missouri, and Wisconsin—have agreed on a list of 13 standard fertilizer formulas in addition to straight acid phosphate, which will meet all the fertilizer requirements of their states. Each state college of agriculture is now to select 12 formulas, including acid phosphate, and to urge farmers not to buy other mixtures, nor to mix at home in any other proportion of ammonia, phosphoric acid, and potash. Officials of 13 fertilizer companies, consulted as to the commercial practicability of the scientists' formulas, said all could be mixed and that standardization on this list will cut costs per unit of plant food by eliminating the present multiplicity of low-analysis brands. No fertilizer on the list contains less than a total of 16 per cent ammonia, phosphoric acid, and potash.

It is reported that several fertilizer manufacturers are producing calcium arsenate as a side line, intending to sell it only for cash, preferably to their fertilizer customers, at as low a price as possible, the purpose being not to make big profits on calcium arsenate, but to provide protection for the cotton of their customers.

The Hartford-Empire Co., of Hartford, Conn., which controls the Hartford-Fairmont Co., has contracted for the control of the business and patents of the Howard Automatic Glass Feeder Company. The Hartford-Fairmont Co., which is the chief representative in the development of automatic glass feeding machines employing the new gob process, has recently been amalgamated with the Empire Machine Co., a leading representative in developing machinery for blowing and forming paste mold ware in general, and especially electric light bulbs. The company will be connected by close contract relations with the Corning Glass Works.

BOOK REVIEWS

Van Nostrand's Chemical Annual. Fifth Issue, 1922. Edited by John C. Olsen. D. Van Nostrand Co., New York. Price, $4.00.

One hundred years ago numerical data on chemistry were relatively unimportant. To-day tables, charts, and mathematical functions *ad infinitum* compose the fundamental base from which arise the vast towers of scientific structure. As the chemical era progresses in complexity, it becomes increasingly imperative to have easily available these basic data freed from the nonpabular quicksands. Thus, "Van Nostrand's Chemical Annual" was conceived in necessity; since 1909 chemists have not been without this needed utility in the architecture of their science. Such an instrument, now issued for the fifth time, truly must be of worth.

The style, general content, and inherent conciseness of the Chemical Annual have been commended repeatedly in previous reviews in This Journal. The last edition does not vary greatly from the former: physical constants, gravimetric factors, calculation aids for volumetric analysis, specific gravity and vapor tension tables, measurement equivalents, thermochemistry, and stoichiometry. Just here, however, is the difficulty. If the book were unrevised, still its value would be great. But in the processes of revisions, it has been customary to presume concomitantly progressive improvement. While the reviewer appreciates the Gargantuan attempt of the editors to digest the many rivulets of scientific information, yet he feels that too much of the epitomized content is simply predigested material—too much is reprinted. Few of the footnotes refer to recent literature. Compounds now made in the United States, prides of American chemistry, are not mentioned, particularly such medicinals as procaine (aminobenzoyl-diethylamino-ethanol hydrochloride), barbital (diethylbarbituric acid), cinchophen, benzocaine, benzyl succinate; even arsphenamine is omitted, about which more chemistry has been written than probably any other compound. There seems to be little value in the numerous problems in stoichiometry; they are reminiscent of the classic "ponies." Nor is there need of so much valuable space devoted to the list of new books; instead, tables on various pH values or partition coefficients would be of decided help. The equations for volumetric computations are at times too rigid and their genesis is of the "paper chemistry" protype; it is suggested that in future editions some of the equations could be explained better from the electronic viewpoint.

One fault, the inconsistency of us scientists, is revealed by this book. Our organizations and leaders are encouraging the universal employment of the metric system. Yet, in actual practice we stand condemned. Tables used every day are printed side by side in Fahrenheit and Centigrade, while specific gravities occur at two or three "standard" temperatures.

Notwithstanding the criticisms, the book deserves high praise: it is undoubtedly valuable; it is compact; it is reasonable in price. The technologic make-up is excellent, reflecting to the credit of both the editors and the printers. Particularly pleasing is the dedicatory courtesy—an excellent photogravure reproduction of Theodore W. Richards. John Tulloch has well said: "*Scientific* facts, unlike facts of mere contingency or incident, are truths of nature which, once discovered, admit of repeated verification." So to Dr. Richards, workers in *scientific* realms are glad to join with the editors of *scientific* data to pay homage for the "truths of nature," he has given us; they will constitute precious contributions in future editions of such books as "Van Nostrand's Chemical Annual."

Paul Nicholas Leech

Liquid Fuel and Its Apparatus. By W. H. Booth, F. G. S. 2nd edition. E. P. Dutton & Co., New York. Price, $4.00.

The first edition of this treatise was published in 1912 as an abridgment of the author's larger work, "Liquid Fuel and Its Combustion" (Constable & Co., 1902). The plates of the first edition have been used, without even the correction of rather numerous typographical errors and incorrect statements. New material equal to about four pages has been added as paragraphs at the ends of some of the chapters where blank space was available and as inserted pages (265–A and 269–A). These sections are dated 1921.

Inaccuracies and careless statements are frequent, particularly in those sections dealing with chemical subjects. On page 50, Russian petroleum is stated to be composed of hydrocarbons of the olefin series, while Beaumont (Texas) petroleum is said to be characterized by the presence of members of the acetylene and benzine (*sic*) series. The "Bombe" calorimeter is mentioned on page 63. The surprising statement that there are thirty different hydrocarbons in crude petroleum appears on page 64. The distillation of petroleum with steam is described as a solution of the petroleum by the steam, an effect peculiar to steam (page 64).

In attempting to cover such subjects as materials of construction (steel, refractories, flue gas analysis, etc.), it has been necessary to limit the space assigned to more important topics. The description of the various types of liquid fuels available is inadequate. The common misstatement that Texas and California petroleums are used principally in the crude form, is repeated (page 45).

The second section of the book, "Practice," is perhaps more satisfactory. However, a thoroughgoing revision would undoubtedly have effected many changes here also. An adequate critical discussion of the various types of burners and furnaces is lacking.

W. F. Faragher

A. S. T. M. Tentative Standards, 1922. 774 pp. Illustrated. American Society for Testing Materials, Philadelphia, 1922. Paper, $7.00; cloth, $8.00.

The method adopted by the A. S. T. M. for arriving at its standards by inviting criticisms of tentative standards is too well known to require comment here. The present volume presents 163 tentative standards chosen by the various committees of the society as best in each case treated, to which the attention of workers in the several fields is directed. The classifications covered by these tentative standards are: Ferrous Metals, Nonferrous Metals, Cement, Lime, Gypsum and Plaster, Preservative Coatings, Petroleum Products and Lubricants, Road Materials, Coal and Coke, Waterproofing, Insulating Materials, Shipping Containers, Rubber Products, Textile Materials, and Miscellaneous. Under these headings are given methods of analysis and tentative specifications for these materials. In this connection it might be noted that approximately half of the tentative standards here published are either new or have been revised for this volume. Suggested revisions and criticisms occupy a small section of the book. Certainly this publication represents the latest and best compilation of matter of the kind at present available.

The Properties of Electrically Conducting Systems. Monograph No. 7. By CHARLES A. KRAUS. 415 pp. The Chemical Catalog Co., Inc., New York. Price, $4.50.

Another valuable contribution has been made to the Monograph Series. As the author indicates in his preface, the importance of "our conceptions of matter in the ionic condition" may readily be shown to account for the rapid strides made in the last few decades in the development of chemistry and molecular physics. The author has collected and correlated a vast amount of literature, together with the result of much work that he personally has done or been in direct contact with.

Owing to the meager data available on this subject, much of the matter presented is purely empiric, but careful consideration and analysis are given to the various theories advanced in recent years, so that a clearer understanding may be had of the various conclusions reached by many investigators in their attempts to establish laws relating to ionization. Obviously, the greater part of the book is devoted to the properties of electrolytic solutions.

The conductance of gaseous systems is not discussed, since "they have been treated extensively in treatises" dealing exclusively with gaseous conducting systems. Metallic conductors are discussed in the closing chapter of the book. The properties of metallic systems are less widely known than electrolytic solutions, but the author carefully outlines the relations between conductance temperature, composition, and pressure of metals, both solid and liquid. The author closes his text with scant reference to theories of metallic conductance, referring the reader to the references given by Koenigsberger.

The various theories relating to electrolytic solutions are clearly explained in the text and their limitations pointed out. It is made plain that no one theory is adequate to explain the multiplicity of phenomena occurring in electrolytic solutions. References to original work are given fully and frequently throughout the text.

Mathematical derivations are given with the usual familiar symbols, and the equations are clearly set forth and can be readily referred to.

More care could have been used in the preparation of graphs. The value of those as given would be mainly for illustration of the various phenomena described, and not for detailed use.

As a textbook, this volume should be of great value for instruction in the theory of ionization as a part of the student's training in physical chemistry, as well as a reference for all those interested in ionization phenomena.

P. E. LANDOLT

Physical and Chemical Examination of Paints, Varnishes, and Colors. By H. A. GARDNER. 215 pp. and appendix. Published by Scientific Section, Paint Manufacturers' Association of the United States, Washington, D. C. Price, $9.00.

There is a need in the paint and varnish industry for a more thorough standardization of specifications for both raw materials and finished products. Such standardization naturally involves the development of methods of physical and chemical examination which will be accurate in the hands of the average analyst.

The Scientific Section, Educational Bureau, Paint Manufacturers' Association of the United States, under H. A. Gardner as director, has been active in advocating such standardization, and through its extensive coöperative work has been an important factor in the success of the efforts of the American Society for Testing Materials, the Federal Specifications Board, State Regulatory Laboratories, and other agencies interested in the standardization of methods for evaluating paints and painting materials. The copies of the 18 U. S. Interdepartmental Specifications appearing as an appendix to the book furnish evidence of the success of this coöperative work.

The volume is practically a compilation of methods and data presented from time to time through bulletins by the author as director of the Scientific Section. The methods and apparatus described are those in use in the author's laboratory and, while not all of them have been accepted by the trade in general, their presentation in this form has served a useful purpose if the book proves to be instrumental in bringing more closely together the producer and consumer of paint and varnish products.

E. E. WARE

The Chemical Engineering Library. Benn Brothers, Ltd., London, 1922. Price, 3s. net, each.

Every chemist entering a plant and every man already in a plant feels at one time or another the need of some knowledge of the wide field of plant equipment in fields other than the narrow one in which he works. Frequently, plant men of various classes are well informed on the actual operation of the machines under their immediate charge, but are completely ignorant of the fundamental principles involved and their application to other machines. This applies as well to the laboratory worker, who is accustomed to carry out extensive researches in glass with little or no thought of later plant equipment, as to the plant worker, whose attention is devoted solely to the operation of a single tool carrying out a single reaction. It is to fill the need of these men that the Chemical Engineering Library is being compiled.

The individual units of the series, of which five have been published, are compact in make-up both as to thought and binding. Possibly they lack something in durability, being bound rather for the library or desk than for withstanding the wear and tear of the reader's pocket. The titles so far published include: "The General Principles of Chemical Engineering Design," by Hugh Griffiths; "Materials of Construction: Nonmetals," by Hugh Griffiths; "Weighing and Measuring of Chemical Substances," by H. L. Malan and A. I. Robinson; "The Flow of Liquids in Pipes," by Norman Swindin, and "Chemical Works Pumping," by Norman Swindin.

The Chemical Engineering Catalog. 7th Annual Edition. 1187 pp. quarto. The Chemical Catalog Co., New York, 1922. Price, $10.00. Leasing fee, $2.00.

The place of the Chemical Engineering Catalog in the working libraries of chemical men has been too well established by the first six annual editions to call for comment here. The compilation of engineering data on chemical plant equipment is the only one of its kind in the world, and serves admirably to give the prospective purchaser of such materials a proper perspective of his sources of supply. Second in importance to this feature is the catalog of chemical products and raw materials, together with their sources of supply. These two sections of the book are well indexed in a preceding section of about 220 pages. In this index is to be found the real improvement of this edition over those previously offered. References and cross references both to equipment and materials have been greatly amplified and the list of sources expanded. A change in the system of indexing to a more logical arrangement of the names of chemical compounds has made the finding of any item sought much easier.

The book section of the catalog has shown a gradual growth, and offers a list of most recent books of interest to the chemical profession, together with short summaries of each. The service offered by the publishers of the catalog in supplying books of any publishers at publishers' prices is gaining in popularity.

The effect of the unfortunate financial condition of the industry is noted in the slight reduction in the number of pages in this edition. However, the growing popularity of the catalog as a reference work and the continued use to which it is put are well illustrated by the fact that the reduction in this instance is considerably less than the proportionate reduction in space taken in other advertising mediums.

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

November

The month of October marked a sharp decrease in Chilean **nitrate** sales. (Pp. 328–9)

The United States supplied 62 per cent of the world's production of **crude petroleum** in 1921 and imported an additional 17 per cent, chiefly from Mexico. While official statistics showing 1921 imports are not available for all countries, it is estimated that approximately 58 per cent of the world's importation of mineral oils in 1921 came from the United States. (Pp. 338–40)

Large distributors of **petroleum** products in the United Kingdom have made drastic cuts in prices of gasoline, kerosene, and aviation spirit. (P. 341)

A new and valuable deposit of **iron ore** has just been discovered near Ipoh in the Federated Malay State of Perak. (P. 350)

Basic slag containing 15 to 20 per cent of phosphoric acid is produced by the Thomas steel factories in Belgium at the rate of about 1 ton of slag to every 4 tons of steel. (Pp. 355–6)

The price on **citrate of lime** in Italy has been fixed for the seasons of 1922 and 1923 at 600 lire per 100 kilos. (P. 356)

French quotations for African **phosphate rock** are cited. (P. 356)

The production of **crude petroleum** in Formosa during 1920 and 1921 was 333,500 gal. each year, with a value of $108,175 in 1920 and $93,135 in 1921.

The British Government Petroleum Department on first of October became a section of the Board of Trade. (P. 403)

Gasoline is sold in the city of Brest and its environs at a much higher price than in most other centers of France. It is believed that if it were imported directly into Brest, instead of passing through an intermediary point, there would be a good opportunity for trade in that district. (P. 403)

Continued improvement is shown in the United States **export trade** in chemicals. Exports of chemicals and allied products for the first 9 mo. of 1922 still fall below the totals for the corresponding period of 1921, but the proportion of decreases continues to diminish until the margin is only one-half of 1 per cent. (P. 404)

The use of American chemical **fertilizers** in Sicily has shown a marked increase during the past few years, and American products have a ready sale and good reputation. (P. 405)

Plans are being perfected for the further development of an **atmospheric nitrogen** products industry in British Columbia. (P. 405)

Conditions in the German **wood-pulp** and **paper** industry are described. (Pp. 418–9)

Japanese **pulp** production has been restricted by suspending the operations of two factories, and the manufacture of bleached pulp will be undertaken with a view to checking importations. (P. 419)

A schedule of modifications in the Spanish **customs tariff** is cited for the following products: pulp wood; crude cod-liver oil; refined cod-liver oil; other crude animal oils, including whale oil; oxalic acid and commercial oxalates; nitrate of soda. (P. 430)

The import prohibition on **coal-tar products** into Italy has been removed. Fuel oil has been placed on the free list and important changes have been made in the import duties on coal-tar dyes and intermediates. (P. 431)

Italy has removed her export embargo on **aluminium** scrap. (P. 431)

The Bureau of Public Health in Peru is authorized to supervise and standardize the sale of **drugs** and **medicines**. (P. 436)

A compilation of Berlin chemical wages is given which illustrates the rapidity with which such wages have increased since June 1922. (P. 440)

Germany's imports of Chilean **nitrates** showed a marked decline in 1921, which is explained by the enforcement of a more rigid import control and by a loss of purchasing power, as well as by the development of domestic production through air fixation. Her present estimated production of nitrates for fertilizers is about 350,000 tons of pure nitrogen content annually. Inland consumption absorbs by far the greater part of the home production, as the needs of German agriculture were never greater. (P. 471)

A recent survey of the local **drug, chemical,** and **pharmaceutical** market has brought out the fact that German manufacturers are firmly established in Sicily in all lines. (Pp. 471–2)

Another advance was made by the German Carbide Syndicate during September in the price of **calcium,** the new price being three times that which prevailed August 1, 1922. (P. 472)

There is a great difference of opinion in Germany as to the use of **acid phosphate** as a fertilizer. Before the war 650,000 tons annually were used, while the present domestic supply is 175,000 tons, mostly Thomas slag. From experiments made during the past 10 years it appears that the soil in various parts of Germany is such as to call for the use of little or no acid phosphate for years at a time. (P. 472)

The directors of the **Anilin Interressen Gemeinschaft** have agreed to the long-expected increase in the capital stocks of the constituent concerns. (P. 472)

Because of the great demand from farmers, the importation of 200,000 tons of Chilean **saltpeter** has been sanctioned by the German Food Ministry. (P. 472)

A method of **waterproofing cloth** by means of the direct application of fresh latex, or sap, is practiced in the Department of Beni, Bolivia. Further details of the process may be obtained from the Textile Division of the Bureau of Foreign and Domestic Commerce. (P. 478)

Successful experiments have been conducted in Germany in obtaining **gas from peat.** This gas produces a higher temperature than is produced through the combustion of bituminous coal. (P. 482)

As the result of numerous tests made by the experimental plant at Stockholm for the extraction of **mineral oil from shale** the general impression seems to be that the problem of profitably producing mineral oils from shale in Sweden has been solved, although the Swedish Academy of Engineering has reserved judgment pending additional tests. (P. 484)

Under the Safeguarding of Industries Act of the United Kingdom, **gallic acid** is dutiable at $33^1/_3$ per cent. (P. 502)

Because of its textile, paper, and leather industries, Czechoslovakia is an important consumer of **coal-tar dyestuffs.** Through long business connections and known quality of product, German dyes have an advantage. There is a certain prejudice against American colors because they are not known and because immediately after the war some American dyestuffs of poor quality were received. It is believed that this prejudice can be overcome, and probably the best opening for American dyes is in direct blacks, blues, reds, and acid colors. (P. 542)

Chile has issued a decision regarding the conditional reduction of import duty on **naphtha** and **gasoline.** (P. 559)

Italy has removed her export embargo on **pyrites.** (P. 559)

STATISTICS OF EXPORTS TO THE UNITED STATES

Madras—(P. 355)
Nux vomica
Sweden—(P. 363)
Sulfite
Kraft pulp
Sulfate pulp

Bolivia—(P. 391)
Tin
Austria—(P. 411)
Copper
Lead
Zinc

SPECIAL SUPPLEMENT ISSUED

Spanish Trade in Petroleum Products. *Trade Information Bulletin* 72.

CURRENT PUBLICATIONS

NEW BOOKS

Aircraft Steels and Materials. R. K. Bagnall-Wild, Leslie Aitchison, A. A. Remington, A. J. Rowledge, and W. A. Thain. 210 pp. Illustrated. Price, 16s. net. Constable & Co., Ltd., London.

Allotropy: The Theory of Allotropy. A. Smits. 397 pp. Price, $7.00. Longmans, Green & Co., New York.

Chemical Reactions and Their Equations. Ingo W. D. Hackh. 138 pp. Price, 6s. Chapman & Hall, London.

Chemicals and Allied Products, 1919 and 1920. 150 pp. Dominion Bureau of Statistics, Ottawa, Canada.

Chemistry: Cours de Chimie. E. Charabot and C. Milhau. 2nd edition. 370 pp. Price, 11fr. Dunod, Paris.

Chemistry of Dental Materials. C. S. Gibson. 176 pp. Price, 12s. 6d. Benn Bros., Ltd., London.

Definition of Relativity. 16 pp. **Definition of the Ether.** 16 pp. **Definition of Equivalence.** 16 pp. **Definition of Isotopes.** 20 pp. F. H. Loring. Science by Definition Series. Price, 1s. each. H. O. Lloyd & Co., Ltd., London.

Engine-Room Chemistry. Augustus H. Gill. 3rd edition. 174 pp. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

Food: Report of the Food Investigation Board for the Year 1921. Department of Scientific and Industrial Research. 47 pp. Price, 2s. H. M. Stationary Office, London.

Gasworks Chemistry: Modern Gasworks Chemistry. Geoffery Weyman. 184 pp. Price, 25s. Benn Bros., Ltd., London.

Gelatin: Die Fabrikation von Leim und Gelatine. Ludwig Thiele. 189 pp. Price, 80 cents. Max Janecke, Leipzig.

Handbook: Agendas Dunod 1923. 12 volumes. Price, 10 fr. 40 each. **Agenda Chimie.** Emile Javet. 425 pp. **Agenda Métallurgie.** Louis Descroix. 312 pp. **Agenda Physique Industrielle.** J. Izart. 315 pp. Dunod, Paris.

Incandescent Lighting. S. I. Levy. 129 pp. Price, 3s. Sir Isaac Pitman & Sons, Ltd., London.

Internal Combustion Engine. H. E. Wimperis. 4th edition, revised and enlarged. 320 pp. Illustrated. Price, 12s. 6d. net. Constable & Co., Ltd., London.

Iron Ore. Part VI. Europe and Africa (Foreign). Summary of Information as to the Recent and Prospective Iron-Ore Supplies of the World. Imperial Mineral Resources Bureau. 275 pp. Price, 6s. H. M. Stationery Office, London.

Laboratory Handbook of Biochemistry. P. C. Raiment and G. L. Peskett. 102 pp. Price, 5s. Edward Arnold & Co., London.

Lubrication and Lubricants. J H. Hyde. 114 pp. Price, 2s. 6d. Edward Arnold & Co., London.

Mechanical Laboratory Methods. The Testing of Instruments and Machines in the Mechanical Laboratory and in Practice. Julian C. Smallwood. 3rd edition, revised and enlarged. 437 pp. 112 illustrations. Price, $3.50. D. Van Nostrand Co., New York.

Nitrogen Industry. J. R. Partington and L. H. Parker. 335 pp. Illustrated. Price, 21s. net. Constable & Co., Ltd., London.

Ore: Technical Methods of Ore Analysis for Chemists and Colleges. Albert H. Low. 348 pp. Price, $3.50. John Wiley & Sons, Inc., New York.

Organic Syntheses. Vol. II. James Bryant Conant, Hans Thacher Clarke, Roger Adams, and Oliver Kamm, Editors. 100 pp. Price, $1.50. John Wiley & Sons, Inc., New York.

Practical Chemical Physiology. W. W. Taylor. 70 pp. Price, 4s. Edward Arnold & Co., London.

Rubber: Les Colloides dans l'Industrie. Le Caoutchouc. Paul Bary. 255 pp. Price, 32 fr. 50. Dunod, Paris.

Rare Metals: Les Métaux des Terres Rares. J. F. Spencer. 280 pp. Price, 36 fr. Dunod, Paris.

Supervised Study in Mathematics and Science. S. Clayton Sumner. 241 pp. Price, $1.40. The Macmillan Co., New York.

Swiss Industry: Rapport sur le Commerce et l'Industrie de la Suisse en 1921. 438 pp. Price, 9 fr. Secrétariat de l'Union Suisse du Commerce et de l'Industrie, Zürich.

Synthetic Coloring Matters: Dyestuffs Derived from Pyridine, Quinoline, Acredine, and Xanthrene. J. T. Hewitt. 405 pp. Price, 14s. Longmans, Green & Co., London.

Volatile Oils. Vol. III. E. Gildemeister and Fr. Hoffman. 2nd edition, translated by E. Kremers. 777 pp. Price, 32s. Longmans, Green & Co., London.

RECENT JOURNAL ARTICLES

Alkaloids: Recent Developments in the Chemistry of Alkaloids. Norman Evers. *The Chemical Age (London)*, Vol. 7 (1922), No. 176, pp. 594–98.

Atmospheric Dust. J. S. Owens. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 20, pp. 438*r*–43*r*.

Biochemical Differentiation of Bacteria. Homer W. Smith. *American Journal of Hygiene*, Vol. 2 (1922), No. 16, pp. 607–55.

Catalytical Activity of Copper. O. W. Brown and C. O. Henke. *Journal of Physical Chemistry*, Vol. 26 (1922), No. 8, pp. 713–27.

Cellulose: L'Industrie de la Cellulose en France. A. R. de Vains. *Chimie et Industrie*, Vol. 8 (1922), No. 4, pp. 767–81.

Chemistry as an Aid in the Detection of Crime. Henry Leffmann. *American Journal of Pharmacy*, Vol. 94 (1922), No. 11, pp. 691–99.

Chrome Tanning: Modern Problems in Chrome Tanning. Donald Burton. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 11, pp. 555–65.

Coal: Comparison of Froth with the Trent Process. Oliver C. Ralston. *Coal Age*, Vol. 22 (1922), No. 23, pp. 911–14.

Coal: Le Chauffage au Charbon Pulvérisé des Chaudières et des Fours en Général. Paul Frion. *Chimie et Industrie*, Vol. 8 (1922), No. 4, pp. 736–57.

Coke: The Structure of Coke: Its Origin and Development. Sir George Beilby. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 21, pp. 341*t*–47*t*.

Fluorspar and Its Uses. G. H. Jones. *Blast Furnace and Steel Plant*, Vol. 10 (1922), No. 11, pp. 563–67.

Gas: The Sampling and Analysis of Automobile Exhaust Gas. A. C. Fieldner and G. W. Jones. *Journal of the Franklin Institute*, Vol. 194 (1922), No. 5, pp. 613–44.

Laundry: Chemical Research in the Power Laundry Industry. A. F. Shupp. *American Dyestuff Reporter*, Vol. 11 (1922), No. 10, pp. 336–38.

Leather: Plan de Travail pour l'Étude des deux Questions Suivantes. I—Caractérisation Analytique Individuelle des Matières Tannantes et des Extraits. II—Recherche des Mélanges—Décèlement des Adulterations. M. Janet. *Journal of the Society of Leather Trades' Chemists*, Vol. 6 (1922), No. 10, pp. 336–50.

Leather: Some Observations on the Histology of Bated Skins. Röhm and Haas Company. *Journal of the American Leather Chemists Society*. Vol. 17 (1922), No. 11, pp. 542–54.

Rubber: Sull' Invecchiamento Naturale ed Artificiale della Gomma Vulcanizzata. C. Pelizzola. *Giornale di Chimica Industriale ed Applicata*, Vol. 4 (1922), No. 10, pp. 458–60.

Scientific Instruments: The Control of Works Operations by Scientific Instruments. Leonard Levy. *The Chemical Age (London)*, Vol. 7 (1922), No. 180, pp. 734–37.

Steel: Repeated Stress Failures of Construction Steel and Their Relation to the Krupp Repeated Impact Test. F. Rittenhausen and F. P. Fischer. *Forging and Heat Treating*, Vol. 8 (1922), No. 11, 519–25. Translated from *Stahl und Eisen*.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Zinc: The Effect of Impurities on the Oxidation and Swelling of Zinc Aluminium Alloys. A booklet of 35 pages, paper of Brauer and Peirce, presented at the joint meeting of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers and the American Foundrymen's Association, June 5, 1922. The New Jersey Zinc Company, New York, N. Y.

Parsons & Petit, selling agents for the Freeport Sulphur Co., have recently published a card which shows on one side pictures of the loading of sulfur at the mines and docks, with a short description of the origin and mining in the United States and Sicily, and statistics covering 1892 to 1921, inclusive, embodying production, imports and exports of the United States, and production and exports of Sicily. The other side shows channels of consumption, with domestic exports to the different countries during 1913 and from 1918 to 1921.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Analysis of Kentucky Coals. *Technical Paper* 308. 92 pp. Paper, 10 cents. 1922.

Bureau of Mines Investigates Gold in Oil Shales and Its Possible Recovery. Thomas Varley. *Reports of Investigations* 2413. 10 pp. Issued November 1922.

Coal-Dust Explosion Tests in the Experimental Mine 1913 to 1918, Inclusive. G. S. Rice, L. M. Jones, W. L. Egy, and H. P. Greenwald. *Bulletin* 167. 639 pp. Paper, $1.00. 1922.

Coke-Oven Accidents in the United States during the Calendar Year 1921. W. W. Adams. *Technical Paper* 318. 34 pp. Paper, 5 cents.

Contraction and Shrinkage of Nonferrous Alloys as Related to Casting Practice. R. J. Anderson. *Reports of Investigations* 2410. 13 pp. Issued November 1922.

Distillation Gases Yielded by Trent Amalgams, and Ethylene Found Therein as a Source of Alcohol. J. D. Davis. *Reports of Investigations* 2413. 8 pp. Issued November 1922.

Fusibility of Ash from Coals of the United States. *Bulletin* 209. W. A. Selvig and A. C. Fieldner. 119 pp. Paper, 15 cents. 1922.

Lessons from the Granite Mountain Shaft Fire, Butte, Montana. Daniel Harrington. *Bulletin* 188. 50 pp. Paper, 15 cents.

Methods for Determining Sediment in Fuel Oils. A. D. Bauer. *Reports of Investigations* 2408. 4 pp. Issued October 1922.

Properties of Typical Crude Oils from the Producing Fields of Southern Louisiana and Southern Texas. (Abstract.) N. A. C. Smith, A. D. Bauer, and N. F. LeJuene. *Reports of Investigations* 2416. 2 pp. Issued November 1922.

Reduction Mills in the Various Western States in 1920. *Reports of Investigations* 2287. 1 p. Issued October 1922.

The Production of Carbon Black from Natural Gas by the High Voltage Arc. J. J. Jakowsky. *Reports of Investigations* 2417. 10 pp. Issued November 1922.

Value of Coke, Anthracite, and Bituminous Coal for Generating Steam in A Low-Pressure, Cast-Iron Boiler. J. Blizard, J. Neil, and F. C. Houghten. *Technical Paper* 303. 56 pp. Paper, 10 cents. 1922.

Bureau of Standards

Caustic Magnesia Cement. *Circular* 135. Paper, 5 cents. Issued December 1922.

Properties of Electrical Insulating Materials of the Laminated, Phenolmethylene Type. J. H. Dellinger and J. L. Preston. *Technologic Paper* 216. Paper, 30 cents.

Reclamation of Used Petroleum Lubricating Oils. W. H. Herschel and A. H. Anderson. *Technologic Paper* 223. 16 pp. Issued October 21, 1922. Paper, 5 cents.

Relative Usefulness of Gases of Different Heating Value and Adjustments of Burners for Changes in Heating Value and Specific Gravity. W. M. Berry, I. V. Brumbaugh, J. H. Eiseman, G. F. Moulton, and G. B. Shawn. *Technologic Paper* 222. Paper, 25 cents. Issued December 1922.

Specification for Numbered Cotton Duck for Government and Commercial Use. *Circular* 136. 4 pp. Paper, 5 cents. 1922.

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MARKET REPORT—DECEMBER, 1922

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

As far as spot business in chemicals is concerned, December saw somewhat of a falling off in buying. Contract business for delivery over 1923, however, has been active. Consumers, evidently warned by the rising prices of the past four months, are reported to have signed up freely for next year's supplies of many items. This may have been occasioned by the fact that consumers have been short of stocks for some time past, and now, admitting that the market has stabilized to their satisfaction, are willing to contract for goods well in advance. When this is compared with the hesitancy of buyers to cover by contract a year ago, the condition in itself is indicative of the changed general situation in the chemical market.

Spot business has been slow primarily because consumers have been holding down stocks of raw materials until after inventory taking. No real lack of demand is evident, as can be concluded from the amount of contract business done and the general stability of prices. In spite of less demand for spot goods and goods for immediate shipment, prices have actually advanced during the past month. Numerous scarcities have been developed, in some cases to the point of acuteness. In most products the market shows that it is easier to sell satisfactorily than it is to buy, particularly in instances like cresylic acid, solvent naphtha, arsenic, formaldehyde, methanol, phenol, salt cake, Glauber's salt, and others. December, like October and November, was almost devoid of genuine price declines.

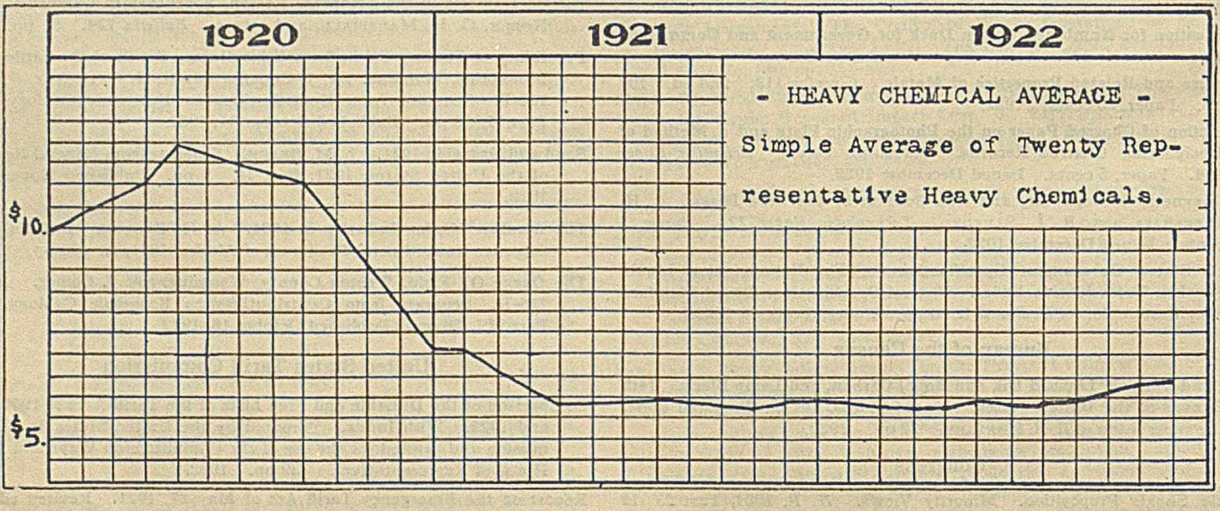
Reports indicate that caustic soda and soda ash are being signed up for delivery over 1923 on contract at approximately the same terms as have ruled the spot markets during the greater part of 1922. Producers state that business has been extremely good during the closing weeks of the year. It is practically impossible to buy salt cake on the open market and has been for some weeks past. Niter cake and Glauber's salt are also in small supply on spot and at producing centers. Very limited spot stocks of potassium prussiate are being held at higher levels by sellers. On the rising market for tin metal, tin crystals have advanced. Two exceptions to the higher price rule during December were yellow sodium prussiate and oxalic acid, both of which dropped off slightly.

One of the most spectacular market developments of the past few months has been in wood chemicals. The rising tendency of all prices in this group continued to manifest itself during December, with higher quotations noted for acetate of lime, acetic acid, acetone, methanol, formaldehyde, and other derivatives. Production is curtailed and has been for many months. Excess stocks are about depleted and it is with difficulty that buyers have been able to cover requirements during the month past. Producers are entering contracts rather warily as they are still uncertain regarding next year's supplies. Lime acetate is now $3.50, acetone 21 cents, methanol $1.25, and formaldehyde 16 cents.

Arsenic continues to play a leading role in the market. January delivery is commanding 15 cents a lb. with little spot material offered. Reports indicate that consumption in 1922 aggregated 4000 tons of As_2O_3, a large portion of which went into the production of some sixteen million pounds of calcium arsenate for the cotton fields. No residual stocks of either remain. Estimates place the requirements of calcium arsenate for 1923 as more than double 1922, but it is difficult to see where the arsenic is coming from to take care of this demand. Reduced smelting operations for several years back, owing to low prices for both copper and arsenic, have permitted all surpluses to be wiped out. American smelters will not produce unless there is some assurance of a continued fair price. An arsenic shortage during 1923 is almost certain.

Although stocks of cresylic acid are in bond at ports of entry, little is to be had on the open market owing to the fact that the duty has not as yet been determined upon by the appraiser's stores. Such small lots as are being sold command 90 cents per gal. for any grade. During December all salicylates went up, the continued high price of phenol being the cause. The latter moved to 35 cents a lb. inside, with only imported goods being offered. No American producer is yet known to have resumed operations. Denatured alcohols are higher. Supplies of alums and aluminium sulfate are somewhat reduced, with consequent rising price tendencies in the latter.

Demand for coal-tar intermediates during the month has been good with prices firm. Aniline oil is moving well at 17 cents. Dimethylaniline is firmer on position of methanol. H-acid is stronger on reduced competition. Animal and fish oils have been steady and prices strong. Cod and menhaden oils are higher on scarcity, as the fishing season is now over and stocks are low. Demand for animal oils has been active. Vegetable oils have been in fair demand with China-wood and linseed oils higher. Turpentine is easier.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

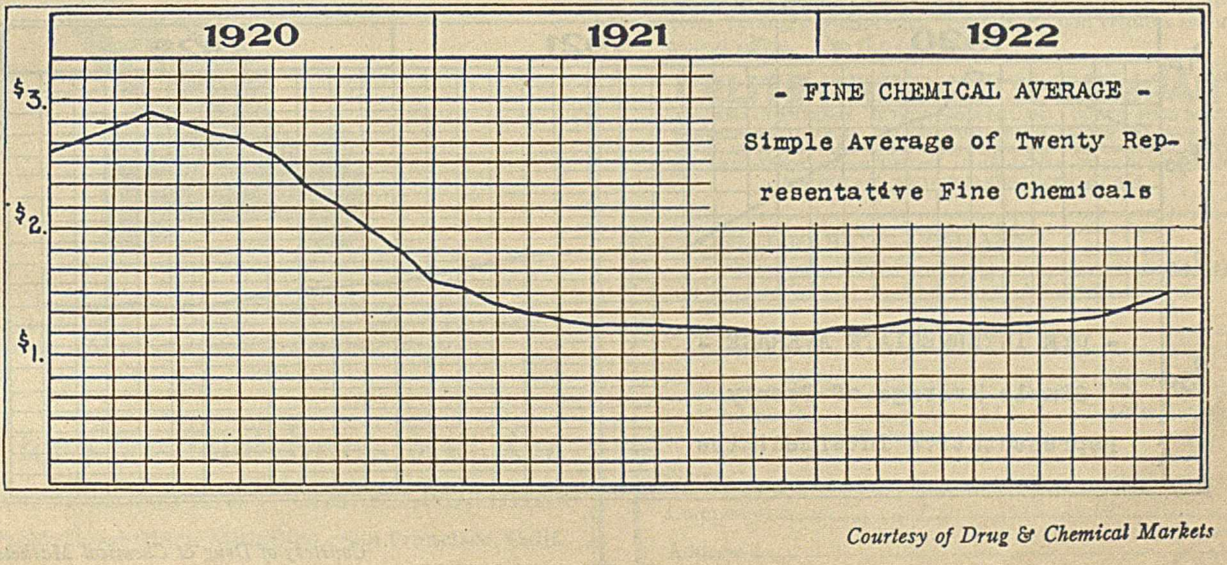
	Dec. 1	Dec. 15	Jan. 1922
Acid, Boric, cryst. bbls.......lb.	.11¾	.11¾	.12¾
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls..lb.	.06	.06	.07
Hydriodic, sp. gr. 1.150...lb.	2.25	2.25	2.00
Nitric, 42°, cbys. c/l wks.lb.	.05½	.05½	.06
Phosphoric, 50% tech.....lb.	.08	.08	.10
Sulfuric, C. P...........lb.	.08	.07	.07
66° tks. wks........ton	15.00	15.00	16.00
Oleum 20%.........ton	18.00	18.00	19.00
Alum, Ammonia, lump........lb.	.03½	.03½	.03½
Potash, lump............lb.	*.03½	*.03½	*.03½
Chrome.............lb.	.06	.06	.07
Soda, ground............lb.	.04	.04	.03½
Aluminium Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.10¾	.10¾	.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.	.14	.15	.06½
Barium Chloride............ton	*100.00	*95.00	*53.00
Nitrate.................lb.	*.08	*.08	*.07
Barytes, white..............ton	33.50	33.50	28.00
Bleaching Powd., 35%, works ....100 lbs.	2.00	2.00	2.25
Borax, cryst., bbls............lb.	.05½	.05½	.05¾
Bromine, pure, wks...........lb.	.29	.29	.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.	5.75	5.75	5.55
Iodine, resublimed...........lb.	4.40	4.40	3.80
Lead Acetate, white crystals...lb.	.12	.12	.11
Nitrate................lb.	.22	.22	.15
Red...................lb.	.08	.09	.08
White (Carb.)...........lb.	.08½	.08½	.07¼
Lime Acetate...........100 lbs.	3.50	3.50	1.75
Magnesium Carbonate, tech...lb.	.07½	.07½	.06
Magnesite, calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow...........lb.	*.28	*.28	*.27
Red...................lb.	*.30	*.30	*.30
Plaster of Paris.............bbl.	4.25	4.25	4.25
Potassium Bichromate........lb.	.10	.10	.10½
Bromide, imported.......lb.	*.19	*.19	*.13
Carbonate, calc., 80-85%.lb.	*.05½	*.05½	*.04½
Chlorate, cryst...........lb.	*.07½	*.07½	*.05½
Hydroxide, 88-92%......lb.	*.06½	*.06½	*.06
Iodide, bulk.............lb.	3.50	3.50	2.90
Nitrate.................lb.	.08	.08	.08
Permanganate, U. S. P....lb.	*.17	*.17	*.15
Prussiate, red...........lb.	*.95	*.95	*.29
Yellow.............lb.	*.39	*.39	*.24½
Salt Cake, bulk.............ton	28.00	28.00	17.00
Silver Nitrate...............oz.	.43	.43	.44½
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.75	3.75	3.80

*Resale or Imported (not an American makers' price).

	Dec. 1	Dec. 15	Jan. 1922
Sodium Acetate..............lb.	.07½	.07½	.04
Bicarbonate.........100 lbs.	2.00	2.00	2.00
Bichromate.............lb.	.07½	.07½	.07¾
Bisulfite, powd...........lb.	.04¼	.04¼	.04¼
Chlorate................lb.	.07	.07	.07½
Cyanide, 96-98%........lb.	.23	.23	.28
Fluoride, tech...........lb.	.09½	.09½	.09½
Hyposulfite, bbls.....100 lbs.	3.20	3.20	3.50
Nitrate, 95%........100 lbs.	2.50	2.57	2.32½
Nitrite..................lb.	.09	.09	.06½
Prussiate, yellow.........lb.	.21	.20	.16½
Phosphate (di-sod.),tech..lb.	.04½	.04½	.04¼
Silicate, 40°..............lb.	.01½	.01½	.01⅛
Sulfide, 60%, fused.......lb.	.04	.04	.05
Strontium Nitrate............lb.	*.10	*.10	*.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.	.20	.20	.35
Oxide, bbls..............lb.	.07½	.07½	.08

ORGANIC CHEMICALS

	Dec. 1	Dec. 15	Jan. 1922
Acetanilide, U. S. P., bbls......lb.	*.34	*.34	*.29
Acid, Acetic, 28 p. c.......100 lbs.	3.17	3.17	2.37½
Glacial..............lb.	.12	.12	.10
Benzoic, U. S. P........lb.	.60	.60	.60
Carbolic, cryst., U. S. P., drs...............lb.	.40	.40	.12
50- to 110-lb. tins....lb.	.45	.45	.18
Citric, crystals, kegs......lb.	*.50	*.50	*.43
Oxalic, cryst., bbls., wks...lb.	.14	.13½	.14
Pyrogallic, resublimed....lb.	1.60	1.60	1.75
Salicylic, U. S. P.........lb.	.38	.38	.24
Tannic, U. S. P., bbls....lb.	.70	.70	.75
Tartaric, cryst., U. S. P...lb.	*.30	*.30	*.25
Acetone, drums..............lb.	.21	.21	.12
Alcohol, denatured, complete.gal.	.40	.40	.45
Ethyl, 190 proof, bbls....gal.	4.75	4.75	4.75
Amyl Acetate................gal.	2.35	2.35	2.00
Camphor, Jap, refined, cases...lb.	.91	.94	.90
Carbon Bisulfide, c/l..........lb.	.06	.06	.06½
Tetrachloride............lb.	.10	.10	.10½
Chloroform, U. S. P., drums...lb.	.35	.35	.43
Creosote, U. S. P.............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.27	.27	.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.	.14	.14½	.10½
Glycerol, dynamite, drums....lb.	.17½	.17	.14½
Methanol, pure, bbls.........gal.	1.05	1.20	.75
Methylene Blue, med.........lb.	3.00	3.00	4.00
Petrolatum, light amber......lb.	.04½	.04½	.05¼
Pyridine.....................gal.	1.75	1.80	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

OILS, WAXES, ETC.

	Dec. 1	Dec. 15	Jan. 1922
Beeswax, pure, white.........lb.	.32	.32	.33
Castor Oil, No. 3.............lb.	.12	.12	.10½
Ceresin, yellow...............lb.	.08	.08	.07½
Corn Oil, crude, tanks, mills...lb.	.07¼	.07¼	.06¾
Cottonseed Oil, crude, f. o. b. mill.....................lb.	.08½	.08½	.07
Linseed Oil, raw, c/l.........gal.	.87	.89	.69
Menhaden Oil, crude, mills...gal.	.53	.46	.35
Neat's-foot Oil, 20°..........lb.	.18	.18	.16¾
Paraffin, 128–130 m. p., ref.....lb.	.03¾	.03¾	.05
Rosin, "F" grade, 280 lbs....bbl.	6.50	6.35	5.30
Rosin Oil, first run...........gal.	.43	.43	.36
Shellac, T. N.................lb.	.70	.70	.66
Sperm Oil, bleached winter, 38°......................gal.	1.05	1.05	1.70
Stearic Acid, double pressed...lb.	.11¼	.11¼	.09¾
Tallow Oil, acidless...........lb.	.11¾	.11¾	.10
Turpentine, spirits of........gal.	1.54	1.43	.82½

METALS

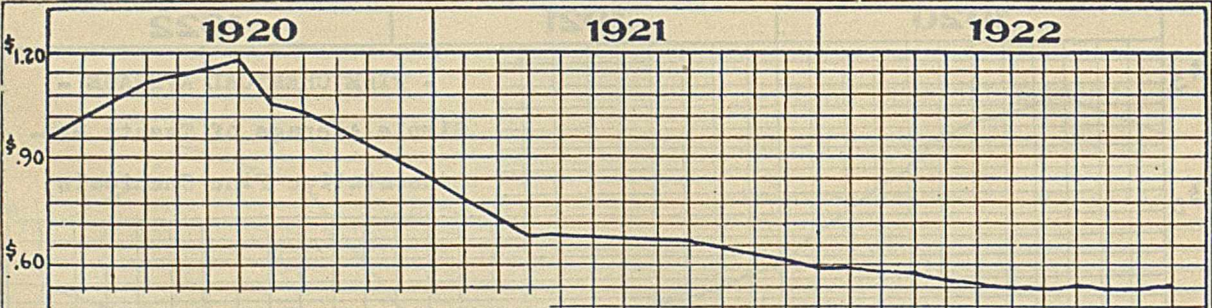
	Dec. 1	Dec. 15	Jan. 1922
Aluminium, No. 1, ingots.....lb.	.23	.23	.17
Antimony, ordinary......100 lbs.	6.50	6.50	4.55
Bismuth......................lb.	2.60	2.65	1.80
Copper, electrolytic..........lb.	.13⅞	.14	.13⅛
Lake....................lb.	.14	.14	.13¾
Lead, N. Y..............100 lbs.	7.25	7.25	4.70
Nickel, electrolytic...........lb.	.36	.36	.45
Platinum, refined, soft........oz.	108.00	108.00	78.00
Quicksilver, flask......75 lbs. ea.	70.00	71.00	52.00
Silver, foreign................oz.	.64¼	.64½	.65¼
Tin..........................lb.	.36¾	.37¼	.32¾
Tungsten Wolframite....per unit	7.50	7.50	2.00
Zinc, N. Y..............100 lbs.	8.25	8.25	5.20

FERTILIZER MATERIALS

	Dec. 1	Dec. 15	Jan. 1922
Ammonium Sulfate, expt..100 lbs.	3.55	3.55	2.60
Blood, dried, f. o. b. N. Y....unit	4.50	4.60	3.50
Bone, 3 and 50, ground, raw..ton	28.00	28.00	30.00
Calcium Cyanamide, unit of ammonia.................	2.25	2.25	2.25
Fish Scrap, dried, wks......unit	5.15	5.25	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	.70	.70	*.75
Tankage, high-grade, f. o. b. Chicago...............unit	4.60 & .10	4.60 & .10	3.00 & .10

COAL-TAR CHEMICALS

	Dec. 1	Dec. 15	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.	.40	.40	.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.	.60	.60	.50
Cleve's..................lb.	1.50	1.50	1.50
Gamma..................lb.	1.80	1.80	2.25
H........................lb.	.75	.78	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	1.15	1.30
Picric...................lb.	.20	.20	.25
Sulfanilic................lb.	.19	.19	.26
Tobias'..................lb.	1.30	1.30	2.00
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.16	.16	.17
Aniline Salt..................lb.	.24	.24	.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.	3.75	3.75	5.50
Dianisidine..................lb.	4.50	4.50	4.75
p-Dichlorobenzene...........lb.	.06	.06	.15
Diethylaniline...............lb.	.60	.60	.90
Dimethylaniline..............lb.	.40	.40	.40
Dinitrobenzene..............lb.	.20	.20	.21
Dinitrotoluene...............lb.	.20	.20	.25
Diphenylamine..............lb.	.52	.52	.58
G Salt......................lb.	.65	.65	.70
Hydroquinol.................lb.	1.15	1.15	1.35
Monochlorobenzene..........lb.	.08	.08	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.24	.24	.30
a-Naphthylamine............lb.	.29	.29	.30
b-Naphthylamine............lb.	.95	.95	1.05
m-Nitroaniline..............lb.	.62	.62	.85
p-Nitroaniline..............lb.	.73	.73	.77
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol..............lb.	.72	.72	.75
o-Nitrotoluene..............lb.	.11	.11	.15
p-Nitrotoluene..............lb.	.60	.60	.70
m-Phenylenediamine.........lb.	.90	.90	1.10
p-Phenylenediamine.........lb.	1.50	1.50	1.60
Phthalic Anhydride..........lb.	.35	.35	.38
R Salt......................lb.	.55	.55	.60
Resorcinol, tech.............lb.	1.30	1.30	1.50
U. S. P..................lb.	2.00	2.00	2.00
Schaeffer's Salt. ....lb.	.60	.60	.70
Sodium Naphthionate........lb.	.56	.56	.70
Thiocarbanilide..............lb.	.35	.35	.40
Tolidine (base)..............lb.	1.15	1.15	1.20
Toluidine, mixed............lb.	.30	.30	.30
o-Toluidine.................lb.	.15	.15	.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

H_2SO_4

does not affect real

Hard Lead Alloy

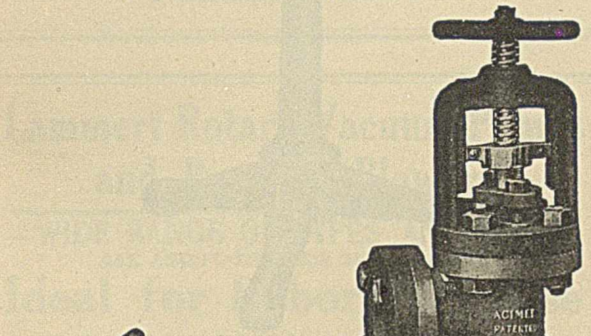
ACIMET

Trade-Mark Reg.

Acid Resisting

VALVES

Patented



We are prepared to co-operate with our customers in all parts of the world. Representation in foreign countries is open for negotiation with responsible concerns.

The Cleveland Brass Mfg. Co.

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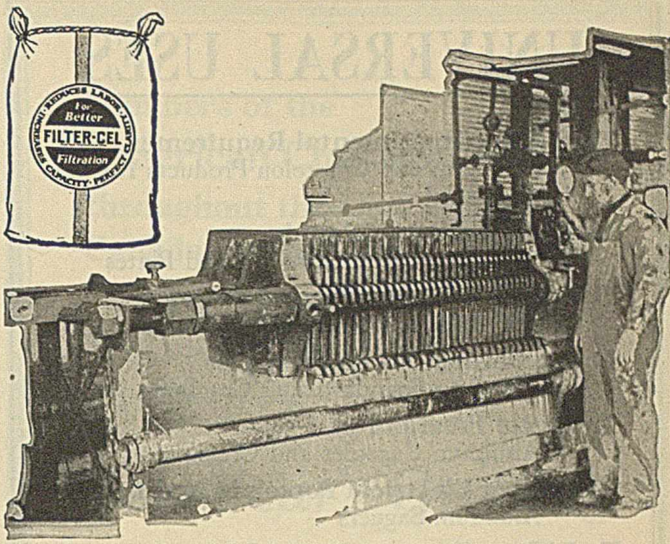

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FILTER-CEL is an extremely porous mineral powder which has no chemical effect upon the liquids. It may be used with all types of pressure filters, and builds up a cake which retains the most minute particles of suspended matter. In addition to greater clarity, it prevents clogging, enables the filter to operate in longer cycles and increases the rate of flow.

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A quantity sufficient for you to determine results will be sent upon request, or we shall be glad to filter a sample of your product in our laboratories and return to you with a detailed report.

The experiences of our chemical engineers in filtering innumerable products of widely divergent nature are contained in a booklet explaining FILTER-CEL in detail and giving typical installations. Sent free upon request from our nearest office. Use the coupon.

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Gentlemen: Without obligation, send Bulletin HH-40 and the additional matter checked below. We use

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(GIVE NAME OF FILTER) (LIST PRODUCTS FILTERED)

☐ Send sufficient quantity of FILTER-CEL for testing.
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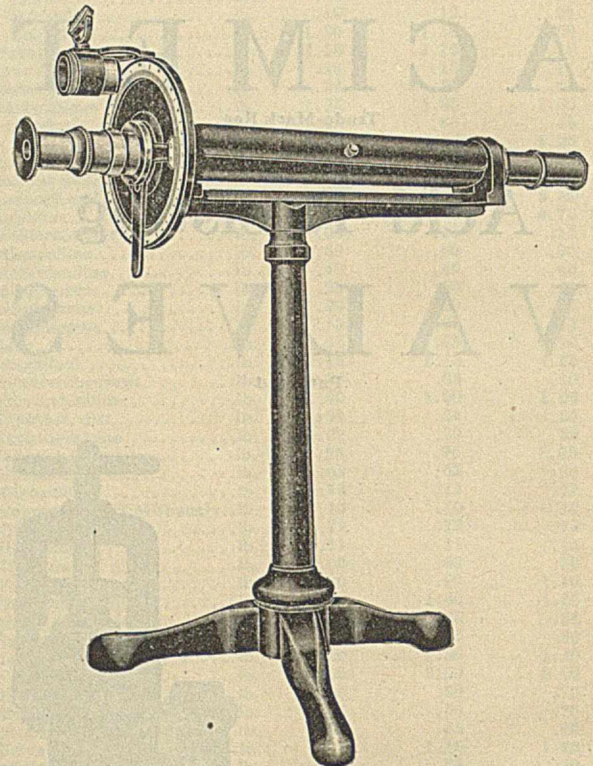

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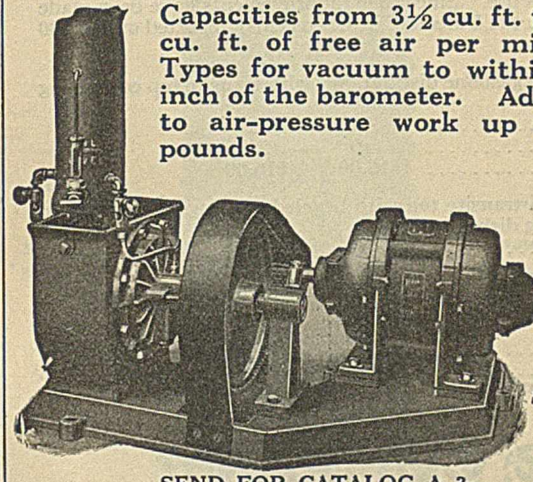

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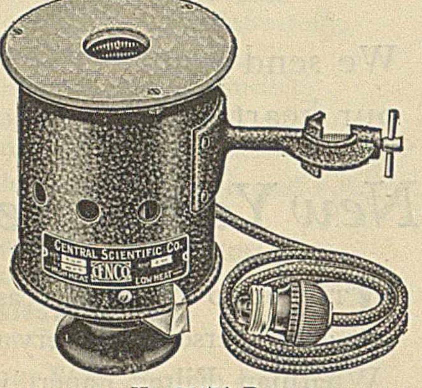

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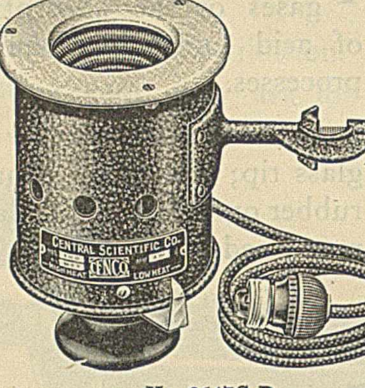

No. 9647C-D.

The design of the **Cenco Elecrtic Heaters** was suggested by Dr. E. W. Dean, of the U. S. Bureau of Mines, and developed by our Engineering Department, in cooperation with the Bureau of Mines Laboratory, to provide a simple, economical heater, for use with the standard gasoline distillation apparatus specified by Committee D-2 of the American Society for Testing Materials for the determination of the initial boiling and end points of gasoline, naphtha, petroleum oils and paint thinners. The idea of simplicity, replaceability and efficiency were always kept in mind.

The **heating unit** is constructed by a special process (patent applied for), which enables the heating coil of chromel wire to be securely held in the form of a conical helix in a solid block of extremely efficient heat insulating material by means of a refractory cement. The separate turns of wire are in contact with the refractory cement for only a small part of their circumference, and as a result, the heat wasted by absorption in and radiation from the block is reduced to a minimum. The maximum exposure of wire surface, the conical shape of the depression in the block and the high heat radiating qualities of the cement combine to concentrate the heat upon the opening in the transite top of the heater. Due to this method of construction the **Cenco Electric Heater** responds readily to changes in current produced by adjusting the rheostat. The heating unit, which includes both the heating coil and heat insulating container, can be easily replaced by the user in case of a burn-out.

A **variable rheostat**, mounted in the same case with the heating coil, permits the temperature to be raised or lowered at will by turning the **adjusting knob** on the under side of the heater, which is always cool. Attached to the adjusting knob is an **index**, which enables the operator to judge the amount of resistance in the circuit. When the entire rheostat is in the circuit, the heater is operating on **low heat** with a current consumption of 165 watts, thereby radiating 2440 calories per minute into the heating chamber. When the entire rheostat is out of the circuit, the heater is operating on **high heat** with a current consumption of 255 watts, thereby radiating 3650 calories per minute.

The **Cenco Electric Heater** is furnished with a **clamp**, permitting it to be mounted on any laboratory support stand, which enables it to be used in many places in the laboratory where a rapid and efficient source of concentrated heat is required. It will be found preferable to a gas flame for many operations.

Since the **Cenco Electric Heater** was first announced, over **1500** have been placed in laboratories, from which have come enthusiastic reports of their performance and of their adaptability for widely varying purposes. A test conducted by the U. S. Bureau of Mines on one of the first models gave over 500 hours of continuous use. Since then, improvements have been made in method of construction and character of materials used, as a result of which the Bureau of Mines recently reported **over 1,000 hours of use and no evidence of deterioration.**

9647. CENCO ELECTRIC HEATER, as used in the A. S. T. M. methods for gasoline distillations, with transite top containing 1¼ inch opening for use in official tests

No.	A	B
For volts	110	220
Each	**$15.00**	**$16.00**

9647. CENCO ELECTRIC HEATER, same as Nos. 9647A and B, but with transite top with beveled openings 2½ inches in diameter, for use with distilling flasks, Kjeldahl flasks, evaporating dishes, etc.

No.	C	D
For volts	110	220
Each	**$15.00**	**$16.00**

9648. HEATING UNITS, for No. 9647, for replacement.

No.	A	B
Each	**$2.50**	**$3.00**

For further description, send for **BULLETINS 93F** and **47F.**

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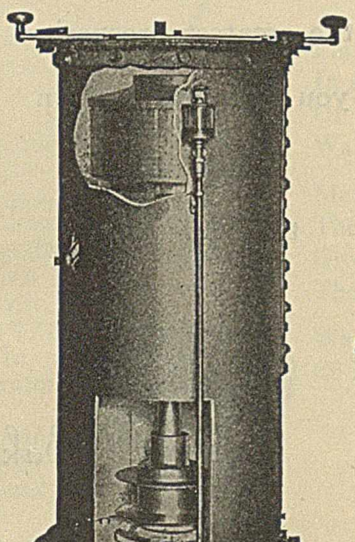

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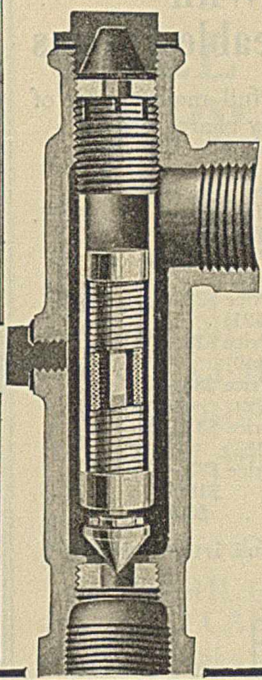

Furthermore, you can guarantee that Sarco Traps will cut down repair bills, for they have but five parts compared with as many as forty-three in some traps. Consequently, there are fewer parts to carry in stock—fewer parts to wear out and need replacement.

You can safeguard your own judgment until you are sure that the Sarco will do as claimed, as we will ship same on 30 days' free trial.

Write for particulars regarding free trial offer and interesting booklet D-31.

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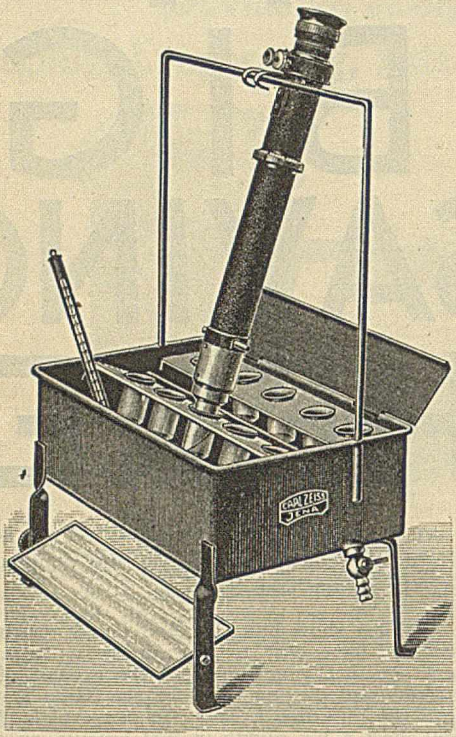
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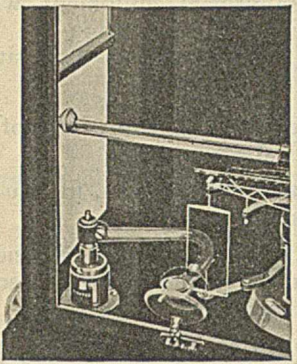
TWIN BENEFACTORS



The pan extractor admits and ejects the button while the balance door is closed. Dust and air-currents need never enter. Readjustment of the instrument is rarely necessary.

THE *HEUSSER multiple-weight-attachment* and *mechanical-pan-extractor* are accessories, patented, obtainable only in a *HEUSSER* Precision Balance.

They are no more a part of the instrument than is the horn a part of the motor in your car.

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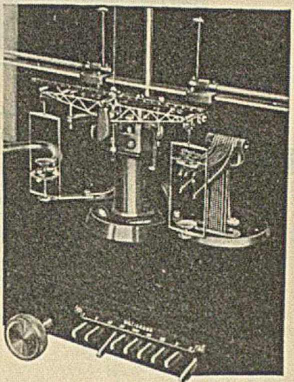
A mighty interesting balance booklet for the asking.



The weight attachment permits the instantaneous changing of weights while the balance swings and the door is closed. Since weights are not handled their accuracy is never impaired.

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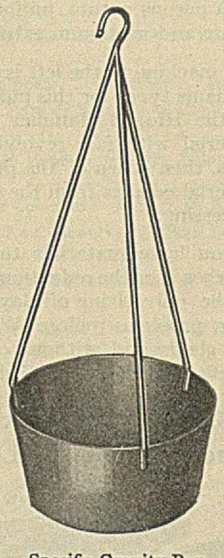

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