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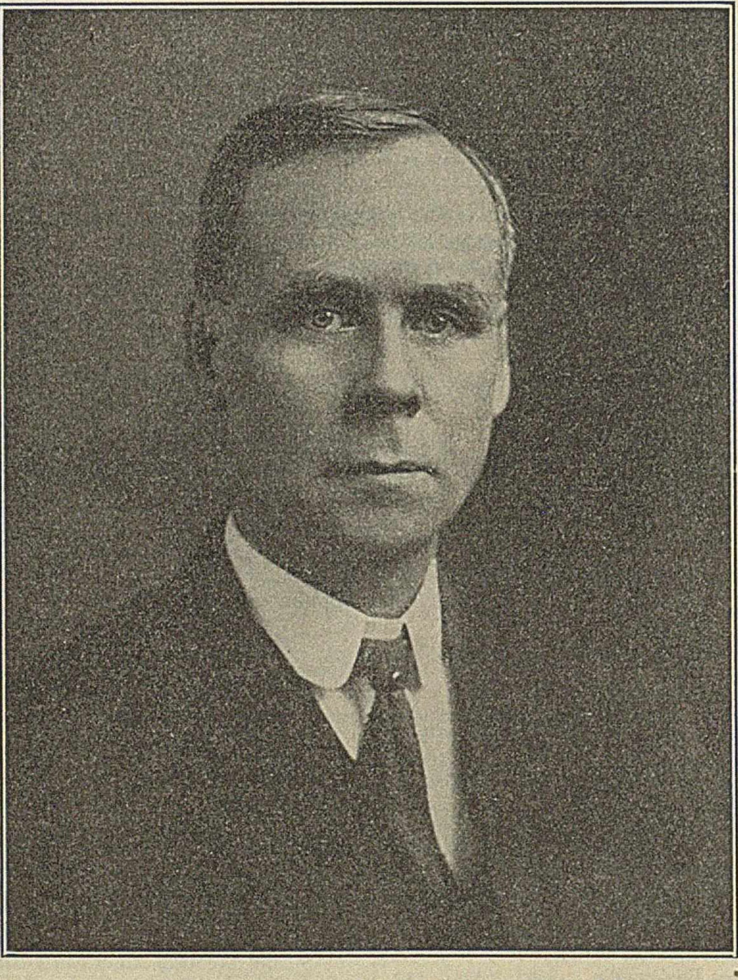
# THE SOCIETY'S PRESIDENT FOR 1920

## WILLIAM ALBERT NOYES

William Albert Noyes, the newly elected president of the AMERICAN CHEMICAL SOCIETY, needs no introduction to its members. Editor of the *Journal of the American Chemical Society* from 1902 to 1917, during the years when it was advancing to its present position as one of the greatest journals of chemistry. Dr. Noyes will be identified by many of our members as the editor to whose guidance the SOCIETY entrusted its one organ of expression. When the SOCIETY recently launched its program to publish a series of chemical monographs on scientific and industrial topics of moment, it promptly made him editor-in-chief of the scientific series.

But to many others Dr. Noyes is identified even more markedly with the development and establishment on a firm basis of America's position in chemical research. The value of this development, from 1890 to 1915, was shown by the supreme test of the war with its problems of chemical warfare, production and creation. In the group of leaders in this development, Dr. W. A. Noyes stood shoulder to shoulder with Remsen, T. W. Richards, Nef, A. A. Noyes, Michael, and other university men, Acheson, Baekeland, Hall, Lovejoy, and other leaders in industrial chemistry, men whose research work commanded the admiration of the world of science, and kindled the enthusiasm of thousands of younger men who were ready when the call came. In token of his position among our research leaders Dr. Noyes was one of the earliest recipients of the Nichols Medal (1908) for his work (in collaboration with Dr. H. C. P. Weber) on the atomic weight of chlorine, and he has recently received the Willard Gibbs Medal for pioneer work on the electrochemical theory of valence. For many years his special field has been organic chemistry, centering in the chemistry of camphor and its derivatives, and in 1904 he gave the address on "The Present Problems of Organic Chemistry" at the gathering of the world's leading chemists in St. Louis. A member of the National Academy of Sciences since 1910, Dr. Noyes has recently been elected chairman of its Chemistry Section. He is also a member of the American Philosophical Society and of the American Academy of Arts and Sciences.



WILLIAM ALBERT NOYES, PRESIDENT AMERICAN CHEMICAL SOCIETY

Many, especially among our younger members, will recall with pride that they are former pupils of Noyes, for he has not only been an eminent investigator and great editor, but also an active and inspiring teacher. His textbooks on general chemistry, organic chemistry and qualitative analysis are characterized by directness and clarity of exposition and sane and up-to-date presentation of facts and theories. Under the leadership of Dr. Noyes the department of chemistry at the University of Illinois has emerged from comparative obscurity to a position among our finest university laboratories. Noyes, with the support of a far-seeing university president, has made his department a beehive of research in practically every line of chemical effort.

We can appreciate the character of the man who has risen to leadership in our national SOCIETY. Honesty and vision have given purpose to his inquiring mind; courage has given point to its thrust; and an indefatigable working capacity has given him the power of successful accomplishment in every field he has touched.

The SOCIETY is to be congratulated on the fact that it has bestowed its brightest honor on one who has devoted the best years of his life to its service in bringing its senior Journal to a position of world authoritativeness, on one who has been and is a leader in research and teaching—on a true and loyal American—William Albert Noyes.

CHICAGO, ILL. JULIUS STIEGLITZ

# EDITORIALS

## CRITICAL DAYS

In a few short weeks public opinion, speaking through the Congress of the United States, will have declared its appraisement of chemistry as a national asset. This judgment is bound up in three important measures soon to be reported by committees which have given painstaking consideration to these matters. We refer to the Longworth bill which seeks to insure the permanency of our coal-tar chemical industry, the Bacharach bill which would provide a permanent domestic supply of the tools of the chemist, and finally the Army Reorganization bill which will determine the status of the Chemical Warfare Service either as a vigorous independent unit of our War Department or as a weakling appendage of some division of that Department.

On January 10, 1920, the very day of the proclamation of the ratification of the Treaty of Versailles, Marshal Foch gave words of warning in an interview from which the following statements are taken:

> It would be foolish to believe there will be no more war merely because we do not wish to fight. * * *
>
> War is not always avoidable. * * *
>
> If it is true two are necessary to make a fight, it is equally true the one best prepared will win. * * *
>
> There are ingenious people who believe that to leave the key in the door is the surest way to prevent entrance of thieves. I think it wiser to be ready for any unfavorable event. * * *
>
> War no longer may be called an art. It now is a science and an industry. * * *
>
> Those who wish to avoid violence cannot afford to ignore anything in the way of scientific and industrial progress.

It is our conviction that the final word of Congress will be such as to fill the hearts of chemists with renewed zeal and enthusiasm. Public opinion, however, must be informed regarding these measures in order to rouse itself to unmistakable expression, and that is the responsibility of the chemists of America. What is the state of public opinion in your neighborhood, fellow chemist? A word in advocacy *now* will be more valuable than whole volumes of regrets later. All together for American security and economic independence!

## A SIGNIFICANT COMBINATION

Announcements of the formation of new corporations in the chemical industry with capitalizations running into millions have become so common in these hustling days that we are prone to take these developments as a matter of course and to give but slight thought to their meaning. However, peculiar and especial interest attaches to the announcement on January 9, 1920, of the formation of the Atmospheric Nitrogen Corporation, capitalized at $5,000,000. No details have been issued by the officers of the company as to the proposed lines of activity of the new organization. President E. L. Pierce, of the new company, announces that the Solvay Process Company has joined forces with the General Chemical Company in the matter of nitrogen fixation. As the establishment of an independent, self-supporting fixed nitrogen industry in America for the increase of crops in time of peace and as a preparedness measure for war is greatly to be desired, this announcement is of extreme economic importance. It is also announced from England that Brunner, Mond and Co., Ltd., operating the Solvay soda plants in that country, have arranged to take over the incomplete Haber plant started by the government and that they will operate the Haber process in addition to their ammonia soda business.

A word of explanation will make these announcements clear. When the various allied commissions visited the Haber ammonia process works at Oppau they found a small ammonia soda plant erected in connection therewith. This was first printed in a British government publication dated February 1919, which had only a very limited and confidential circulation. Later, the significance of the association of these two plants and its relation to the future of the nitrogen industry was clearly brought out by M. Georges Claude, first in a note in the *Comptes Rendus* of May 19, 1919, and later and more fully in *Chimie et Industrie* for August 1919.

In the Haber synthetic ammonia process, the chief item of expense is the cost and purification of the hydrogen required for the reaction

$$N_2 + 3H_2 = 2NH_3.$$

The cheapest known method of producing hydrogen in quantity for the Haber process and the one used at Oppau is illustrated by the following reactions for the production of water gas and for the treatment of this water gas with steam in the presence of a catalyst:

$$C + H_2O = CO + H_2 \qquad (1)$$

$$(CO + H_2) + H_2O = CO_2 + 2H_2 \qquad (2)$$

It will be observed at once that eleven tons of carbon dioxide are produced for every ton of hydrogen set free. For a long time this carbon dioxide was considered as a useless waste product, and such appears to have been the case in Germany until early in 1918. Some bright chemist, however, finally remembered that in the Solvay soda process thousands of tons of carbon dioxide are used each year and many hundred thousand tons of limestone burned for this specific purpose. A short study at once made plain that the ammonia industry and the soda industry for most civilized countries is or should be of the same order of magnitude and a further interesting interdependence was at once brought out.

The Solvay soda process is usually considered as involving the following reactions:

$$CaCO_3 + C\ (+\ O_2) = CaO + 2CO_2 \qquad (3)$$

$$NaCl + H_2O + CO_2 + NH_3 = NaHCO_3 + NH_4Cl \qquad (4)$$

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O \qquad (5)$$

$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O \qquad (6)$$

By adding the rich carbon dioxide from (5) to the much leaner gas from (3) a carbon dioxide of around 55 per cent $CO_2$ is obtained for use in (4). The waste carbon dioxide from the Haber process is much purer and varies from about 75 per cent, if nitrogen is mixed with the water gas, to approximately 90 per cent if it is not. One of the great drawbacks of the Solvay process is the waste of ammonia in recovery (6), and of lime and chlorine, as calcium chloride, the latter being a waste nuisance that is present at every ammonia soda plant. At the same time one of the problems of any plant fixing nitrogen as ammonia is to produce the ammonia in a form suitable for application to the soil. This is commonly done by neutralizing with sulfuric acid to form the sulfate. Any neutral, fixed, and nonhygroscopic salt of ammonia, of which there are few, would probably do as well. Georges Ville and others have shown that ammonium chloride, which is a more concentrated nitrogen product than the sulfate and meets the other requirements also, is equal to sulfate as a fertilizer, just as potassium chloride is as available for crops, with the possible exception of tobacco, as potassium sulfate.

Accordingly, a synthetic ammonia plant and a Solvay soda plant supplement each other perfectly when the above method of producing hydrogen is utilized. If the waste carbon dioxide, together with the ammonia, is passed into brine the products obtained at once are sodium bicarbonate and ammonium chloride, the one ready for sale or conversion into soda ash, the second ready for the fertilizer markets.

For the recovery of ammonium chloride in solid form, suitable for fertilizers, it seems that it will not be necessary to resort to evaporation, for Claude states that in collaboration with Mittau he has worked out an adaptation of the method of Schreib for alternative precipitation of the sodium bicarbonate and of the ammonium chloride, depending upon the very slight solubility of the ammonium chloride in cold solutions of neutral ammonium carbonate of appropriate concentration.

By the coördination of these two processes to meet America's needs for fixed nitrogen, there will result lower installation costs for both processes, the saving of several hundred thousand tons of sulfuric acid, several hundred thousand tons of lime, several thousand tons of coke, and the elimination of a waste product that has always been considered a nuisance. The saving made may be credited to either product at will.

Necessary information for the installation of the Haber process is at hand or is rapidly being acquired. The Chemical Foundation, Inc., has control of the Haber patents. A new day is evidently at hand for two fundamental chemical industries in America—nitrogen fixation and soda manufacture.

## THE JOY AND THE SORROW OF M. I. T.

The juxtaposition of light and shadow in earthly affairs has been strongly illustrated during the past month at Massachusetts Institute of Technology. $8,000,000 was needed to enable that splendid institution to continue fittingly its work. Spurred on by the announcement that the mysterious "Mr. Smith" had again come to "Tech's" aid with an offer of one-half the needed amount, provided the other half were raised, there began a drive for the goal. As a part of the drive, a novel plan of coöperation with the industries was evolved. Details of a joint contract have been worked out by which the industries agree to contribute definite amounts annually for a period of five years. These funds are to be used chiefly to increase the salaries of the instructing staff. In return the Institute offers contributors the use of its libraries, files, and plant, the members of its staff are to be available as consultants, and a classification of its alumni and undergraduates, detailing special qualifications of each, is to be maintained. The plan is bold in its conception and may prove one of the most important steps of recent years in technical education. Its proponents look forward with confidence to the future and answer in advance objections which might be raised.

The net result of the drive was success, and a dinner followed where alumni and friends could voice their joy. At this dinner the identity of "Mr. Smith" was revealed, Mr. George Eastman, of Rochester, N. Y., whose contributions to this institution now total $11,000,000.

However, there was a vacant seat at the dinner, that of President R. C. Maclaurin, whose staunch spirit had supported and inspired every feature of that drive. Only a few days later came the announcement of his death. Just at the moment of his greatest triumph for the institution he loved so well he passed away.

Fortunate the institution which enjoyed for twelve years the far-seeing leadership of such a man as President Maclaurin and can still count as one of its most valuable assets the memory of all for which he stood.

## STUDENT OPINION

The Bacharach bill passed the House of Representatives on August 2, 1919. This bill increases the duties on imports of chemical glassware, porcelain, and scientific instruments and repeals that clause of existing legislation which gives to educational institutions the right to import such articles free of duty.

In the debate on the bill Representative Kitchin, strongly opposing its passage, laid great stress upon the "poor, hard-working students in this country," and emphasized the point that no student or representative of the students had been heard by the Ways and Means Committee. Our own feeling all along has been that if student opinion could be ascertained, it would show a strong majority in favor of the bill. This, however, was a mere matter of opinion based upon the conviction that the spirit of independence is still strong in the hearts of young Americans.

Through the courtesy of Professor Pond of Stevens Institute we have been given opportunity to put the matter before the students in the chemistry courses of that institution. In our remarks we emphasized cold-bloodedly that this bill meant a tax upon the students of the country. We leaned over backward in the effort to avoid any plea for the bill. No reference whatever was made to the resolutions passed by the Council of the AMERICAN CHEMICAL SOCIETY, urging repeal of the duty-free privilege. We wanted no hasty judgment, and so the subject was left for discussion among themselves and for a vote at whatever time and in whatever manner they might decide upon.

To-day we received from the student chairman of the meeting the result of the ballot as it was taken by classes, on the Bacharach bill:

| CLASS | Favor | Against | Per cent Favoring |
|---|---|---|---|
| Senior.......... | 66 | 11 | 86 |
| Junior.......... | 113 | 15 | 88 |
| Sophomore...... | 133 | 18 | 88 |
| Freshman....... | 245 | 55 | 82 |
| TOTAL...... | 557 | 99 | 85 |

We commend these figures to the subcommittee of the Senate Committee on Finance which is now considering the Bacharach bill. We believe that this judgment, deliberately expressed by the students of Stevens Institute, is thoroughly representative of student opinion throughout the country.

## SAFETY IN SPEECH

To the scientist the approach of a newspaper reporter has long been a signal for withdrawal into a shell of silence. For this restraint he could not justly be blamed, for there stood before his memory the distorted condition in which an expert opinion ventured in an unguarded moment by some colleague had appeared in print.

There are times, however, when the scientist holds the responsibility of safely guiding public opinion. He should speak, and his views should be made known through the widest medium of reaching the public, namely, the press. The difficulty in the past has been the channel through which these views reached the make-up room of the newspaper.

In the hope of overcoming this difficulty, the A. C. S. News Service has just made an experiment, the success of which has proved so remarkable that it should be recorded, in the confident hope that when members of the AMERICAN CHEMICAL SOCIETY understand what is being attempted they will give the same generous measure of coöperation as was given recently by Dr. Reid Hunt of the Harvard Medical School.

It is not exaggeration to say that the recent extraordinary number of deaths from drinking wood alcohol presented the possibility of a national disaster. Quick, full, and responsible publicity was needed. In this situation Dr. Hunt was asked to prepare a statement which could be sent out over his name to the press of the country by our News Service. The request was promptly complied with; the material was put into newspaper shape by the technical manager, Mr. Harrington; and a few hours later the distribution through the mails was in progress.

Returns from the clipping bureaus show how broadly this material was utilized, in most cases in full as issued by the News Service, and as it appears on page 197 of this issue. The Associated Press, the United Press, and other news agencies gave the material immediate distribution. Not only was the matter used in the news columns, but it formed the basis of much sound editorial discussion. It is a significant fact that every clipping received to date not only quotes Dr. Hunt as authority for the statements, but says also that the bulletin was prepared at the request of the AMERICAN CHEMICAL SOCIETY.

Thus a national obligation and responsibility has been effectively met. Your equally generous coöperation is urged, if it should be requested.

## NOTES

Last October the Société de Chimie Industrielle passed the six-thousand mark in its membership list. Congratulations and best wishes to this young organization, whose founders had the courage to launch it upon its career of usefulness during the darkest days of the war.

Still heartier will be the congratulations if some day the present two great French chemical societies are combined.

In St. Louis recently a jury disagreed in the suit brought by our Government against a manufacturer of saccharine and the matter will again have to go to trial. In France it was decided last fall to continue as a peace measure the war-time repeal of anti-saccharine legislation, the revenue from the government monopoly of this industry continuing to aid the national exchequer.

There is humor even in Congressional hearings, for example, this extract from the testimony of January 12, 1920, on the Longworth bill:

> MR. METZ. On the contrary, I have stated my position here. I am a consumer. It is not selfish on my part, but the other men are selfish; that is the difference. It is the consumer I am looking out for. I have done that from the beginning.

Toy sets for chemical experiments are indicative of the present general interest in matters chemical. May it not be well, however, to offer the manufacturers of such toys, through a committee of the SOCIETY, expert advice on the character of experiments which may safely be placed in children's hands? Already one young lad has been severely burned by the breaking of a test tube in which he was boiling concentrated sulfuric acid.

We were not satisfied with our page of Market Reports, and even doubted its usefulness in a monthly publication, but inquiry among our readers developed the fact that it was of value to them. Beginning with this issue the list has been revised, a page has been added to include the new dye industry, and quotations on all items are given as of the beginning and the middle of the previous month, so that the trend of the market may be noted. It is hoped that these changes will increase the usefulness of this section.

# THE CHEMICAL INDUSTRY AND TRADE OF JAPAN

By O. P. Hopkins, Washington, D. C.

Received January 3, 1920

The war has stimulated industrial development in Japan in a most remarkable manner, and no lines have been more favorably affected than those concerned with the production of chemicals and allied products. It is safe to say that the American chemical manufacturer is not quite so much interested at this moment in the markets offered for his goods in Japan as he is in the future competition he may expect from the Japanese manufacturer in the growing markets of the Far East and even in the Western Hemisphere.

The boom in the Japanese chemical industry resulted from the same circumstances that brought about a similar development in the United States—the cutting off of European supplies, with the consequent rise in prices, and the insistent demand for munitions at very high prices. The Japanese were even more unprepared than we were to meet the situation that arose when war was declared, and they have naturally not been able to achieve the same measure of success as we have. But in many lines they have made sound progress, and their present position is deserving of the most careful study.

Their efforts have been directed mainly toward the development of a coal-tar industry, the production of alkalies for the paper, glass, textile, and soap industries, progress in metal refining, and the greatest possible utilization of water power in electrochemical processes. The manufacture of iodine and potash from kelp, of glycerin, paints, fertilizers, the tanning of skins and hides, and many minor lines have also been pushed energetically. The match industry was well established before the war.

There are many factors that favor the present program. Water power is abundant, cheap, and well distributed throughout the industrial regions. Few concerns pay as high as two cents per kilowatt-hour and some pay less than one cent. The coal supplies are adequate, although not conveniently located. The price is somewhat higher at the pit-mouth than with us, and by the time the costly transportation is added, the price to the consumer is very high—$4.73 a metric ton at Yokohama, for instance, in 1913, and $17.80 in 1918. Certain raw materials are had in great abundance, either from Japanese sources or from easily accessible sources in nearby countries, such as sulfur, camphor, menthol, vegetable oils of all kinds, kelp, phosphate, lime, silica, and wood. The salt supply is something of a problem, as the government monopoly is considered by the manufacturers not to have worked out to the best advantage of the alkali industry, but a satisfactory supply is expected eventually. The attitude of the government may be considered a favorable factor, as every encouragement has been given the growing industries, including subsidies to one large company each in the dyestuff, medicinal, and glycerin industries. One of the most favorable factors is the low-priced labor, although it is well known that labor costs are not relatively so high in the chemical as in some other industries. But Japanese labor is very low priced, despite even war wages. Wages have not risen any more rapidly, proportionally, than in western countries, and while improvements in the standard of living may be expected, it is not reasonable to suppose that the standard will ever be so high as with us while there are so many millions to be fed, sheltered, and clothed in so small an area. The country is badly overpopulated. In this fact lies the "necessity" upon which the whole political program of the statesmen is based.

There are also unfavorable factors which tend to hold back the expansion of the chemical industry. The supply of technically trained men is inadequate, although a great many foreign engineers have been induced to come in. The failure of certain individual enterprises is attributed to faulty engineering. For the most part the laborers have had no experience that fits them for the new work, although there are exceptions, such as the facility with which ceramic workers adapt themselves to glass-making. This lack of trained chemists and laborers is a very serious one, but it is something that can be overcome in time. It should not be considered a permanent factor—witness the remarkable manner in which the Japanese have learned to manufacture the electrical equipment required to utilize their water power. Lack of equipment has also limited progress, as suitable outfits were difficult to buy abroad during the war, and manufacturing them at home has been a slow job. This is another shortcoming that can be remedied in time. A further obstacle in the way of some branches of the industry has been the methods used in selling to the new foreign markets. All sorts of irregularities have been charged to the exporters and much harm done which it will take a long time to undo. Business immorality is not of course a matter to be determined by geographical boundaries, and much can be said, and has been said, in extenuation of the faults of the Japanese trader, but at any rate the harm done in this direction is now well recognized by the Japanese themselves, and the government and commercial organizations are coöperating to remedy the trouble. Matches and glassware, for example, must now pass inspection before they can be exported.

The purpose of this paper is to bring together statistics of production and trade that will give the American manufacturer some definite idea of what the Japanese are actually accomplishing in the field of industrial chemistry. A study of the import statistics will also show what lines can be sold in Japan. A number of industries have been singled out for separate discussion. For the most part they are the lines to which the Japanese are paying particular attention, but it has been impossible to treat all such lines in this manner, as details for all are not available. As a matter of fact, it has been difficult to assemble the facts into an orderly treatment of the subject, for much of this business is new to Japanese economists, statisticians, and writers, and the sources of information still leave much to be desired. Even in the official statistics, the statisticians working on the production, import, and export returns have at times used different classifications, units, and arrangements. For this paper it was decided to use quantities wherever possible, even when that course did preclude interesting totals, for prices have varied so much that they now mean very little in such statistics.

Figures are from official Japanese statistics unless otherwise indicated. Some of the descriptive facts have been taken from Japanese trade papers, organs of commercial organizations, and the unofficial but authoritative Japan Year Book; some have been obtained from officials recently returned from Japan, and some are to be found in material published by the United States Bureau of Foreign and Domestic Commerce.

## ACIDS

Not many details are available that bear on the production and use of acids in Japan. Abundant supplies of native sulfur and pyrites make it possible for manufacturers to supply the country's needs for sulfuric acid and to do some exporting. The production of hydrochloric acid increased from about 8,000,000 lbs. in 1913 to nearly 25,000,000 lbs. in 1917, but it evidently does not enter foreign trade, as no official figures for imports or exports are given. The domestic output of nitric acid went up from 1,077,100 lbs. in 1913 to 4,942,070 lbs. in 1917 (no foreign trade figures available). Imports of carbolic acid fell from 4,731,134 lbs. in 1917 to 2,950,867 lbs. in 1918. It has not been produced in large enough quantities to obtain notice in the official returns. Of the 6,993,760 lbs. of acetic acid produced in 1917, 5,632,007 lbs. were exported. There was a falling off in exports of about a million pounds in 1918. Boric, citric, oxalic, salicylic, and tartaric acids are imported in varying quantities, as shown in the complete table of imports.

## CAMPHOR AND MENTHOL

More than half of the world's production of natural camphor comes from Formosa (now called "Taiwan" by the Japanese) and Japan proper. Wasteful methods of production and the greatly increased demands for the product have recently made it advisable for the Japanese government to regulate the exports by allocating supplies to the various consuming countries. The causes for the increased demand are well known, and the reasons assigned for the inability to meet the demands are scarcity of labor, the destruction of easily accessible trees, and the difficulties and dangers attending the exploitation of forests in the wilder sections of Formosa, where hostile savage tribes still make the camphor worker hesitate about sticking to his job even at higher wages than most other industries offer. Under government auspices, the situation is being very carefully studied and constructive plans put into operation for improving the output. Much planting of new trees is being done and a careful survey of all existing sources is going forward. It is also hoped that all districts now menaced by savages will soon be brought under control. In the meantime all the camphor companies have united to form one big company and expect to compete to better advantage for labor in the future.

The following figures will give a general idea of the magnitude of the industry and the export trade (crude, oil, and refined camphor have been lumped together without reducing them to a common basis):

| | 1913<br>Lbs. | 1917<br>Lbs. | 1918<br>Lbs. |
|---|---|---|---|
| Production | 6,284,087 | 7,334,737 | (1) |
| Exports | 3,278,200 | 4,126,928 | 2,333,652 |

[1] Not obtainable.

The government is now discouraging the exports of crude camphor, with the idea that the country can profitably do its own refining. The war served to revive interest in the manufacture of celluloid, which, for some reason or other, had been languishing, and unmanufactured celluloid and such celluloid products as combs, hair pins, and toys are now exported in considerable quantities.

The menthol trade, which has virtually been controlled by the Japanese in times past, was hit rather hard by the war. Japanese exports reached their highest point in 1916, when sales abroad amounted to 511,168 lbs., and since then have declined. There has been an increasing tendency on the part of the farmers to cut down the acreage devoted to peppermint in favor of grain and beans, which pay better. In two of the principal districts the cut in acreage has amounted to 50 per cent during the last year.

## DYESTUFFS

When the exports of dyes from Germany were shut off, Japan found herself in the same boat with the United States, England, and France; that is, with extensive dye-using industries and practically no domestic production of dyes to meet their demands. As a matter of fact, Japan was in a worse plight than any of the others, because there was practically no experience to fall back upon. She had to build from the ground up so far as raw materials, personnel, and equipment went.

In 1915 an act was passed to subsidize one company for the manufacture of dyestuffs, and under this act was organized the Japan Dyestuff Manufacturing Joint Stock Co., with 160,000 shares of $24.90 each. The government guaranteed dividends of 8 per cent, and there was a disposition at first on the part of unprotected manufacturers to fear the competition from this firm and resent the action of the government. In a short time, however, the demand for dyestuffs sent prices up to a point that brought them enthusiastically into the business, and early in 1916 it was announced unofficially that the total production of aniline oil by all companies was 60,000 lbs. a month. By the middle of 1918 there were 100 factories in existence, exclusive of small concerns manufacturing inferior goods, with a total capitalization of about $7,500,000.

The Japanese dye makers have naturally had difficulty in satisfying their customers in the matter of quality, and there has been much dissatisfaction on the score of prices also, but the fact of the matter seems to be that the staple dyes are coming forward in large quantities and that the industry seems pretty well established. The leading manufacturers have started a movement to induce the government to impose a high enough tariff wall to make certain that outside competition will not undo the progress made under the stimulation of war prices.

The United States now has the major portion of the import trade in aniline dyes and logwood extract, and is doing a considerable business in both lines. In the following table are shown Japanese imports from all countries for three different years. The supplies of aniline and artificial indigo in 1913 originated almost exclusively in Germany, while the logwood extract came largely from France. The natural indigo purchased in 1918 came from China.

PRINCIPAL IMPORTS OF DYES INTO JAPAN

| | 1913<br>Lbs. | 1917<br>Lbs. | 1918<br>Lbs. |
|---|---|---|---|
| Aniline dyes | 9,738,863 | 832,947 | 2,538,725 |
| Artificial indigo | 2,186,513 | 1,910 | 143 |
| Natural indigo | 27,432 | 85,664 | 1,444,856 |
| Logwood extract | 955,992 | 1,649,205 | 3,588,288 |

It is the opinion of Japanese manufacturers that the future of American participation in the trade will depend upon the ability of Germany to supply her former customers at competitive prices, and that the future of both German and American exporters, and therefore of the Japanese dye manufacturers, depends to a considerable extent upon the attitude of the Japanese government on the tariff question.

### FERTILIZERS

It is probably safe to say that fertilizers play a more vital part in the agriculture of Japan than in that of any other country in the world. For centuries the intensive cultivation of the soil has demanded their liberal use. Twenty-five years ago dependence was placed mainly on such "natural" manures as nightsoil, stable manure, and fish, and to some extent upon rice bran and cake from vegetable-oil presses. Then artificial fertilizers were gradually introduced and large quantities of Chilean nitrate, phosphate, ammonium sulfate, and bean cake were imported. Still later, the war stimulated home production of fertilizers and to-day enormous quantities of ammonium sulfate and superphosphates, as well as other chemical salts of minor importance, are manufactured by Japanese firms. Potash salts as such do not seem to play an important part in Japanese agriculture. Production of chemical fertilizers some time ago reached a point where exports on a considerable scale were made at fancy prices, but this development was considered detrimental to the interests of the country until such time as the home demand was really met, so the government stepped in and exercised a rigorous control over exports.

Before the war ammonium sulfate was imported from England to the extent of about 115,000 tons, but when this source was cut off, its production was undertaken successfully by the electrochemical plants, which had already made strides in the manufacture of calcium carbide and atmospheric nitrogen. The gas industry also produces important quantities as a by-product. At this writing the domestic product is high priced and some fear is felt that English supplies may injure the industry. Latest unofficial figures indicate that the domestic production is somewhat more than half the pre-war consumption. Prohibition of exports led some manufacturers to export calcium carbide, for which there has been a good outside demand.

Phosphate rock for the superphosphate industry is obtained from islands in the South Seas and the Indian Ocean. Production of the finished fertilizer has reached something like 500,000 tons a year, which is more than sufficient for home use, and export markets have become a necessity. Most of the surplus is sold in the Dutch East Indies and in Siberia.

The soy-bean cake and meal used so extensively as a fertilizer comes from oil mills in Manchuria and Japan. The consumption of this fertilizer amounts to more than 1,300,000 tons. It is exported to the Pacific Coast of the United States when shipping rates are normal, and the exporters hope to develop this trade further in the future.

Sodium nitrate comes from Chile. The fish and other animal products used as fertilizers are from domestic sources. Packing-house fertilizers, so extensively used in the United States, are not in evidence in Japan, as the people are not meat eaters. There are no statistics showing the quantities of nightsoil and stable manure used, but it is well known that the Japanese, like the Chinese, make the most of these materials.

So far as opportunities for American fertilizers in Japan are concerned, they will probably be limited in the future to packing-house products, specialized mixed fertilizers, and possibly sulfate of ammonia, if competition from English and Japanese producers can be met.

### GLASS AND GLASSWARE

The removal of Belgium, Germany, and France from the glass trade in the Far East has stimulated the Japanese industry to a remarkable degree, and this is a line in which the Japanese seems certain to hold his own at least, even when the European competition returns. Recent developments are shown statistically in the following table:

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| Production | $2,914,036 | $13,626,403 | ([1]) |
| Imports | 1,646,758 | 1,261,233 | $1,223,614 |
| Exports | 1,652,791 | 6,669,672 | 8,007,614 |

[1] Not obtainable.

It is evident that export markets opened to the Japanese through the absence of European competition were the prime factor in this sudden development, and these markets are found chiefly in easily accessible Asiatic countries, although some of the product has found its way to the United States and other distant fields. The following official United

States statistics show how the trade with this country has been affected:

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| Imports from Japan | $9,053 | $ 98,087 | $351,713 |
| Exports to Japan | 9,117 | 623,014 | 500,232 |

The increased imports from Japan have consisted of beads and a large total still included under "all other" in the statistics of both governments. The increased exports to Japan have been largely plate glass, formerly supplied by Europe in qualities apparently not yet produced in sufficient quantities by Japanese manufacturers.

According to a statement recently prepared by the Far Eastern Division of the Bureau of Foreign and Domestic Commerce, the Japanese glass manufacturers have a decided advantage over their competitors in the matter of wages, and the laborers are said to adapt themselves readily to the industry because of previous experience in pottery making and similar lines. The average daily wage in glass factories in 1917, according to this statement, was 38 cents for males and 17 cents for females over 15 years of age, and 14 cents for males and 11 cents for females under that age. During the war large quantities of soda ash have been imported from the United States, but the domestic production of soda ash and sodium sulfate has rapidly increased, as explained elsewhere in this paper. The silica used in a large factory having an output of 100,000,000 sq. ft. of window glass a year is obtained from Korea and Anam and is said to be of excellent quality. It is interesting to note that the machinery in this factory is practically all driven by electric power. Much of the machinery in the larger factories is of American manufacture. The latest production figures are for 1917, but the expansion of the industry has continued since that date, according to later but unofficial reports.

### MATCHES

Matches are one of the most important of the Japanese chemical manufactures, and the bulk of the production goes into foreign trade. Before the war the value of the match exports was about half that of the total for all chemicals and chemical manufactures; since then it has dropped down to about 40 per cent of that total. The following summary will give some idea of the size of the industry and the extent to which the product goes into foreign trade:

| | 1913<br>Gross | 1917<br>Gross | 1918<br>Gross |
|---|---|---|---|
| Production | 51,731,010 | 52,531,551 | (1) |
| Exports | 44,009,245 | 44,150,011 | 39,467,420 |

[1] Not obtainable.

The industry supplies all domestic needs, and, with the exception of phosphorus, depends upon domestic materials. China, India, and other Asiatic countries take most of the exports, although they have found their way to America and Europe since the war started. The cost of labor has gone up in recent years, but the price of matches has advanced even more rapidly, as is shown by the fact that while exports have decreased somewhat in quantity, they have doubled in value. The low cost of labor is the most important factor in the success of the Japanese match industry, for the product is admittedly inferior in quality. The Japan Year Book confesses that the boxes and splints are weak and liable to break, while the friction surface is easily affected by dampness. This same authority states that Japanese matches are sold in Chinese and other nearby Asiatic markets at about 45 per cent less than their rivals.

As this matter of wages is important in appraising the chemical industries of Japan, it will be worth while to devote a little space here to a study of that phase of the match industry, as some figures given in the Industrial Census (in Japanese) make it possible to compare establishments with five or more operatives with American establishments included in the census of 1914. Wages, of course, have gone up in both countries since that time, but if it is borne in mind that the rise has been somewhat more rapid in this country than in Japan, a general idea of the present relative wage costs in the two countries can be formed. The comparison for 1914 follows:

| | UNITED STATES | JAPAN |
|---|---|---|
| Wage earners: | 3,800 | 17,677 |
| Over 14 years: | | |
| Male | .......... | 4,075 |
| Female | .......... | 10,972 |
| Under 14 years: | | |
| Male | .......... | 538 |
| Female | .......... | 2,092 |
| Wages | $1,757,975 | $752,258 |
| Average wage | $463 | $43 |
| Horsepower | 7,465 | 335 |
| Production: | | |
| Gross[1] | 49,050,229 | 60,315,973 |
| Value | $12,556,279 | $9,120,562 |
| Average production: | | |
| Gross per wage earner | 12,908 | 3,412 |
| Gross per wage dollar | 28 | 80 |
| Average value of product: | | |
| Per wage earner | $3,304 | $516 |
| Per wage dollar | $7.14 | $12.12 |
| Wages per 1,000 gross | $35.84 | $12.47 |

[1] For United States, estimated by the United States Tariff Commission.

### PAINTS

Japan is not a very great paint-consuming country, little being used on such things as houses and fences, yet the sudden demand for paints in the shipbuilding industry and the high prices offered in other Far Eastern countries have brought into being a considerable industry. Even the imports of shipsbottom paints have fallen off recently, and the decline in imports of other paints has been most striking. On the other hand, exports have increased from less than half a million to more than 15,000,000 lbs. since the war started, as the following summary shows:

| | 1913<br>Lbs. | 1917<br>Lbs. | 1918<br>Lbs. |
|---|---|---|---|
| Imports: | | | |
| Ship's-bottom | 547,091 | 500,026 | 376,062 |
| Other | 1,774,597 | 471,585 | 264,888 |
| Exports | 474,708 | 2,420,850 | 15,034,236 |

There are no official statistics of paint production in the country. It is known that materials are to be found at home or in nearby China, although something like 52,000 gal. of turpentine oil were imported in 1918, almost entirely from the United States.

### PAPER

Two general classes of paper are produced in Japan—Japanese and "European." The former has been made for centuries and is especially adapted to Japanese and Chinese needs. The latter is a comparatively new product, the manufacture of which has been greatly stimulated by the high war prices. It meets a growing demand at home and markets abroad are eagerly sought. China, Kwantung Province, and Hongkong take about 60 per cent of the exports of machine-made paper, which have been increasing rapidly. During the war India also became prominent as an importer of this paper. Good grades of printing paper are still imported, however, and in the absence of effective competition from England, the United States has become the chief source of supply.

A statistical summary of the situation follows:

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| Production: | | | |
| "European" | $11,455,823 | $29,490,458 | (1) |
| Japanese | 10,425,814 | 18,069,209 | (1) |
| Imports | 3,604,262 | 2,035,693 | $4,678,954 |
| Exports: | | | |
| "European" | 943,381 | 7,038,377 | 12,481,933 |
| Japanese | 598,604 | 977,090 | 1,695,530 |

[1] Not obtainable.

The timber resources of Japanese Saghalien and Hokkaido have made possible a rapid development of the pulp industry under the stimulus of war prices, as the following figures show:

| | 1913<br>Tons | 1917<br>Tons | 1918[1]<br>Tons |
|---|---|---|---|
| Production | 85,050 | 189,350 | 231,550 |
| Imports | 53,850 | 18,050 | 32,200 |
| Exports | ..... | 4,150 | ? |
| Consumption | 138,900 | 201,550 | 263,750 |

[1] 1918 production total on authority of Japan Paper Guild.

Japanese enthusiasts believe that eventually enough pulp will be made at home to meet all domestic needs, and that all foreign competition can be met in spite of the rising cost of labor and materials. It is a difficult matter to determine costs in this industry, but the following figures per 100 lbs. of pulp in a single large mill will be of interest (they are from the "Keizai Shimpo" for October 18, 1919):

| | 1915 | 1918 (August) |
|---|---|---|
| Mechanical pulp: | | |
| Wood | $0.773 | $1.780 |
| Labor, including bleaching | 0.100 | 0.670 |
| Power | 0.205 | 0.410 |
| Miscellaneous | 0.067 | 0.135 |
| TOTAL | 1.145 | 2.995 |
| Sulfite pulp: | | |
| Wood | 1.250 | 2.855 |
| Sulfur | 1.120 | 0.188 |
| Coal | 0.023 | 0.033 |
| Labor | 0.125 | 1.190 |
| Power | 0.250 | 1.200 |
| Miscellaneous | 0.085 | 0.173 |
| TOTAL | 1.853 | 5.639 |
| Bleaching sulfite pulp: | | |
| Bleaching powder | 0.340 | 0.575 |
| Labor | 0.025 | 0.035 |
| TOTAL | 0.365 | 0.610 |

Detailed statements covering the recent developments in the Japanese paper industry have been printed by the United States Bureau of Foreign and Domestic Commerce.

### SOAP AND GLYCERIN

With the unlimited supplies of oils available it is not surprising that the Japanese have turned to soap-making on a large scale. It is not possible to show the development by quantity, as different units are used for different soaps and for production, imports, and exports, but the following values will be better than nothing:

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| Production | $3,195,650 | $9,744,127 | (1) |
| Imports | 78,883 | 57,632 | $ 70,367 |
| Exports | 754,013 | 1,913,165 | 2,301,119 |

[1] Not obtainable.

A factory established in 1913 by a well-known English company has been producing soap on a large scale, including the finest grades of toilet soap. The unlimited markets that can be developed among the hundreds of millions of Asia seem to assure a prosperous future for the Japanese industry. At present the exports go chiefly to China, with important quantities to the Dutch East Indies.

No production figures are available for glycerin, but it is known that the output is increasing and the imports falling off. The 600,000 lbs. imported in 1918 was the semi-refined and refined product.

### SODA AND BLEACHING POWDER

Caustic soda, soda ash, sodium sulfate and bleaching powder are all being turned out on an increasing scale by the Japanese to meet the demands of the soap, glass, and paper industries. A handicap in the past has been the high price of salt, which is a government monopoly, but recent concessions have been made in that respect as a result of heavy pressure brought to bear by the manufacturers. Details are difficult to get hold of, but the following statistics will help to explain the situation:

| | 1913<br>Lbs. | 1917<br>Lbs. | 1918<br>Lbs. |
|---|---|---|---|
| Caustic soda: | | | |
| Production | 9,535,621 | 19,979,742 | (1) |
| Imports | 26,810,066 | 47,877,323 | 16,350,847 |
| Exports | ...... | 881,031 | 1,455,815 |
| Soda ash: | | | |
| Production | 4,756,402 | 7,597,771 | (1) |
| Imports | 68,521,861 | 98,060,756 | 124,159,672 |
| Sodium sulfate: | | | |
| Production | 3,138,682 | 18,657,527 | (1) |
| Bleaching powder: | | | |
| Production | 33,114,094 | 47,528,123 | (1) |
| Exports | 2,235,591 | 14,261,615 | 10,904,580 |

[1] Not obtainable.

It can be assumed from the foregoing figures that Japan is rather a long way from being independent so far as these three salts go, and that therefore American exporters can expect to find markets for some time to come. Before the war the imports came mostly from England, but the United States is now the chief factor. In soda ash, England predominated until 1917, but in 1918 America took the lead. The newer Japanese plants use electrochemical processes, but a number of the older concerns use the LeBlanc process. A plant has been established in Manchuria, where salt is cheap.

### SULFUR

Japan is blessed with extensive deposits of sulfur and recovers enough of it each year to supply her own needs and to export extensively to Australia, British India, and other points in the east. Production and exports are shown by the following figures, which are supplemented with production figures for iron pyrites:

| | 1913<br>Lbs. | 1917<br>Lbs. | 1918<br>Lbs. |
|---|---|---|---|
| Sulfur: | | | |
| Production | 131,059,061 | 260,329,009 | 156,634,240[1] |
| Exports | 119,613,792 | 188,375,054 | 119,263,386 |
| Iron pyrites: | | | |
| Production | 252,586,826 | 267,559,347 | (2) |

[1] Estimated from official returns for the first 6 mo.

[2] Not obtainable.

The war stimulated the production of sulfur, but by 1918 high freight rates and transportation difficulties had cut down exports and discouraged production.

### STATISTICS OF PRODUCTION

The statistics of production contained in the following table have been compiled from official reports of the Japanese Department of Agriculture and Commerce. As a whole, the table will give a fairly definite idea of the recent developments in the chemical and allied industries, although a number of branches will be found missing, presumably because they are of minor importance, or because they are so new that data have yet to be collected.

JAPANESE PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS

| ARTICLES | QUANTITY PRODUCED 1909 | 1913 | 1917 |
|---|---|---|---|
| Acetone, lbs. | (1) | (1) | 728,900 |
| Acids: | | | |
| Acetic, lbs. | (1) | (1) | 6,993,760 |
| Hydrochloric, lbs. | 3,989,409 | 7,748,555 | 24,951,527 |
| Nitric, lbs. | 1,160,333 | 1,077,100 | 4,942,070 |
| Sulfuric, lbs. | 150,251,336 | 413,613,139 | 741,039,167 |
| Alum, lbs. | 7,455,051 | 12,464,338 | 22,059,722 |
| Ammonium sulfate, lbs[2] | 1,847,349 | 1,818,658 | 24,122,051 |
| Bleaching powder | 14,453,362 | 33,114,094 | 47,528,123 |
| Camphor: | | | |
| Crude, lbs. | 1,111,073 | 1,292,267 | 1,299,767 |
| Oil, lbs. | 1,363,944 | 2,231,538 | 2,451,096 |
| Refined, lbs. | 1,101,345 | 2,760,282 | 3,583,874 |
| Fertilizers, artificial:[3] | | | |
| Animal, lbs. | (1) | 297,946,698 | 296,785,631 |
| Vegetable, lbs. | (1) | 495,647,166 | 895,563,490 |
| Mineral, lbs. | (1) | 1,207,959,705 | 1,102,234,108 |
| Superphosphate, lbs. | ..... | 1,132,838,096 | 982,192,275 |
| Double superphosphate, lbs. | ..... | ..... | 5,945,279 |
| Ammonium sulfate, lbs. | ..... | 35,349,130 | 89,711,450 |
| Potassium sulfate, lbs. | ..... | 11,431,500 | 1,269,464 |
| Calcium cyanamide, lbs. | ..... | 9,101,529 | 8,559,569 |
| Potash salts, lbs. | ..... | 1,542,730 | 2,478,240 |
| Other, lbs. | ..... | 17,696,720 | 12,077,831 |
| Mixed | ..... | 559,066,581 | 459,229,775 |
| Iodine, lbs. | 76,773 | 152,566 | 484,138 |
| Iron pyrites, lbs. | 47,416,891 | 252,586,826 | 267,559,347 |
| Peppermint: | | | |
| Crude, lbs. | 226,899 | 803,040 | 1,094,711 |
| Menthol crystals, lbs. | 147,921 | 258,060 | 561,843 |
| Oil, lbs. | 142,182 | 272,006 | 564,964 |
| Potash: | | | |
| Iodide, lbs. | 153,457 | 158,234 | 222,150 |
| Chlorate, lbs. | ..... | ..... | 13,294,721 |
| Chloride, lbs. | 1,044,011 | 4,451,967 | 19,466,656 |
| Soda: | | | |
| Ash, lbs. | 2,892,835 | 4,756,402 | 7,597,771 |
| Caustic, lbs. | 8,378,257 | 9,535,621 | 19,979,742 |
| Sulfate, lbs. | 2,420,833 | 3,138,682 | 18,657,527 |
| Sulfur, lbs. | 81,349,740 | 131,059,061 | 260,329,009 |
| Wood spirit, gal. | (1) | (1) | 281,185 |
| Candles, lbs. | (1) | (1) | 22,255,234 |
| Glass | $2,088,940 | $2,914,036 | $13,626,403 |
| Lacquer, lbs. | 553,352 | 664,245 | 714,914 |
| Matches, gross | 49,972,039 | 51,731,010 | 52,531,551 |
| Oils: | | | |
| Petroleum, gal. | 78,964,394 | 80,705,957 | 119,706,578 |
| Fixed vegetable | (1) | (1) | $18,998,865 |
| Volatile | (1) | (1) | $112,088 |
| Paper: | | | |
| Japanese | $9,072,837 | $10,425,814 | $18,069,209 |
| "European" | $7,051,340 | $11,455,823 | $29,490,458 |
| Soap: | | | |
| Toilet | $1,298,377 | $2,484,678 | $4,712,541 |
| Industrial | $ 114,726 | $167,930 | $493,315 |
| Laundry and other | $ 492,614 | $543,042 | $4,538,271 |
| Sugar:[4] | | | |
| Jaggery, lbs. | 116,386,420 | 112,303,332 | 179,276,939 |
| Muscovado, lbs. | 26,911,705 | 34,696,008 | 76,177,965 |
| Brown, lbs. | 171,884 | 7,905,413 | 27,414,464 |
| White, lbs. | 1,130,533 | ..... | ..... |
| Waxes: | | | |
| Unbleached, lbs. | 18,967,887 | 12,935,334 | 15,816,499 |
| Refined, lbs. | 9,900,716 | 10,263,120 | 11,168,734 |

[1] Not shown separately.
[2] Year ended March 1918.
[3] Figures for 1914 and 1917.
[4] Figures for 1910, 1913, and 1917.

## STATISTICS OF IMPORTS

The imports statistics given in the following table are based upon the annual returns of the Japanese Department of Finance. Only principal countries of origin are given.

JAPANESE IMPORTS OF CHEMICALS AND CHEMICAL PRODUCTS

| CHEMICALS, DRUGS, ETC. | 1913 | 1917 | 1918 |
|---|---|---|---|
| Acids: | | | |
| Boric, lbs. | 1,185,000 | 788,875 | 1,019,638 |
| United Kingdom | 326,933 | 641,468 | 513,425 |
| United States | 2,189 | 147,396 | 506,211 |
| Germany | 711,471 | ..... | ..... |
| Carbolic, lbs. | 978,598 | 4,731,134 | 2,950,867 |
| United States | ..... | 4,715,000 | 2,573,409 |
| Germany | 409,118 | ..... | ..... |
| Citric, lbs. | 62,662 | 99,790 | 36,302 |
| United Kingdom | 32,061 | 83,303 | 17,102 |
| Italy | ..... | 7,840 | 2,688 |
| United States | ..... | 7,975 | 6,169 |
| Germany | 27,235 | ..... | ..... |
| Oxalic, lbs. | (1) | 51,292 | 366,505 |
| United Kingdom | ..... | 13,492 | 212,705 |
| United States | ..... | 22,450 | 153,800 |
| Salicylic, lbs. | 320,868 | 90,377 | 516,292 |
| United States | ..... | 88,138 | 485,163 |
| United Kingdom | 2,241 | 2,239 | 31,129 |
| Germany | 290,294 | ..... | ..... |
| Tartaric, lbs. | 159,380 | 341,170 | 269,086 |
| United Kingdom | 122,708 | 217,125 | 89,274 |
| France | 1,120 | 64,797 | 72,319 |
| Italy | 4,409 | 44,063 | 84,669 |
| United States | ..... | 15,185 | 2,239 |
| Germany | 25,201 | ..... | ..... |
| Alcohol, gal. | 6,602 | 506 | 5 |
| United States | 112 | 73 | 5 |
| Germany | 4,827 | ..... | ..... |
| Alum, lbs. | (1) | 572,950 | 110,179 |
| China | ..... | 572,300 | 71,795 |
| Ammonium carbonate, lbs. | 433,757 | 982,073 | 299,854 |
| United Kingdom | 416,532 | 833,022 | 297,299 |
| United States | ..... | 149,051 | 2,595 |
| Germany | 11,605 | ..... | ..... |
| Ammonium chloride, lbs. | 1,095,218 | 904,430 | 224,244 |
| United Kingdom | 646,198 | 887,562 | 217,963 |
| United States | 251 | 13,935 | 5,581 |
| Germany | 448,748 | 2,933 | ..... |
| Bismuth subnitrate, lbs. | 31,463 | 6,868 | 1,599 |
| United States | 1,000 | 6,668 | 1,149 |
| Germany | 17,245 | ..... | ..... |
| Calcium acetate, lbs. | 9,033,606 | 255,326 | 1,368,479 |
| United States | 9,033,578 | 255,326 | 1,360,688 |
| Germany | 28 | ..... | ..... |
| Fertilizers: | | | |
| Ammonium sulfate, lbs. | 245,858,923 | 33,289,035 | 2,400,039 |
| United Kingdom | 230,534,365 | 24,743,532 | 561,253 |
| Australia | 4,155,888 | 2,906,265 | 1,771,987 |
| Kwangtung Prov. | 307,016 | 4,951,139 | 66,668 |
| United States | ..... | 225,268 | ..... |
| Bone dust, lbs. | (1) | ..... | 42,574,107 |
| China | ..... | ..... | 24,217,068 |
| British India | ..... | ..... | 11,515,136 |
| Kwangtung Prov. | ..... | ..... | 6,627,754 |
| Sodium nitrate, lbs. | 58,919,948 | 121,443,199 | 107,818,225 |
| Chile | (1) | 121,215,534 | 106,910,898 |
| British India | (1) | ..... | 896,014 |
| United States | (1) | 224,004 | 745 |
| Bean cake, lbs. | (1) | 2,185,407,850 | 2,530,188,786 |
| Kwangtung Prov. | ..... | 1,289,574,438 | 1,691,808,703 |
| China | ..... | 460,733,075 | 353,281,592 |
| Asiatic Russia | ..... | 63,708,318 | 11,048,197 |
| Cottonseed cake, lbs. | (1) | 63,558,313 | 102,821,921 |
| China | ..... | 63,558,313 | 102,325,880 |
| Rapeseed cake, lbs. | (1) | 99,110,886 | 58,828,079 |
| British India | ..... | 34,358,499 | 526,596 |
| China | ..... | 64,725,267 | 57,997,117 |
| Other oil cake, lbs. | (1) | 22,236,611 | 22,001,417 |
| Asiatic Russia | ..... | 2,812,348 | 121,034 |
| China | ..... | 12,488,829 | 14,504,078 |
| Kwangtung Prov. | ..... | 2,386,018 | 1,976,620 |
| Glycerin, lbs. | 1,892,785 | 887,997 | 600,464 |
| United Kingdom | 1,251,486 | 724,243 | 45,113 |
| United States | ..... | 133,387 | 518,132 |
| Germany | 588,273 | ..... | ..... |
| Phosphorus: | | | |
| Red, lbs. | 455,630 | 260,644 | 129,839 |
| United Kingdom | 76,767 | 259,905 | 660 |
| Germany | 121,632 | ..... | ..... |
| Yellow, lbs. | 377,682 | 47,589 | ..... |
| United Kingdom | 254,504 | 31,979 | ..... |
| United States | ..... | 15,610 | ..... |
| Germany | 105,201 | ..... | ..... |
| Potash: | | | |
| Bichromate, lbs. | 591,945 | 584,688 | 221,615 |
| United States | 408,640 | 584,688 | 221,615 |
| Germany | 10,930 | ..... | ..... |
| Bromide, lbs. | 92,701 | 3,410 | 335 |
| United States | 3,926 | 3,300 | 333 |
| Germany | 86,515 | ..... | ..... |
| Chlorate, lbs. | 7,527,720 | 235,244 | 67,201 |
| France | 2,436,664 | 211,741 | 67,210 |
| United States | ..... | 23,503 | ..... |
| Germany | 3,071,533 | ..... | ..... |
| Cyanide, lbs. | 1,100,671 | 652,165 | 607,810 |
| United Kingdom | 553,525 | 651,717 | 605,958 |
| Germany | 544,391 | ..... | ..... |
| Nitrate, lbs. | 1,291,351 | 174,424 | 1,680,022 |
| China | ..... | 149,185 | 1,131,434 |
| Germany | 1,280,215 | ..... | ..... |
| Soda: | | | |
| Ash, lbs. | 68,521,861 | 98,060,756 | 124,159,672 |
| United States | 8,979 | 54,382,470 | 76,709,247 |
| United Kingdom | 68,510,677 | 40,880,290 | 46,983,738 |
| Germany | 2,205 | ..... | ..... |
| Bicarbonate, lbs. | 9,910,039 | 6,881,352 | 7,331,829 |
| United Kingdom | 9,882,581 | 6,548,997 | 3,627,901 |
| United States | 112 | 220,405 | 3,662,187 |
| Germany | 27,346 | ..... | ..... |
| Borate, lbs. | 1,401,041 | 3,373,388 | 2,348,931 |
| United Kingdom | 856,137 | 3,156,684 | 2,083,045 |
| United States | 148,640 | 216,704 | 265,887 |
| Germany | 396,274 | ..... | ..... |
| Caustic, crude, lbs. | 26,810,066 | 47,877,323 | 16,350,847 |
| United States | 361,495 | 47,255,852 | 15,024,902 |
| United Kingdom | 26,412,689 | 603,804 | 789,976 |
| Germany | 32,501 | ..... | ..... |
| Cyanide, lbs. | ..... | 535,820 | 1,576,669 |
| United Kingdom | ..... | 524,734 | 1,553,261 |
| United States | ..... | 11,086 | 23,308 |
| Germany | ..... | ..... | ..... |

[1] Not shown separately.

apanese Imports of Chemicals and Chemical Products (*Continued*)

| Chemicals, Drugs, Etc. (*Concluded*) | 1913 | 1917 | 1918 |
|---|---|---|---|
| Peroxide, lbs. | 392,083 | 55,345 | 21,826 |
| United Kingdom | 83,442 | 30,213 | 7,275 |
| Sweden | ..... | 17,334 | ..... |
| Italy | ..... | 7,275 | 14,551 |
| Germany | 117,259 | ..... | ..... |
| Tanning materials: | | | |
| Galls, oak bark, and similar tanning materials, lbs. | 3,646,810 | 13,351,834 | 10,861,048 |
| Cape Colony and Natal | ..... | 7,166,922 | 3,215,980 |
| British India | 223,860 | 4,238,570 | 1,558,106 |
| China | 590,860 | 997,863 | 589,460 |
| Argentina | ....... | 393,422 | 68,281 |
| United States | 2,012,742 | 195,033 | 1,674,070 |
| Australia | 273,871 | 179,004 | 1,308,854 |
| Africa, n. e. s.[2] | ..... | ..... | 1,505,610 |
| Germany | 225,492 | ..... | ..... |
| Catechu and other tanning extracts, lbs. | 6,049,553 | 10,415,490 | 7,744,914 |
| Argentina | 88,185 | 3,858,817 | 180,049 |
| Dutch East Indies | 1,186,804 | 3,027,173 | 2,299,574 |
| Straits Settlements | 1,000,390 | 1,844,674 | 2,817,730 |
| British India | 37,703 | 668,764 | 1,508,436 |
| China | 20,663 | 546,352 | 6,667 |
| Cape Colony and Natal | ....... | 158,600 | 91,030 |
| United Kingdom | 507,204 | 111,936 | 388,203 |
| United States | 910,604 | 110,230 | 452,724 |
| Germany | 1,382,930 | ..... | ..... |
| Drugs, medicines, etc.: | | | |
| Alcoholic medicinal preparations, gal | 6,927 | 9,227 | 11,697 |
| United Kingdom | 4,774 | 7,536 | 9,872 |
| United States | 1,461 | 1,619 | 1,611 |
| Germany | 556 | ..... | ..... |
| Antifebrin, lbs. | 88,747 | 105,151 | 204,613 |
| United States | ..... | 94,960 | 201,009 |
| Germany | 46,755 | ..... | ..... |
| Antipyrin, oz. | 731,694 | 54,359 | 94,259 |
| France | 75,818 | 29,879 | 33,903 |
| Switzerland | 25,832 | 13,141 | 36,748 |
| United Kingdom | ..... | 9,732 | 23,608 |
| Germany | 630,044 | ..... | ..... |
| Aromatic chemicals | $24,990 | $26,454 | $112,861 |
| United Kingdom | 5,383 | 16,397 | 48,389 |
| United States | ..... | 6,648 | 53,412 |
| Cocaine, oz. | 52,228 | 90,049 | 45,634 |
| United Kingdom | 1,763 | 30,426 | 17,356 |
| United States | ..... | 30,404 | 15,228 |
| France | ..... | 14,473 | 6,298 |
| Holland | 2,500 | 13,746 | 1,095 |
| Germany | 47,965 | ..... | ..... |
| Formalin, lbs. | 946,562 | 571,865 | 730,840 |
| United States | ..... | 534,957 | 724,943 |
| Germany | 535,976 | ..... | ..... |
| Guaiacol carbonate, lbs. | 27,879 | 258 | 200 |
| Switzerland | 3,737 | 221 | ..... |
| Kwangtung Prov. | ..... | 30 | ..... |
| Germany | 12,927 | ..... | ..... |
| Milk sugar, lbs. | 427,003 | 65,743 | 499,816 |
| United States | ..... | 24,530 | 499,373 |
| United Kingdom | 51,551 | 22,400 | ..... |
| Kwangtung Prov. | ..... | 12,998 | ..... |
| Morphine, oz. | 91,128 | 600,229 | 165,087 |
| United Kingdom | 73,303 | 598,749 | 119,722 |
| Germany | 17,327 | ..... | ..... |
| Perfumed waters, lbs. | 87,218 | 76,046 | 62,147 |
| France | 55,874 | 49,104 | 25,985 |
| United Kingdom | 10,668 | 24,630 | 29,430 |
| Germany | 8,047 | ..... | ..... |
| Quinine, oz. | 253,829 | 513,763 | 452,799 |
| Dutch East Indies | 180,819 | 503,683 | 415,523 |
| Santonin, lbs. | 4,492 | 1,697 | 3,665 |
| Russia | ..... | 1,157 | 3,556 |
| United States | ..... | 463 | 110 |
| United Kingdom | 1,282 | 77 | ..... |
| All other chemicals, drugs, etc. | $1,665,673 | $2,441,177 | $4,855,881 |
| United States | 97,110 | 1,296,113 | 2,306,812 |
| United Kingdom | 172,409 | 353,466 | 397,925 |
| China | 97,933 | 249,762 | 485,885 |
| British India | 22,393 | 83,420 | 277,318 |
| France | 35,847 | 91,197 | 51,688 |
| Peru | ..... | 67,393 | 331,127 |
| Germany | 1,049,996 | 11,018 | 3,845 |
| All other preparations or compds. of chemicals, drugs, etc. | $173,248 | $245,336 | $268,743 |
| United Kingdom | 29,344 | 39,329 | 24,682 |
| France | 13,320 | 19,509 | 4,517 |
| Switzerland | 2,334 | 19,195 | 9,190 |
| Germany | 68,901 | 1,635 | ..... |
| United States | 57,916 | 160,881 | 228,287 |
| Dyes, Paints, Etc.: | | | |
| Aniline dyes, lbs. | 9,738,863 | 832,947 | 2,538,725 |
| United States | ..... | 337,115 | 1,841,808 |
| Germany | 8,585,797 | 279,987 | 462,445 |
| Switzerland | 662,861 | 160,898 | 165,782 |
| France | 269,749 | 21,876 | 14,398 |
| Holland | 23,035 | 14,201 | ..... |
| United Kingdom | 178,373 | 4,462 | 31,442 |
| Other coal-tar dyes, lbs. | (1) | 13,978 | 29,840 |
| Germany | (1) | 13,978 | 10,599 |
| Aniline salts, lbs. | 648,730 | 1 | 175,713 |
| United States | ..... | 1 | 175,713 |
| United Kingdom | 138,338 | ..... | ..... |
| Germany | 360,644 | ..... | .... |

[1] Not entered.

Japanese Imports of Chemicals and Chemical Products (*Continued*)

| Dyes, Paints, Etc. (*Concluded*) | 1913 | 1917 | 1918 |
|---|---|---|---|
| Indigo: | | | |
| Natural, lbs. | 27,432 | 85,664 | 1,444,856 |
| British India | 25,450 | 56,162 | 1,310,025 |
| Dutch East Indies | 1,214 | 29,502 | 122,632 |
| Artificial, lbs. | 2,186,513 | 1,910 | 143 |
| Germany | 1,974,432 | 1,870 | 69 |
| Logwood extract, lbs. | 955,992 | 1,649,205 | 3,588,288 |
| United States | 4,508 | 1,303,737 | 3,483,008 |
| France | 878,149 | 283,507 | 61,571 |
| United Kingdom | ..... | 61,865 | 42,757 |
| Germany | 73,223 | ..... | ..... |
| Oxide of cobalt, lbs. | 40,169 | 116,347 | 103,598 |
| United Kingdom | 39,284 | 108,984 | 10,601 |
| United States | 884 | 7,363 | 92,998 |
| Saffron, lbs. | 5,025 | 3,329 | 3,758 |
| France | 3,148 | 1,720 | 3,024 |
| Spain | 1,190 | 1,609 | ..... |
| Germany | 485 | ..... | ..... |
| Ultramarine blue, lbs. | 322,406 | 91,316 | 167,165 |
| United States | ..... | 50,908 | 144,063 |
| United Kingdom | 30,384 | 22,908 | 8,816 |
| France | 14,393 | 17,084 | 14,286 |
| Germany | 258,467 | ..... | ..... |
| Carbon black, lbs. | 356,819 | 407,285 | 971,718 |
| United States | 325,287 | 407,044 | 968,024 |
| Germany | 7,449 | ..... | ..... |
| Lacquer, lbs. | 1,587,784 | 1,657,637 | 2,064,038 |
| China | 1,542,734 | 1,616,253 | 2,038,927 |
| French Indo-China | 45,036 | 41,371 | 21,121 |
| Liquid gold, silver platinum, oz. | 44,923 | 20,210 | 23,836 |
| United States | 7,791 | 16,410 | 21,482 |
| United Kingdom | 10,284 | 3,800 | 2,200 |
| Germany | 24,794 | ..... | ..... |
| Ship's-bottom paints, lbs. | 547,091 | 500,026 | 376,062 |
| United Kingdom | 437,075 | 390,503 | 218,877 |
| United States | 98,209 | 108,291 | 146,971 |
| Other paints, lbs. | 1,774,597 | 471,585 | 264,888 |
| United States | 81,784 | 139,781 | 176,322 |
| United Kingdom | 1,621,299 | 327,613 | 88,095 |
| Germany | 24,355 | ..... | ..... |
| Varnishes, lbs. | 603,102 | 741,227 | 311,381 |
| United States | 188,891 | 493,946 | 286,620 |
| United Kingdom | 376,500 | 246,345 | 22,973 |
| Germany | 23,647 | ..... | ..... |
| White lead, red lead, and litharge, lbs. | 130,061 | 14,855 | 18,256 |
| United States | 13,298 | 8,700 | 112 |
| United Kingdom | 103,191 | 6,151 | 16,984 |
| Germany | 12,582 | ..... | ..... |
| Zinc white | (1) | 96,258 | 493,175 |
| United Kingdom | ..... | 22,407 | 17,426 |
| Printing ink, lbs. | 334,613 | 116,105 | 212,740 |
| United States | 240,692 | 88,033 | 188,031 |
| United Kingdom | 26,895 | 27,336 | 22,901 |
| Germany | 59,998 | ..... | ..... |
| Other ink, lbs. | 212,870 | 11,186 | 59,580 |
| United States | 90,117 | 4,989 | 23,188 |
| United Kingdom | 121,850 | 4,963 | 33,053 |
| France | 257 | 1,188 | 3,315 |
| Germany | 646 | 46 | ..... |
| All other dyes and pigments | $259,301 | $267,594 | $552,824 |
| United Kingdom | 56,798 | 119,400 | 125,891 |
| United States | 8,916 | 91,906 | 349,998 |
| China | 5,421 | 28,314 | 42,186 |
| France | 24,058 | 15,509 | 7,468 |
| Germany | 135,373 | 3,036 | ..... |
| All other coatings and fillers | $91,116 | $84,308 | $92,111 |
| United States | 24,427 | 61,109 | 74,235 |
| United Kingdom | 46,122 | 21,783 | 16,860 |
| France | 1,950 | 580 | .... |
| Germany | 12,208 | ..... | ..... |
| Oils, Fats, Waxes, and Manufactures thereof: | | | |
| Oil-bearing materials: | | | |
| Soy beans, lbs. | 235,521,849 | 185,616,327 | 258,322,752 |
| Peanuts, lbs. | ..... | 3,718,040 | 14,060,680 |
| Sesame, lbs. | 13,129,316 | 12,085,122 | 25,795,264 |
| Perila ocimoide, lbs. | 9,883,760 | 17,604,130 | 17,055,967 |
| Rape and mustard, lbs. | 35,573,334 | 78,439,933 | 127,505,661 |
| Linseed, lbs. | ..... | 8,269,715 | 14,528,942 |
| Hempseed, lbs. | ..... | 17,110,470 | 7,131,334 |
| Cottonseed, lbs. | 26,540,382 | 47,405,818 | 32,696,701 |
| Copra, lbs. | 5,639,797 | 89,678,340 | 165,184,726 |
| Vegetable oils: | | | |
| Castor oil, lbs. | 970,148 | 730,040 | 1,044,503 |
| China | 426,159 | 405,706 | 758,860 |
| Kwangtung Prov. | 185,338 | 77,710 | 11,158 |
| United States | ..... | 5,740 | 16,088 |
| Germany | 37,765 | ..... | ..... |
| Coconut oil, lbs. | 1,128,489 | 2,003,237 | 681,319 |
| Straits Settlements | 107,978 | 1,372,548 | 113,158 |
| Linseed oil, lbs. | 582,257 | 147,103 | 438,426 |
| United Kingdom | 509,553 | 72,572 | 7,822 |
| China | ..... | 59,730 | 327,929 |
| United States | 11,320 | 13,045 | 231 |
| Germany | 5,122 | ..... | ..... |
| Olive oil, lbs. | 197,036 | 118,070 | 140,595 |
| France | 121,436 | 47,944 | 20,929 |
| Italy | 30,489 | 35,563 | 1,746 |
| United States | 3,167 | 14,610 | 37,515 |
| Spain | 2,493 | 8,820 | 17,637 |
| Germany | 35,229 | ..... | ..... |
| Soy-bean oil, lbs. | 6,249,522 | 1,024,240 | 2,633,915 |
| Turpentine oil, gals. | 38,731 | 51,690 | 88,047 |
| United States | 38,100 | 51,642 | 88,026 |
| Vegetable tallow, lbs. | ..... | 20,915 | 5,483 |

[1] Not shown separately.

JAPANESE IMPORTS OF CHEMICALS AND CHEMICAL PRODUCTS (*Continued*)

| OILS, FATS, ETC. (*Concluded*) | 1913 | 1917 | 1918 |
|---|---|---|---|
| Mineral oils: | | | |
| Crude, gal. | 3,519,619 | 3,242,766 | 1,271,108 |
| United States | 159 | 3,242,766 | 1,127,825 |
| Gasoline, gal. | 296,065 | 1,139,712 | 2,757,799 |
| United States | 295,360 | 383,594 | 321,339 |
| Dutch East Indies | ..... | 345,512 | 2,404,460 |
| Kerosene, gal. | 48,174,840 | 19,426,787 | 23,276,881 |
| United States | 33,145,387 | 17,943,857 | 19,752,947 |
| Dutch East Indies | 15,029,453 | 1,482,791 | 3,513,369 |
| Mineral colza, gal. | 565,449 | 537,382 | 291,254 |
| United States | 565,409 | 537,382 | 291,254 |
| Paraffin wax, lbs. | 17,902,123 | 23,780,672 | 34,040,882 |
| British India | 3,650,442 | 7,495,273 | 8,069,098 |
| Dutch East Indies | 636,979 | 9,239,780 | 15,385,960 |
| United States | 7,252,562 | 6,621,634 | 9,995,959 |
| Vaseline, lbs. | 910,291 | 689,837 | 576,290 |
| United States | 13,221 | 659,074 | 576,290 |
| United Kingdom | 127,341 | 28,117 | ..... |
| Other mineral, lbs. | 19,572,190 | 15,767,900 | 33,787,687 |
| United States | 18,101,324 | 15,709,430 | 33,720,643 |
| Dutch East Indies | 23,246 | ..... | 97 |
| Tallow, beef, lbs. | 9,943,623 | 16,813,550 | 20,056,708 |
| China | 6,659,223 | 9,390,834 | 8,756,427 |
| Australia | 2,747,315 | 7,298,393 | 10,740,643 |
| Other animal fats, lbs. | 3,647,573 | 2,101,764 | 2,255,668 |
| Australia | 2,445,510 | 1,247,822 | 1,350,311 |
| China | 124,181 | 843,865 | ..... |
| Olein, lbs. | 971,335 | 864,378 | 1,565,142 |
| Australia | 971,324 | 700,160 | 1,002,642 |
| Stearin, lbs. | 721,532 | 603,657 | 246,486 |
| United States | ..... | 391,330 | 87,114 |
| United Kingdom | 263,848 | 147,010 | 37,438 |
| Australia | ..... | 58,796 | 117,282 |
| Soap: | | | |
| Perfumed, lbs. | 377,576 | 103,940 | 1,235,548 |
| United States | 111,776 | 53,466 | 57,842 |
| United Kingdom | 78,377 | 39,577 | 59,635 |
| Germany | 113,400 | 3 | ..... |
| Other, lbs. | 1,380,355 | 160,885 | 14,697 |
| France | 1,110,041 | 92,749 | 3,295 |
| United Kingdom | 115,014 | 45,743 | 37,039 |
| United States | 60,967 | 14,752 | 9,998 |
| Oils, fats and waxes, perfumed, lbs. | 58,576 | 42,064 | 20,631 |
| France | 45,809 | 32,524 | 8,792 |
| United Kingdom | 5,784 | 7,099 | 3,732 |
| United States | 831 | 2,180 | 7,659 |
| Germany | 6,023 | ..... | ..... |
| Volatile oils, lbs. | 285,956 | 426,310 | 673,832 |
| United Kingdom | 64,177 | 113,474 | 179,315 |
| China | 39,338 | 77,440 | 73,623 |
| Dutch East Indies | 106 | 67,493 | 170,783 |
| France | 34,905 | 52,828 | 42,748 |
| British India | 12,433 | 48,487 | 90,642 |
| United States | 108 | 35,220 | 93,923 |
| Germany | 120,735 | ..... | ..... |
| All other oils, fats, and waxes, and manufactures thereof | $113,569 | $221,810 | $471,824 |
| GUMS, RESINS, ETC.: | | | |
| India rubber and gutta percha, crude, lbs. | 2,660,702 | 8,327,903 | 16,231,322 |
| Straits Settlements | 1,644,139 | 6,136,580 | 15,127,412 |
| British India | 337,647 | 1,603,330 | 522,001 |
| United Kingdom | 437,311 | 344,575 | 147,476 |
| United States | 138,518 | 122,325 | 93,717 |
| Germany | 15,343 | ..... | ..... |
| Rosin, lbs. | 15,648,616 | 26,082,035 | 26,141,718 |
| United States | 11,108,305 | 24,404,825 | 21,805,808 |
| China | 416,106 | 1,407,937 | 4,217,514 |
| Straits Settlements | ..... | 141,140 | 30,497 |
| United Kingdom | 723,815 | 126,494 | 10,925 |
| Germany | 3,378,866 | ..... | ..... |
| Shellac, lbs. | 452,607 | 1,172,053 | 2,236,891 |
| British India | 450,964 | 1,168,470 | 2,202,859 |
| Other gums and resins, lbs. | (1) | 1,068,210 | 1,952,086 |
| Straits Settlements | ..... | 440,780 | 542,719 |
| Dutch East Indies | ..... | 236,162 | 702,301 |
| China | ..... | 169,978 | 74,181 |
| Gelatin, lbs. | 118,782 | 26,568 | 98,836 |
| United Kingdom | 27,717 | 19,643 | 68,427 |
| United States | 17 | 4,990 | 23,079 |
| Germany | 82,033 | ..... | ..... |
| Glue, lbs. | 3,014,168 | 892,370 | 881,891 |
| United Kingdom | 547,149 | 466,297 | 37,923 |
| France | 73,690 | 187,353 | 31,262 |
| United States | 1,329 | 107,802 | 462,018 |
| Switzerland | 13,779 | 46,214 | ..... |
| Italy | ..... | 44,798 | ..... |
| Germany | 1,045,307 | ..... | ..... |
| Gum arabic, lbs. | 615,273 | 359,575 | 309,924 |
| British India | 55,443 | 187,729 | 247,819 |
| United Kingdom | 77,393 | 82,095 | ..... |
| Germany | 144,463 | ..... | ..... |
| Pitch and asphalt, lbs. | 1,053,884 | 1,448,712 | 1,971,064 |
| United States | 637,983 | 1,312,971 | 1,450,960 |
| United Kingdom | 219,273 | 115,333 | 210,644 |
| Germany | 190,383 | 20,408 | 318,460 |
| ORES, ETC.: | | | |
| Antimony ore, lbs. | (2) | 8,739,828 | (2) |
| China | ..... | 8,542,735 | ..... |
| French Indo-China | ..... | 197,093 | ..... |
| Iron ore, lbs. | 617,837,109 | 655,327,868 | 795,715,024 |
| China | 613,393,915 | 652,695,417 | 792,997,387 |
| Lead ore, lbs. | (2) | 50,120,413 | 7,926,188 |
| China | ..... | 30,684,110 | 880,967 |
| Asiatic Russia | ..... | 11,561,040 | 1,729,261 |
| Kwangtung Province | ..... | 3,360,374 | 2,116 |
| Russia | ..... | 3,360,110 | ..... |

[1] Not given in 1913.

[2] Not shown separately.

JAPANESE IMPORTS OF CHEMICALS AND CHEMICAL PRODUCTS (*Concluded*)

| ORES, ETC. (*Concluded*) | 1913 | 1917 | 1918 |
|---|---|---|---|
| Zinc ore, lbs. | (1) | 205,807,535 | 132,038,936 |
| Australia | ..... | 151,356,625 | 98,955,854 |
| French Indo-China | ..... | 38,362,942 | 29,578,527 |
| Asiatic Russia | ..... | 9,067,347 | 2,968,038 |
| Other ores | $134,450[2] | $2,154,763 | $2,702,522 |
| French Indo-China | ..... | 215,285 | 112,068 |
| Clay, lbs. | (1) | 41,997,480 | 9,792,176 |
| China | ..... | 21,270,040 | 1,701,382 |
| Kwangtung Province | ..... | 19,930,385 | 6,890,854 |
| United States | ..... | 671,156 | 285,088 |
| Cryolite, lbs. | (1) | 44,342 | 63,682 |
| Sweden | ..... | 22,046 | ..... |
| Denmark | ..... | 22,046 | ..... |
| United States | ..... | 250 | ..... |
| Gypsum, lbs. | 3,458,124 | 11,449,284 | 10,448,743 |
| China | 1,906,732 | 7,711,200 | 10,447,743 |
| United States | ..... | 2,835,550 | ..... |
| United Kingdom | ..... | 902,490 | ..... |
| Phosphorite, lbs. | 730,364,000 | 197,472,700 | 342,700,600 |
| Australia | ..... | 132 | 324,364,900 |
| United States | 85,924,700 | ..... | ..... |
| United Kingdom | 48,859,600 | ..... | ..... |
| Egypt | 65,578,100 | ..... | 8,640,700 |
| MISCELLANEOUS MANUFACTURES: | | | |
| Glass and glassware | $1,696,758 | $1,261,233 | $1,223,614 |
| Explosives: | | | |
| Dynamite, lbs. | 2,145,280 | 1,415,873 | 2,638,856 |
| United States | ..... | 1,000,966 | 1,874,683 |
| Canada | ..... | 409,607 | 759,213 |
| China | ..... | ..... | 4,960 |
| United Kingdom | 520,757 | 5,300 | ..... |
| Germany | 1,612,022 | ..... | ..... |
| Detonators, lbs. | 69,684 | ..... | ..... |
| Germany | 54,152 | ..... | ..... |
| United Kingdom | 15,532 | ..... | ..... |
| Other explosives | $47,329 | $11,879 | $7,209 |
| Paper | $3,604,262 | $2,035,693 | $4,678,954 |
| United Kingdom | 1,073,164 | 608,009 | 458,074 |
| Germany | 1,267,540 | 7,328 | ..... |
| Belgium | 232,247 | ..... | ..... |
| Austria-Hungary | 177,006 | 3,200 | ..... |
| Sweden | 506,692 | 256,371 | 58,981 |
| Norway | 99,234 | 111,338 | 86,697 |
| United States | 146,098 | 993,454 | 4,011,609 |
| Photographic films, sensitized, lbs. | 36,768 | 65,644 | 71,805 |
| United States | 21,949 | 53,556 | 59,599 |
| United Kingdom | 9,414 | 12,088 | 12,082 |
| France | 3,216 | ..... | 8 |
| Germany | 2,124 | ..... | ..... |
| Sugar: | | | |
| Under No. 21 Dutch standard, lbs. | 708,149,914 | 174,011,370 | 462,418,829 |
| Dutch East Indies | 618,094,310 | 121,706,660 | 378,514,386 |
| Philippines | 82,017,770 | 45,245,464 | 76,629,983 |
| Other, lbs. | 3,051,903 | 68,784 | 30,365,454 |
| Rock candy, cube, loaf and similar, lbs. | 187,486 | 11,992 | 2,062 |
| Grape sugar, malt sugar, molasses and the like, lbs. | 2,024,528 | 91,966 | 477,849 |

[1] Not shown separately.

[2] Other than iron ore.

## STATISTICS OF EXPORTS

The following table of exports has been compiled from the annual returns of the Japanese Department of Finance:

JAPANESE EXPORTS OF CHEMICALS AND CHEMICAL PRODUCTS

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| CHEMICALS, DRUGS, ETC.: | | | |
| Acids: | | | |
| Acetic, lbs. | (1) | 5,632,007 | 4,663,924 |
| Straits Settlements | ..... | 3,759,263 | 2,342,510 |
| Dutch East Indies | ..... | 1,120,300 | 1,282,508 |
| British India | ..... | 617,271 | 803,672 |
| Sulfuric, lbs. | 3,368,497 | 9,192,039 | 7,754,090 |
| Straits Settlements | 208,381 | 3,077,489 | 1,051,865 |
| China | 1,482,166 | 1,620,324 | 1,266,329 |
| Egypt | ..... | 1,136,716 | 2,463,983 |
| Asiatic Russia | 315,545 | 1,114,249 | 2,534 |
| Hongkong | 409,813 | 773,395 | 1,238,424 |
| Bleaching powder, lbs. | 2,235,591 | 14,261,615 | 10,904,580 |
| British India | 132 | 8,384,777 | 6,199,441 |
| China | 1,828,436 | 3,926,623 | 2,805,811 |
| Calcium carbide, lbs. | (1) | 7,198,619 | 28,616,157 |
| Australia | ..... | 3,855,964 | 10,334,972 |
| China | ..... | 737,185 | 1,179,797 |
| Hongkong | ..... | 641,717 | 2,072,626 |
| Straits Settlements | ..... | 540,803 | 2,743,357 |
| British India | ..... | 523,327 | 6,558,946 |
| Camphor, lbs. | 3,278,200 | 4,126,928 | 2,333,652 |
| United States | 659,647 | 1,975,073 | 787,873 |
| British India | 1,164,835 | 1,431,885 | 477,758 |
| Coal tar and pitch, lbs. | (1) | 27,079,515 | 19,394,700 |
| French Indo-China | ..... | 18,356,922 | 7,612,252 |
| Hongkong | ..... | 1,408,154 | 7,159,709 |
| Copper sulfate, lbs. | (1) | 3,726,754 | 3,454,618 |
| Australia | ..... | 1,678,503 | 1,913,053 |
| British India | ..... | 711,978 | 316,000 |
| Dutch East Indies | ..... | 402,068 | 491,692 |
| China | ..... | 400,361 | 144,900 |

[1] Not shown separately.

Japanese Exports of Chemicals and Chemical Products (*Continued*)

| CHEMICALS, DRUGS, ETC. (*Concluded*) | 1913 | 1917 | 1918 |
|---|---|---|---|
| Dried plants for insecticides, lbs. | 346,458 | 3,304,297 | 3,197,320 |
| United States | 30,492 | 2,370,259 | 2,700,376 |
| United Kingdom | 183,465 | 612,469 | 412,073 |
| Canada | ..... | 298,571 | 23,600 |
| Fertilizers: | | | |
| Artificial, lbs. | 330,459 | 11,808,924 | 1,836,671 |
| Dutch East Indies | ..... | 5,824,831 | 1,595,926 |
| Asiatic Russia | ..... | 4,485,920 | ..... |
| Straits Settlements | 153,873 | 79,895 | ..... |
| Phosphatic, lbs. | 41,306,486 | 43,892,522 | 14,945,750 |
| Dutch East Indies | ..... | 16,065,736 | 5,236,197 |
| New Zealand | ..... | 8,483,605 | ..... |
| Straits Settlements | 94,380 | 6,521,932 | 1,937,995 |
| Asiatic Russia | ..... | 4,989,235 | ..... |
| British India | 312,448 | 3,711,436 | ..... |
| Cape Colony and Natal | ..... | 784,272 | 6,998,395 |
| Australia | 27,742,507 | 132 | ..... |
| Oil cake, lbs. | (1) | 2,512,343 | 1,749,499 |
| Dutch East Indies | ..... | 61,641 | 1,538,253 |
| United States | ..... | 1,182,295 | ..... |
| Ginseng, lbs. | 331,039 | 350,383 | 277,687 |
| China | 178,669 | 185,944 | 194,117 |
| Hongkong | 151,325 | 163,913 | 83,021 |
| Insect powder, lbs. | 209,340 | 666,576 | 808,594 |
| China | 76,473 | 180,143 | 205,046 |
| Australia | 143 | 117,769 | 162,626 |
| Kwangtung Province | 27,818 | 80,435 | 55,965 |
| Asiatic Russia | 9,665 | 72,710 | 15,062 |
| United States | 15,902 | 47,776 | 119,991 |
| Argentina | ..... | 36,613 | 25,368 |
| United Kingdom | ..... | 20,618 | 63,886 |
| Iodine, lbs. | 26,733 | 62,660 | 81,204 |
| United States | ..... | 26,758 | 23,629 |
| United Kingdom | 11,393 | 15,042 | 29,843 |
| Kaki and other tanning materials, lbs. | (1) | 3,299,658 | 591,580 |
| Asiatic Russia | ..... | 2,600,739 | 1,177 |
| China | ..... | 637,157 | 393,143 |
| United Kingdom | ..... | ..... | 75,134 |
| Menthol: | | | |
| Cane, doz. | 100,681 | 195,137 | 269,052 |
| Dutch East Indies | 26,545 | 66,858 | 76,277 |
| China | 50,523 | 57,891 | 103,129 |
| Hongkong | 14,232 | 30,540 | 43,561 |
| Straits Settlements | 2,487 | 19,028 | 12,781 |
| Crystals, lbs. | 308,089 | 332,293 | 313,908 |
| United States | 54,843 | 196,503 | 99,687 |
| United Kingdom | 83,918 | 83,163 | 155,954 |
| Naphthalene, lbs. | (1) | 1,394,290 | 1,463,838 |
| China | ..... | 566,262 | 627,030 |
| British India | ..... | 328,837 | 161,954 |
| Dutch East Indies | ..... | 191,708 | 56,400 |
| Australia | ..... | 67,213 | 416,840 |
| Potash: | | | |
| Chlorate, lbs. | (1) | 3,415,669 | 4,772,690 |
| United States | ..... | 1,617,233 | 228,485 |
| China | ..... | 913,718 | 1,301,727 |
| Brazil | ..... | ..... | 1,228,860 |
| Iodide, lbs. | 71,727 | 218,790 | 244,643 |
| United Kingdom | 63,474 | 86,930 | 36,559 |
| United States | ..... | 38,294 | 72,303 |
| Asiatic Russia | ..... | 33,373 | 13,786 |
| British India | 417 | 14,420 | 32,399 |
| Soda, caustic, lbs. | (1) | 881,031 | 1,455,815 |
| British India | ..... | 655,917 | 11,487 |
| China | ..... | 145,621 | 195,747 |
| Dutch East Indies | ..... | 2,210 | 810,775 |
| Sulfur, lbs. | 119,613,792 | 188,375,054 | 119,263,386 |
| Australia | 53,782,290 | 109,692,364 | 79,247,950 |
| British India | 2,343,702 | 23,697,560 | 19,045,363 |
| Cape Colony and Natal | ..... | 15,388,857 | 5,072,301 |
| Dutch East Indies | 642,681 | 14,766,798 | 5,172,619 |
| Asiatic Russia | 32,506 | 8,144,242 | 4,876 |
| New Zealand | ..... | 5,523,743 | 1,729,720 |
| Toilet powders | $58,727 | $141,614 | $176,641 |
| China | 36,477 | 79,207 | 82,311 |
| Other prepared perfumes | $105,628 | $139,064 | $218,488 |
| China | 59,279 | 46,955 | 63,123 |
| Tooth powder, paste | $119,286 | $212,857 | $330,176 |
| China | 82,155 | 132,165 | 182,719 |
| Prepared medicines | $828,121 | $799,723 | $953,828 |
| China | 528,516 | 406,528 | 487,783 |
| Kwangtung Province | 64,848 | 97,948 | 106,305 |
| British India | 16,741 | 70,385 | 92,612 |
| All other drugs, chemicals and medicines | $413,177 | $4,596,798 | $6,173,595 |
| United States | 5,448 | 1,098,776 | 976,429 |
| Dutch East Indies | 8,329 | 999,230 | 777,445 |
| China | 183,116 | 776,769 | 1,289,023 |
| Asiatic Russia | 5,730 | 457,413 | 233,917 |
| British India | 19,755 | 391,889 | 353,632 |
| Germany | 6,620 | ..... | ..... |
| Argentina | 508 | 46 | 456,162 |
| United Kingdom | 13,940 | 135,606 | 442,033 |
| DYES, PAINTS, ETC.: | | | |
| Paints, lbs. | 474,708 | 2,420,850 | 15,034,236 |
| Kwangtung Province | 435,107 | 758,763 | 1,179,955 |
| China | 35,765 | 567,675 | 1,541,667 |
| Straits Settlements | ..... | 308,324 | 1,795,357 |
| British India | ..... | 284,697 | 8,010,602 |
| Dutch East Indies | ..... | 235,797 | 1,696,666 |
| Red lead, lbs. | (1) | 1,895,086 | 4,596,276 |
| British India | ..... | 1,391,191 | 3,059,014 |

[1] Not shown separately.

Japanese Exports of Chemicals and Chemical Products (*Continued*)

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| DYES, PAINTS, ETC. (*Concluded*) | | | |
| All other dyes, pigments, coatings and filling matters | $150,907 | $712,706 | $1,752,643 |
| China | 74,990 | 245,316 | 819,552 |
| United States | 2,220 | 110,636 | 13,878 |
| Asiatic Russia | 3,501 | 91,668 | 43,974 |
| Kwangtung Province | 32,224 | 85,245 | 193,908 |
| British India | 10,253 | 63,498 | 237,700 |
| Dutch East Indies | 534 | 39,771 | 181,561 |
| Inks, lbs. | 509,019 | 1,088,601 | 1,392,150 |
| China | 281,649 | 368,730 | 442,109 |
| Hongkong | 129,026 | 193,737 | 188,572 |
| British India | 3,069 | 133,015 | 236,373 |
| Dutch East Indies | 1,320 | 98,406 | 143,650 |
| OILS, FATS, WAXES, AND MANUFACTURES THEREOF: | | | |
| Oil-bearing materials: | | | |
| Linseed, lbs. | (1) | 11,279,488 | 4,322,980 |
| Peanuts, lbs. | 13,070,157 | 18,627,100 | 18,705,620 |
| Rape and mustard, lbs. | (1) | 13,253,105 | 2,721,652 |
| Soybeans, lbs. | (1) | 3,379,985 | 1,594,854 |
| Vegetable oils: | | | |
| Camphor oil, lbs. | 2,594,590 | 2,266,742 | 1,813,344 |
| United States | 1,623,410 | 1,687,055 | 1,048,932 |
| Coconut oil, lbs. | (1) | 34,639,635 | 53,522,777 |
| United States | ..... | 24,742,022 | 48,854,624 |
| United Kingdom | ..... | 2,914,270 | 75 |
| Asiatic Russia | ..... | 2,878,511 | 1,308,784 |
| Canada | ..... | 1,518,996 | 1,681,681 |
| Colza oil, lbs. | 11,664,630 | 19,521,925 | 26,620,762 |
| United States | 314,310 | 12,279,266 | 22,585,710 |
| United Kingdom | 5,711,063 | 4,748,987 | 181,133 |
| Cottonseed oil, lbs. | (1) | 1,599,957 | 2,427,019 |
| United States | ..... | 1,353,868 | 1,179,792 |
| Peppermint oil, lbs. | 373,173 | 343,548 | 283,912 |
| United Kingdom | 118,663 | 185,585 | 193,969 |
| United States | 11,210 | 55,840 | 8,302 |
| France | 58,490 | 41,601 | 1,377 |
| Hongkong | 45,043 | 29,758 | 23,963 |
| Soybean oil, lbs. | 1,879,682 | 7,307,968 | 6,518,898 |
| United States | 658,382 | 6,946,348 | 5,085,155 |
| Vegetable wax, lbs. | 6,261,004 | 6,582,226 | 11,804,465 |
| United Kingdom | 972,884 | 2,690,668 | 6,050,266 |
| United States | 1,244,983 | 2,320,502 | 3,782,461 |
| France | 1,004,590 | 523,087 | 1,167,228 |
| British India | 271,490 | 317,333 | 282,487 |
| Mineral oils: | | | |
| Kerosene, gal. | (1) | 3,594,024 | 1,655,878 |
| China | ..... | 2,438,082 | 841,669 |
| Kwantung Province | ..... | 1,151,189 | 658,926 |
| Other mineral oils, lbs. | (1) | 14,592,340 | 14,521,094 |
| Kwangtung Province | ..... | 7,873,458 | 8,472,919 |
| China | ..... | 5,950,480 | 3,131,906 |
| Fish and whale oil | 54,023,876 | 31,955,843 | 31,382,184 |
| United States | 246,350 | 15,470,291 | 16,173,741 |
| United Kingdom | 12,706,558 | 12,480,904 | 9,005,762 |
| Soap: | | | |
| Toilet, doz. | 2,342,606 | 5,040,409 | 4,732,659 |
| Hongkong | 92,125 | 735,491 | 397,461 |
| Kwantung Prov. | 228,164 | 414,351 | 524,585 |
| British India | 72,198 | 281,804 | 183,059 |
| China | 1,930,129 | 3,365,235 | 3,074,647 |
| Dutch East Indies | 1,469 | 162,855 | 374,886 |
| United States | 22 | 11,116 | 1,008 |
| Washing, lbs. | 261,010 | 576,558 | 1,913,943 |
| China | 194,125 | 175,860 | 959,434 |
| Kwangtung Prov. | 13,407 | 111,172 | 170,790 |
| Hongkong | 7,446 | 80,390 | 272,695 |
| Dutch East Indies | ..... | 6,197 | 366,297 |
| Toilet water and hair oil | $258,474 | $496,036 | $579,060 |
| Dutch East Indies | 49,263 | 148,116 | 187,220 |
| China | 70,002 | 88,319 | 119,523 |
| Straits Settlements | 41,908 | 54,606 | 72,938 |
| All other oils, fats, and waxes, and manufactures thereof | $179,583 | $1,116,532 | $2,297,789 |
| United States | 7,892 | 363,906 | 441,808 |
| China | 27,673 | 248,102 | 392,837 |
| Kwangtung Province | 70,374 | 118,943 | 203,570 |
| United Kingdom | 11,014 | 111,876 | 178,463 |
| Asiatic Russia | 635 | 95,207 | 24,265 |
| Dutch East Indies | 114 | 98,416 | 366,205 |
| ORES, ETC.: | | | |
| Manganese ore, lbs. | (1) | 12,179,700 | 5,188,447 |
| United Kingdom | ..... | 5,721,524 | 1,207,957 |
| United States | ..... | 5,208,288 | 1,392,748 |
| Tungsten ore, lbs. | (1) | 1,586,534 | 2,644,092 |
| United States | ..... | 1,379,124 | 2,644,092 |
| Zinc ore, lbs. | 60,366,044 | 381,576 | 11,244 |
| United Kingdom | 270,770 | 381,576 | 11,244 |
| Other ores | $680 | $380,116 | $244,573 |
| United States | 3 | 192,839 | 178,294 |
| Asiatic Russia | ..... | 89,556 | 50 |
| Antimony, lbs. | 3,533,080 | 31,466,564 | 6,038,036 |
| United States | 1,210,945 | 18,786,698 | 2,943,786 |
| United Kingdom | 1,810,525 | 10,000,745 | 1,669,054 |
| Plumbago, lbs. | (1) | 5,608,570 | 4,442,308 |
| United Kingdom | ..... | 4,030,243 | 3,972,881 |
| Zinc dust, lbs. | (1) | 2,178,787 | 1,589,460 |
| United Kingdom | ..... | 1,019,122 | 1,228,526 |
| United States | ..... | 634,303 | 45,760 |
| MISCELLANEOUS MANUFACTURES: | | | |
| Celluloid, lbs. | (1) | 956,514 | 1,339,445 |
| United Kingdom | ..... | 855,890 | 352,864 |
| France | ..... | 58,583 | 915,610 |

[1] Not shown separately.

JAPANESE EXPORTS OF CHEMICALS AND CHEMICAL PRODUCTS (*Continued*)

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| MISCELLANEOUS MANUFACTURES (*Continued*) | | | |
| Explosives | (1) | 443,076 | 638,090 |
| Kwangtung Province | ..... | 203,626 | 356,048 |
| Asiatic Russia | ..... | 173,061 | 7,216 |
| China | ..... | 62,425 | 110,385 |
| Glass | $1,652,791 | $6,669,672 | $8,007,614 |
| Matches: | | | |
| Safety, gross | 24,300,108 | 31,457,573 | 29,621,324 |
| British India | 6,064,182 | 12,489,216 | 8,768,973 |
| Hongkong | 9,529,743 | 5,302,284 | 5,920,397 |
| Dutch East Indies | 2,273,838 | 3,243,224 | 4,315,164 |
| Straits Settlements | 2,615,230 | 2,364,568 | 2,539,625 |
| United States | 63,347 | 2,311,854 | 1,545,631 |
| Asiatic Russia | 17,859 | 2,211,811 | 15,619 |
| China | 3,397,332 | 1,455,912 | 1,781,053 |
| Other, gross | 19,709,139 | 12,702,438 | 9,846,096 |
| China | 17,184,529 | 8,591,817 | 6,168,131 |
| British India | 453,980 | 2,968,973 | 2,675,084 |
| Kwangtung Prov. | 1,921,302 | 1,105,276 | 979,460 |
| Metal powders, lbs. | (1) | 834,382 | 551,092 |
| China | ..... | 145,596 | 108,413 |
| France | ..... | 138,285 | 24,719 |
| United Kingdom | ..... | 128,548 | 87,430 |
| United States | ..... | 110,537 | 9,593 |
| British India | ..... | 61,986 | 91,794 |
| Paper: | | | |
| "European" | $943,381 | $7,038,377 | $12,481,933 |
| China | 471,928 | 2,819,543 | 4,186,413 |
| Kwangtung Province | 201,028 | 841,121 | 1,180,881 |
| Hongkong | 29,308 | 886,544 | 945,148 |
| British India | 64,539 | 1,111,541 | 1,869,431 |

[1] Not shown separately.

JAPANESE EXPORTS OF CHEMICALS AND CHEMICAL PRODUCTS (*Concluded*)

| | 1913 | 1917 | 1918 |
|---|---|---|---|
| MISCELLANEOUS MANUFACTURES (*Concluded*) | | | |
| Straits Settlements | 9,184 | 166,469 | 513,291 |
| Dutch East Indies | 773 | 458,166 | 1,631,012 |
| Asiatic Russia | 9,147 | 128,709 | 436,259 |
| Philippine Islands. | 5,674 | 252,552 | 400,378 |
| Egypt | 14 | 56,530 | 236,540 |
| Australia | 24,305 | 160,787 | 490,295 |
| United States | 70,255 | 37,044 | 68,844 |
| Japanese: | $598,604 | $977,090 | $1,695,530 |
| China | 195,790 | 344,990 | 582,424 |
| Kwangtung Province | 62,200 | 117,580 | 217,951 |
| Hongkong | 8,251 | 42,555 | 70,763 |
| Dutch East Indies | 4,569 | 36,943 | 218,109 |
| United Kingdom | 111,357 | 82,870 | 86,977 |
| United States | 127,400 | 246,554 | 194,839 |
| Shoe polishes, lbs. | (1) | 373,796 | 481,378 |
| Asiatic Russia | ..... | 124,044 | 89,934 |
| China | ..... | 113,852 | 88,332 |
| Kwangtung Province | ..... | 50,136 | 73,938 |
| Straits Settlements | ..... | 41,323 | 3,315 |
| Dutch East Indies | ..... | 18,647 | 177,622 |
| Soy, gal. | 1,529,444 | 1,868,143 | 844,861 |
| United States | 539,932 | 764,530 | 123,199 |
| Hawaii | 349,820 | 395,627 | 134,312 |
| Sugar: | | | |
| Refined, lbs. | 223,240,395 | 292,205,874 | 252,488,563 |
| China | 202,051,400 | 197,065,352 | 211,632,629 |
| Kwangtung Prov. | 16,173,920 | 44,253,340 | 31,725,978 |
| Rock candy, lbs. | 94,492 | 4,975,830 | 6,698,942 |

[1] Not shown separately.

# ORIGINAL PAPERS

## THE COMMERCIAL OXIDATION OF AMMONIA

By George Arthur Perley

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Received September 4, 1919

(*Concluded from January issue*)

PURITY OF GAS MIXTURES—To review the previous pages, it may be said that the early work in the United States upon the oxidation of ammonia had developed a better understanding of the requirements of a gauze catalyst as far as the general effects of temperature, oxygen, and contact surface were concerned. A nonconducting converter and a cylindrical multi-layer catalyst had been produced which gave as satisfactory results upon a high-grade coke oven ammonia gas as did the electrically heated single-layer gauze catalyst. It was realized that one pound of nitric acid (as anhydrous) could be produced in the form of 50 per cent nitric acid at the following costs:

| | |
|---|---|
| For electrical heat at $0.004 per k. w. h. with a single gauze | $0.00071 per lb. |
| For loss of platinum, by dusting of sprouts | $0.00031 per lb. |

but for an average large oxidation plant, complete charges per lb. $HNO_3$ (100 per cent) are

| | |
|---|---|
| Power | $0.0013 per lb. |
| Operating labor | 0.0011 per lb. |
| Repairs, labor | 0.00036 per lb. |

and an increase of 1 per cent in conversion of 10 per cent ammonia only decreases the cost of the resultant nitric acid by $0.0003 per lb.

After making such comparisons, attempts were made to eliminate electrical heating for all types of ammonia and to increase the capacity of a given weight of platinum. Offhand, there was no available information which would indicate why one common type of catalyst could not be applied to the general ammonia oxidation reaction for ammonia from all sources.

The first attempts to apply the new ideas to the oxidation of cyanamide ammonia resulted in a sad failure. When the multi-layer cylindrical gauze was employed in the oxidation of normal autoclave cyanamide gas it was found that the catalyst rapidly developed inactive dark spots. The only means of maintaining the gauze in the active state was by operating at a ridiculously low capacity. Even under these conditions the gauze finally became inactive.

The first government experimental data upon this problem were secured at the Warners, N. J., plant of the American Cyanamid Company.

Such an exhibition was most startling to those who had seen the success of a similar converter when operating upon a high-grade coke oven ammonia. This was the beginning of the realization of the importance of the factor known as "catalyst poisons." Since this particular observation the writer has noted[1] that German Patent 276,720 covers a process of purifying ammonia as produced from cyanamide by means of sodium hydroxide solution. It was then noted that the platinum became brittle and could be used only for a short time. The presence of silicon hydride, phosphine, and acetylene was considered the cause of the trouble. These were removed by a caustic scrubber.

It should be noted that at the time when the test upon the multi-layer cylindrical gauze was made at the Warners, N. J., plant in March 1918, there were three electrically heated single-layer gauze catalysts in operation. The converters were of the so-called Landis type. A careful examination of the action of the single-layer electrically heated gauze was simultaneously made. It was noted that at periodic intervals this type of converter would also develop dark inactive spots even when heated electrically, but that the externally applied source of heat tended to stabilize the gauze action. The multi-layer nonheated gauze lacked such a stabilizer. An examination as to the oxidation con-

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[1] *Chem.-Ztg.*, **848** (1915).

versions which were being secured on the electrically heated type of gauze was distinctly interesting in view of what has been published along these lines. Table 6 gives the data secured upon the American Cyanamid Company converters.

TABLE 6

SOURCE OF $NH_3$—Normal autoclave cyanamide ammonia

DATE—Week of March 1 to 8, 1918

GAUZE TEMPERATURE—As corrected for optical measurements, always between 790° C. to 870° C.

SIZE OF GAUZE—13 in. × 27 in.; exposed surface 12 in. × 24 in., Landis type

| Total Cu. Ft. Gas per Min. | Vol. $NH_3$ Per cent | Wt. $NH_3$ Per cent | Lbs. $NH_3$ per Oz. Pt per Day | Efficiency Per cent |
|---|---|---|---|---|
| 40–46 | 9.61 | 5.98 | 53.6 | 79.7 |
| 40–46 | 9.65 | 5.99 | 53.9 | 84.5 |
| 40–46 | 9.56 | 5.92 | 53.4 | 87.5 |
| 40–46 | 8.64 | 5.34 | 48.5 | 81.9 |
| 40–46 | 8.68 | 5.35 | 48.5 | 84.8 |
| 40–46 | 8.66 | 5.34 | 48.5 | 84.0 |
| 40–46 | 9.74 | 6.03 | 54.4 | 65.2 |
| 40–46 | 9.71 | 6.02 | 54.3 | 67.0 |
| 40–46 | 9.66 | 6.00 | 53.9 | 85.2 |
| 40–46 | 10.87 | 6.79 | 60.6 | 82.9 |
| 40–46 | 10.98 | 6.86 | 61.4 | 83.3 |
| 40–46 | 9.70 | 6.02 | 54.2 | 87.8 |
| 40–46 | 9.84 | 6.11 | 55.0 | 86.4 |
| 40–46 | 9.80 | 6.09 | 54.7 | 83.4 |
| 40–46 | 8.86 | 5.48 | 49.5 | 79.3 |
| 40–46 | 9.48 | 5.89 | 53.0 | 79.9 |
| 40–46 | 9.40 | 5.83 | 52.5 | 78.2 |
| 40–46 | 8.82 | 5.46 | 49.6 | 78.3 |
| 40–46 | 9.80 | 6.09 | 54.7 | 80.1 |

The above tests were made on two different converters. This same state of erratic results existed for the several succeeding weeks. Such a state of affairs had not been disclosed by previous workers.

A commercial type of ammonia gas existed which caused a serious drop in the oxidation efficiencies of a single electrically heated platinum gauze and which destroyed the catalytic activity of a nonheated platinum multi-layer gauze. An examination of a platinum gauze which had been used in the oxidation of normal autoclave cyanamide ammonia disclosed a very marked contrast to a similar gauze which had served only on high-grade coke oven ammonia. A gauze which has been used in the oxidation of a high grade of coke oven ammonia exhibits a uniformly gray sprouted upper surface. The platinum which has served in the oxidation of cyanamide ammonia presents a multiplicity of shining or sparkling masses all over the sprouted surfaces. These observations as to the relative differences were made for the first time on February 28, 1918, when the first tests of the multi-layer type of converter upon cyanamide ammonia were made. A microscopic examination of the two different types of gauze disclosed the fact that the sparkling masses on the gauze surface first appeared in the form of long crystal-like formations, and that these developed into a sort of skin over the sprouts. The preliminary examination indicated a sort of sintering of the platinum sprouts first formed.

Such observations as the above clearly indicated the necessity of rigidly defining the composition of the ammonia gas which was to be subject to oxidation. It must be noted that the cyanamide ammonia which was being produced at this period was the result of an abnormal war-time overproduction. Poor grades, as well as high, of lime nitrogen were used in the autoclaves, and it is recognized that the tests were made at an unusual period. Nevertheless, the facts were established, and another apparently very important variable had been discovered. Were there constituents in ammonia gas from other sources, such as the coke oven aqua, which accounted for the occasional inconsistencies?

A test with the same multi-layer platinum gauze which failed to function on cyanamide ammonia was made in a similar type of converter upon $NH_3$ from high-grade coke oven aqua on April 25 to May 18, 1918. The previously mentioned article by Dr. C. L. Parsons has given these particular data in full. It was evident that the same multi-layer gauze and type of converter which failed entirely on cyanamide ammonia yielded an average commercial oxidation conversion of 90.7 per cent at a capacity of approximately 70 lbs. of $NH_3$ oxidized per oz. of platinum per day at about 780° C. to 850° C. catalyst temperature.

The interesting feature of the comparison test upon coke oven aqua ammonia arose from the observation that a pure platinum gauze, which had been rendered quite inactive upon cyanamide gas, recovered its full capacity and efficiency of conversion, on a commercial scale, within a short time after operating on $NH_3$ produced from high-grade coke oven aqua.

PHOSPHINE INFLUENCE—Many hasty investigations were begun by several parties in an examination of the possible gas constituents of cyanamide ammonia or their effects. At this time there was practically no information available as to the nature of impurities in either cyanamide ammonia gas or in ammonia-air mixtures, as produced from poor grades of coke oven aqua.

The investigators of the Nitrate Division were misled for a short time by the presence of excessive amounts of acetylene within the normal autoclave cyanamide ammonia gas. The erroneous conclusions were soon checked. It was found possible to add acetylene from a cylinder to the ammonia-air-gas mixture without causing any serious disturbance, other than an increased temperature, upon the multi-layer nonheated gauze. This increase in the gauze temperature was a very logical effect after a consideration of the great calorific value of acetylene. Rather good evidence indicated that the troublesome constituent in the cyanamide ammonia was some form of a phosphorus compound. Whether the particular catalyst poison was phosphine has not as yet been definitely established. Lieut. C. F. Brush, Jr., was transferred from the cyanamide ammonia oxidation plant to the coke oven ammonia oxidation plant in order to work on the effect of adding phosphorus compounds to the gas entering the commercial sized cylindrical multi-layer converter which was operating on coke oven ammonia. The commercial data secured by Lieutenant Brush from June 19 to 23, 1918, while using a cylindrical multi-layer gauze, and adding varying amounts of phosphine, may be summarized in Table 7. It was observed that platinum which had been poisoned by the phosphine could be brought back to its normal operation and physical conditions within a short time. This depended upon the degree it had been poisoned and the temperature of the gauze during the succeeding oxidation with the coke oven ammonia. A laboratory series of experiments along these lines was also made by G. B. Taylor and J. H. Capps, of the Bureau of Mines, and their data were published at a later date.[1] It should be noted that the phosphine which was used in the commercial studies by Lieutenant Brush was carefully prepared by him from C. P. chemicals.

TABLE 7

TYPE OF CONVERTER—Cylindrical 9 in. × 12 in. multi-layer (4) gauze in continuous operation

PHOSPHINE CONTENT—The absolute $PH_3$ content cannot be guaranteed, but the figures are very close approximations

SOURCE OF $NH_3$—High-grade coke oven aqua

| DATE 1918 | | Total Cu. Ft. Gas per Min. | Approx. Lbs. $NH_3$ per Oz. Pt per Day | Vol. $NH_3$ Per cent | P. p. m. of $PH_3$ | Oxidation Efficiency Per cent |
|---|---|---|---|---|---|---|
| June 10 | | 204 | 78.8 | 10.30 | None | 92.6[1] |
| | | 203 | 76.1 | 10.14 | None | 94.1[1] |
| June 11 | | 203 | 75.7 | 10.11 | None | 93.4[1] |
| | | 200 | 80.2 | 10.70 | None | 93.6[1] |
| June 14 | | 201 | 72.8 | 9.67 | None | 97.9[1] |
| | | 201 | 79.5 | 10.60 | None | 90.8 |
| | | 201 | 80.2 | 10.70 | None | 90.4 |
| June 15 | | 200 | 73.2 | 9.70 | None | 90.5[1] |
| June 19 | (2:20 P.M.) | Began adding phosphine | | | | |
| | (4:20 P.M.) | 200 | 73.5 | 9.81 | 1 in 10,000,000 | 59.1[1] |
| June 20 | (11:45 A.M.) | 200 | 80.2 | 10.71 | None | 94.6[1] |
| | (2:30 P.M.) | Began adding phosphine | | | | |
| | (2:45 P.M.) | 200 | 76.5 | 10.20 | 1 in 10,000,000 | 58.5[1] |
| | (4:15 P.M.) | 200 | 76.5 | 10.17 | 1 in 10,000,000 | 57.7[1] |
| | (6:00 P.M.) | Phosphine shut off | | | | |
| | (6:10 P.M.) | 200 | 78.4 | 10.45 | None | 86.3[1] |
| June 22 | (12:40 P.M.) | 200 | 76.1 | 10.33 | None | 90.5[1] |
| | (1:00 P.M.) | Began adding phosphine | | | | |
| | (3:12 P.M.) | 200 | 76.1 | 10.33 | 1 in 50,000,000 | 77.4[1] |

[1] Refers to an average of two simultaneous determinations.

Qualitative tests showed that when one part $PH_3$ per million of mix was used large inactive areas were formed. No inactive spots were formed in the above use of one part of $PH_3$ in ten million of mix.

However, after a gauze had been subjected to one part of $PH_3$ per million of mix, the subsequent addition of one part of $PH_3$ per ten million of mix caused the formation of inactive spots. This certainly indicated the quantitative action of the phosphine poison and showed the limitation to the use of such a type of catalyst for a normal autoclave cyanamide gas which varies in the total phosphorus content from hour to hour. For instance, the first few minutes of supply of ammonia produced by an autoclave steaming must contain the larger bulk of acetylene and phosphine (approximately 90 per cent).

The influence of the addition of small traces of phosphine upon the commercial oxidation of ammonia as obtained from coke oven aqua was most conclusive.

Although no absolutely ultimate analysis could be secured upon the cyanamide gas, it was known that the $NH_3$ gas leaving the cyanamide autoclaves contained distinct amounts of acetylene, phosphorus compounds (some of which reacted completely like phosphine), complex sulfur compounds, etc. To say the least, the normal cyanamide ammonia gas was a complex mixture, but the amounts of these impurities were exceedingly small. A more or less elaborate study of the situation was then begun by the members of the technical staff of the American Cyanamid Company. Simple commercial methods were developed for decreasing the content of phosphorus compounds within the cyanamide gas mixture. The test at U. S. Nitrate Plant No. 2, which has been mentioned in the article by Dr. Landis,[1] was fortunately conducted after certain of the above improvements in the autoclave operations had been made. The average 10 per cent ammonia-air mixture from the autoclave ammonia, as operated prior to June 1918, was generated from an ammonia gas containing from 50 to 100 parts of total phosphorus, expressed as phosphine, per million parts of ammonia. Reports indicate that this same ammonia probably contained from 30 to 80 parts of combined sulfur, as sulfur, per million of $NH_3$, and from 0.3 to 0.5 per cent of acetylene by volume. The improvements as made with the U. S. Nitrate Plant No. 2 installation in autoclave operation decreased the total phosphorus to from 2 to 8 parts of phosphorus, as phosphine, per million. This is certainly a distinct decrease, particularly as applied to a 10 per cent $NH_3$ mixture.

It is also most interesting to note that at a later date U. S. Patent 1,296,820 was granted to Dr. Landis, covering the blowing of air, or other inert gas, through a slurry of water and lime nitrogen to remove such impurities as acetylene and phosphine.

The records of the operations on the oxidation of normal cyanamide ammonia from February 1918 to June 1918 established facts which have been exceedingly helpful in advancing the general knowledge in the field of ammonia oxidation as a whole, and particularly as applied to cyanamide ammonia. There is still a great deal of interesting research that can be conducted along these lines. Even to-day no method has been established for quantitatively separating and determining the various small amounts of impurities within the cyanamide ammonia gas. As a result, a synthetic method of study was adopted for determining the influence of each separate constituent of cyanamide ammonia. Experimental data have been secured by other investigators in this field upon a gas mixture which had been subjected to a partial purification through the intermediate stage of the production of aqua ammonia. When an ammonia-air-gas mixture is produced from this so-called cyanamide aqua it is reported to eliminate only about 50 to 75 per cent of the total phosphorus. The relative distribution of the various phosphorus compounds has not been determined. As no method has been developed for distinguishing the amount of phosphorus present as phosphine and that present in complex ammoniacal or organic combinations, it is most dangerous to draw too rigid conclusions as to the meaning of such tests, or the action of a platinum gauze in the presence of such compounds. Up to the present time only the total phosphorus has been determined in the ammonia-gas mixtures. The facts have shown that exceedingly small amounts of phosphine exert a distinct poisonous action upon the platinum catalyst. Whether all phosphorus compounds react in the same manner is still an unsolved problem.

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[1] THIS JOURNAL, 10 (1918), 459; 11 (1919), 27.

[1] *Chem. & Met. Eng.*, 20 (1919), 476.

Investigations were being conducted upon these various problems at the time of the signing of the armistice, but these have never been completed. It may be said that practically the whole field of catalytic poisons, as applied to the oxidation of all types of commercial ammonia, still remains essentially unsolved. The incomplete investigation of the phosphine factor as carried on in the oxidation laboratories at U. S. Nitrate Plant No. 1 had indicated that phosphine in even exceedingly small amounts reacts with the surface of the platinum gauze to form possibly more than one compound. At low temperature, or from 400° C. to 575° C., there is every indication of the formation of platinum phosphide. The stability of this compound in the presence of ammonia-air mixtures is limited to a certain temperature range. The phosphide is apparently oxidized to pyrophosphate in the presence of air. By a careful control of the temperature conditions it was found possible to increase the gauze temperature to such a point as to exceed the temperature of decomposition of these compounds. A laboratory size converter was utilized in the study of the temperature-phosphine relationships. It was found possible to use ammonia-air mixtures, containing much higher quantities of phosphine than corresponds to the total phosphorus of autoclave cyanamide gas mixtures, without any apparent poisonous actions. The operations at U. S. Nitrate Plant No. 2 were discontinued just as plans were being made to test this out on a large scale. All preliminary indications pointed to the fact that certain of the phosphorus compounds within the cyanamide gas mixture reacted with the platinum to form well-established compounds. These compounds appeared to be decomposed above a certain maximum temperature. By the use of a properly adjusted platinum catalyst temperature it should be possible to prevent the formation of these compounds and thus eliminate the poisonous action. It is unfortunate that this work could not have been continued on a semi-commercial development. It seems as if the stabilizing action of the electrical heat upon a single platinum gauze is possibly a result of continually maintaining the gauze temperature above a certain minimum as demanded by the above-suggested reactions. The method of determining the exact gauze temperature for a single layer of catalyst, by means of an optical pyrometer, is unquestionably quite inaccurate. The pyrometer cannot be focused on the single wires without introducing the large error of the colder spaces between the wires. The uses of thermocouples are limited because of the activations and resultant inconstancy of such.

In view of the possibility that all grades of ammonia might have to be utilized in another period of emergency it seems as if this whole problem of poisons as applied to cyanamide gas mixtures should be thoroughly worked out. A very large amount of preliminary data upon the oxidation of cyanamide ammonia has been secured. Only a very brief synopsis of this is given above. Future investigations will meet success only after developing quantitative methods of analysis as applied to the specific problem. A complete micrographic study will also be required.

### COKE OVEN AQUA IMPURITIES

Almost simultaneously with the above experience with cyanamide ammonia, it was learned that all grades of coke oven aqua did not perform well with a non-externally heated type of catalyst.

The original experimental data upon the utilization of nonelectrically heated platinum catalysts for the oxidation of ammonia had been conducted with a high grade of coke oven aqua. While the exact composition of the impurities in the so-called Grade A aqua was known to vary within certain limits, this variation apparently had involved no serious commercial troubles. A certain amount of the so-called R & H, or B, grade of aqua had been used, with apparent success, in the work by the Semet-Solvay Company. This second-grade quality of liquor was utilized in the initial operations at the oxidation unit of U. S. Nitrate Plant No. 1. Analysis of a rather high-grade R & H aqua shows it to consist of:

| | |
|---|---|
| Per cent $NH_3$ | 29.53 per cent |
| $H_2S$ | 0.00 g. per liter |
| $CO_2$ | 0.06 g. per liter |
| Pyridine | 0.11 g. per liter |
| Organic | 100 cc. of liquor takes 114 cc. *N*/100 $KMnO_4$ |
| Naphthalene | 0.084 g. per liter or 0.0095 per cent |
| Soluble tar | 0.037 per cent |

This represents an exceptionally high grade of the B liquor, as the normal Grade B liquor has an organic number of more nearly 200.

In a Grade A liquor the organic matter, naphthalene, and soluble tar content is approximately 50 per cent of the above. For instance, the typical Grade A aqua shows:

| | |
|---|---|
| $NH_3$ | 25–28 per cent |
| $H_2S$ | 0.00 g. per liter |
| $CO_2$ | Never over 0.50 g. per liter |
| Pyridine | Less than 0.1 g. per liter |
| Organic | 100 cc. of liquor must take less than 50 cc. *N*/100 $KMnO_4$ |
| Naphthalene | Less than 0.01 g. per liter |

In view of the fact that these last-mentioned differences are small, and since, at that time, the cost of Grade A liquor was 5 cents per pound of $NH_3$ more than a Grade B material, it was a matter of economics to utilize the Grade B liquor. It is quite clear that with this difference in the $NH_3$ cost of the two grades of liquor it would only be necessary to obtain a 75 per cent conversion with the B liquor to compete with a 100 per cent conversion on the A liquor.

Prior to this time, the matter of the gas composition and the distribution of the impurities of the aqua into the ammonia-air mixture had received but meager attention. It was learned that the large portion of the pyridine, naphthalene and soluble tar was removed with the ammonia when blowing air through a stripping column such as was used for the production of the ammonia-air mixtures from aqua ammonia.

However, the effect of a substance like naphthalene ($C_{10}H_8$) upon the oxygen concentration is very important when using air as the source of the oxygen, A comparison of the oxidation reactions of ammonia and naphthalene shows that the oxidation of one per cent of naphthalene by volume requires roughly the same volume of oxygen as the oxidation of 10 per cent ammonia. Since both of these reactions occur at the platinum gauze it is quite important that information be secured as to the nature of the gas mixture. It will be noted that the naphthalene content of an ammonia-air mixture produced from Grade B aqua is distinctly high, and thus greatly decreases the active oxygen concentration at the catalyst.

### PREHEATED AIR DEVELOPMENT

The result secured by the use of the secondary grade of coke oven aqua at the oxidation unit of U. S. Nitrate Plant No. 1, over a period of several weeks, was considerably below the standard previously secured on the test converter at Syracuse, N. Y., when operating on somewhat better grades of aqua. The only apparent variable which had been altered from the previous commercial tests was that of gas composition. The data of Table 8, using the cylindrical four-layer nonexternally heated gauze, are typical. In all of the work after June 1918 the modified gravimetric analytical method, similar to that described by Captain Gaillard[1] was used.

TABLE 8

OPERATION—At Oxidation Unit of U. S. N. P. No. 1

SOURCE OF $NH_3$—Grade B coke oven ammonia (composition given above)

DATE—April 4, 1919

CATALYST—Cylindrical 4-layer 0.0026 in. wire, 9 in. diameter × 10 in. high; 13.7 oz.

ANALYSTS—Montilion, Newton, Kennedy, and Coe

| HOUR | Cu. Ft. Gas per Min. | Vol. $NH_3$ Per cent | Lbs. $NH_3$ per Day per Oz. Pt | Gauze Temp. Corr. (as per B. of S. Meas.) | Conversion Per cent |
|---|---|---|---|---|---|
| 9.58 | 113 | 10.6 | 53.8 | 820 | 86.1 |
| 9.58 | 113 | 10.6 | 53.8 | 820 | 86.1 |
| 10.50 | 122 | 12.3 | 67.8 | 912 | 90.7 |
| 10.50 | 122 | 12.3 | 67.8 | 912 | 92.2 |
| 11.50 | 112 | 11.6 | 58.7 | 890 | 89.0 |
| 11.50 | 112 | 11.3 | 57.2 | 890 | 87.3 |
| 12.30 | 112 | 11.7 | 59.2 | 912 | 90.2 |
| 12.30 | 112 | 11.7 | 59.2 | 912 | 90.7 |
| 4.25 | 112 | 9.0 | 45.6 | 780 | 87.1 |
| 4.25 | 112 | 9.1 | 45.6 | 780 | 87.3 |
| 5.45 | 117 | 11.4 | 60.2 | 925 | 86.1 |
| 5.45 | 117 | 11.4 | 60.2 | 925 | 88.6 |
| 6.40 | 112 | 11.2 | 56.6 | 912 | 88.6 |
| 6.40 | 112 | 11.2 | 56.6 | 912 | 89.4 |
| 7.15 | 100 | 10.4 | 47.1 | 890 | 88.0 |
| 7.15 | 100 | 10.4 | 47.1 | 890 | 90.3 |
| 8.30 | 152 | 9.50 | 65.4 | 780 | 84.0 |
| 8.30 | 152 | 9.47 | 65.4 | 780 | 85.7 |
| 8.30 | 152 | 9.45 | 65.4 | 780 | 86.2 |
| 8.30 | 152 | 9.45 | 65.4 | 780 | 87.6 |
| 10.10 | 168 | 10.50 | 80.0 | 870 | 85.6 |
| 10.10 | 168 | 10.65 | 81.0 | 870 | 82.8 |
| 10.35 | 152 | 10.5 | 72.1 | 850 | 84.8 |
| 10.35 | 152 | 10.4 | 72.1 | 850 | 87.3 |

The temperature corrections used in all this work for the modified Morse optical pyrometer observed readings are given in the curve of Fig. 3. It must be noted that the data as secured in Table 8 represent ideal commercial operation and much care was employed in maintaining good operating conditions. A very large amount of data has been accumulated on the same converter and gauze and with a slightly poorer Grade B of aqua which gave averages nearer to 85 per cent oxidation efficiency. However, with a Grade B coke oven aqua, of an organic number around 114, the above is quite characteristic. The poisonous action, when using a multi-layer catalyst, begins to increase in activity as the organic content of the coke oven aqua increases. The variation in the gauze action was distinctly evident. Similar variations had been encountered with the electrically heated single gauze on cyanamide ammonia gas. It is not necessary to cite more data to show the limitations of a nonexternally heated multi-layer gauze catalyst for the use of other than very pure $NH_3$. Many hundred commercial efficiency determinations have been secured upon the impure grades in an effort to solve the problem, but to no avail.

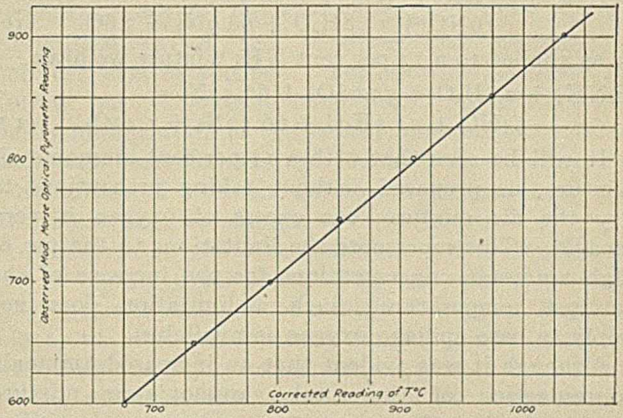

FIG. 3

The indications of all the work upon a multi-layer type of catalyst, as applied to less pure grades of $NH_3$, pointed to the great desirability of oxidation at the highest possible temperatures. The increased catalyst temperature apparently selectively favors the velocity of the nitrogen oxide formation reaction. In other words, when oxidizing ordinary commercial grades of ammonia the relationship between time of catalyst contact and speed of reaction is distinctly important. After a thorough realization of the vast importance of the above-mentioned factors, attempts were made to speed up the velocity of the nitrogen oxide formation reaction and thus greatly decrease the catalyst contact time.

While Dr. Landis[1] has considered "the experiments were critically reviewed and it was concluded that the hot gauze radiated heat to the oncoming ammonia-air mixture and decomposed some of the ammonia" it did not seem physically possible that the oncoming gas could be heated by radiated heat. However, the ready catalysis of ammonia-air mixtures to nitrogen by contact with hot iron tubes, etc., had been recognized. While silica tubes have but little influence upon the catalytic decomposition of ammonia-air mixtures, such a fragile and nonconducting material does not lend itself particularly well to a commercial heat exchange. Aluminum exchanger tubes would unquestionably soften or melt at the temperatures employed. From this standpoint, the use of a heat exchanger on the oncoming ammonia-air mixture seemed distinctly undesirable as a means of increasing the gauze temperature.

The two most obvious methods for increasing the

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[1] *Loc. cit.*

[1] *Chem. & Met. Eng.*, **20** (1919), 472.

temperature of the catalyst, without the use of external energy, were operation with a higher ammonia concentration, or else the use of a heat exchanger upon the oncoming air, and mixing this with the required ammonia just prior to the catalyst entrance.

When using air as the source of the oxygen we can consider the reaction at 800° as

$$4NH_3 + 5O_2 + 18.8\ N_2 + Pt = 4NO + 18.8\ N_2 + 6H_2O + Pt + 211{,}750\text{ g. cals.} \quad (15)$$

As applied to a 10 per cent $NH_3$ commercial gas mixture we have

$$10NH_3 + 2.8H_2O + 18.3O_2 + 68.9N_2 = 10NO + 17.8H_2O + 68.9N_2 + 5.8O_2 \quad (16)$$

or as applied to a 13 per cent $NH_3$ mixture we have

$$13NH_3 + 2.8H_2O + 17.68O_2 + 66.52N_2 = 13NO + 22.3H_2O + 66.52N_2 + 1.43O_2 \quad (17)$$

It will be seen that with a 13 per cent ammonia-air mixture, as prepared without taking precautions to dry the air mixture, the excess of oxygen is very meager. This represents the limitations to the use of high ammonia concentrations for the increase of the catalyst temperature. Such a limitation does not apply in case spillage oxygen is available.

Although it was evident that an increased ammonia concentration of the intake ammonia-air mixture would increase the gauze temperature, a maximum in the efficiency-temperature curve would result when an ammonia-air mixture which yielded insufficient excess oxygen was obtained. The typical commercial data upon 12 per cent $NH_3$ mixtures are given in Table 9. These data were secured on the same Grade B aqua as that of Table 8 and represent the comparison to the operation at lower catalyst temperatures.

TABLE 9

OPERATION—At Oxidation Unit of U. S. N. P. No. 1

SOURCE OF $NH_3$—Grade B coke oven aqua

DATE—April 8, 1919

CATALYST—Cylindrical 4-layer, 0.003 in. wire, 9 in. diameter × 11 in. high; 21.5 oz.

ANALYSTS—Montillon, Newton, Kennedy, and Coe

| HOUR | Cu. Ft. Gas per Min. | Vol. $NH_3$ Per cent | Lbs. $NH_3$ per Day per Oz. Pt | Gauze Temp. Corrected | Conversion Per cent |
|---|---|---|---|---|---|
| 9.50 | 150 | 11.1 | 47.5 | 915 | 85.7 |
| 9.50 | 150 | 11.1 | 47.5 | 915 | 86.2 |
| 10.35 | 165 | 11.5 | 54.6 | 925 | 88.9 |
| 10.35 | 165 | 11.5 | 54.6 | 925 | 87.8 |
| 12.00 | 150 | 12.5 | 54.3 | 990 | 87.0 |
| 12.00 | 150 | 12.5 | 54.3 | 990 | 87.6 |
| 1.00 | 145 | 12.6 | 52.6 | 990 | 90.4 |
| 1.00 | 145 | 12.6 | 52.6 | 990 | 88.6 |
| 2.00 | 145 | 12.3 | 51.4 | 980 | 88.7 |
| 2.00 | 145 | 12.3 | 51.4 | 980 | 89.3 |
| 3.15 | 145 | 12.5 | 52.2 | 995 | 90.6 |
| 3.15 | 145 | 12.4 | 52.2 | 995 | 88.6 |
| 4.15 | 145 | 13.3 | 55.5 | 1030 | 86.9 |
| 4.15 | 145 | 13.4 | 55.5 | 1030 | 89.5 |
| 5.20 | 120 | 13.5 | 56.2 | .. | 88.2 |
| 5.20 | 120 | 13.5 | 56.2 | .. | 89.8 |
| 6.25 | 122 | 12.4 | 43.5 | 995 | 91.9 |
| 6.25 | 122 | 12.3 | 43.5 | 995 | 92.4 |
| 7.15 | 122 | 11.7 | 41.2 | 975 | 91.8 |
| 7.15 | 122 | 11.7 | 41.2 | 975 | .. |
| 8.19 | 145 | 12.1 | 50.5 | 980 | 90.9 |
| 8.19 | 145 | 12.0 | 50.5 | 980 | 90.5 |
| 8.50 | 145 | 12.1 | 50.2 | 995 | 90.2 |
| 8.50 | 145 | 12.1 | 50.2 | 995 | 89.0 |
| 9.15 | 152 | 12.05 | 50.2 | 915 | 92.2 |
| 9.15 | 152 | 12.00 | 50.2 | 915 | 91.2 |

It is quite evident that there was less variation in the operation when the high ammonias and temperatures were employed. A distinct advantage results from the oxidation of high concentrations of ammonia, since a correspondingly high NO gas mixture results. The absorption of the resultant oxides becomes much more efficient. An important limiting factor to the use of any nonexternally heated multilayer type of converter lies in the lack of an adequate temperature control. Such a control as is secured by auxiliary electrical energy, or a suitable heat exchanger, is distinctly a commercial advantage. There was still such an opportunity for improvement that it was decided to operate a heat exchanger of commercial size and thus obtain the corresponding data as to the selective temperature-reaction velocity effects.

A heat exchanger was constructed at the Oxidation Unit of U. S. Nitrate Plant No. 1 out of standard 12-in. pipe and fittings which were readily available. The interchanger casing was 14.5 ft. long by 12 in. diameter and contained 19 standard 2-in. boiler tubes. The 144 sq. ft. of steel tubes did not present sufficient heat transfer surface. However, sufficient data were secured during the plant operations for the design of a proper exchanger. A by-pass is also an essential requirement.

The only available source of ammonia was in the form of Grade B coke oven liquor. The apparatus at Plant No. 1, for the production of ammonia-air mixtures from such, consisted of a countercurrent stripping column. Ammonia-air mixtures of varying $NH_3$ content could be produced at will, depending upon the feed of 29 per cent liquor into the top of the column, and the flow of air and temperature at the base of the same. It was realized that separate mains of air and $NH_3$ would be far more desirable than the above system. Future equipments should be thus installed.

An approximately 30 per cent $NH_3$-70 per cent air mixture was continuously generated in the ammonia column. Air was allowed to pass through the exchanger tubes, while the hot NO gases from the oxidation reaction surrounded the tubes; the air which was thus heated through proper interchange from the gases of the reaction, and the cold ammonia air were allowed to mix within a heat-insulated, 6-in. aluminum pipe just prior to the entrance to the catalyzer holder. A silica-lined iron pipe with a silica baffle plate would be preferable for this mixing chamber. Decomposition of the mixture was thus prevented. This is due to the high velocity within the line and the short period of contact of the hot ammonia-air mixture with any material prior to the gauze entrance. A general tabulation of the average data on the heat exchanger is given in Table 10.

TABLE 10

| APPLIANCE | Total Cu. Ft. Gas per Min. | TEMPERATURE ° C. |
|---|---|---|
| Air intake to tubes | 175 | At 30 |
| Heated air exit from tubes | 504 | At approx. 500 |
| Hot NO mix outside tubes entering | 903 | 800 |
| Cooled NO mix outside tubes leaving | ... | 450 |
| 30 per cent $NH_3$-70 per cent air entering mixer | 80 | 30 |
| Heated 10 per cent $NH_3$-90 per cent air | ... | 300 |
| Heated mix at cylinder entrance | ... | 650 |
| Gauze | ... | 1025 |

Since the 144 sq. ft. of exchange tube surface served to cool the exit NO-$H_2O$ gas mixture only to 450°, it is quite evident that a transfer surface of 200 sq. ft. should be provided for a converter oxidizing 1800 lbs. of $NH_3$ per day. It is undoubtedly safe to cool the hot gases from the temperature at which they leave the gauze to 140° C. Greater cooling than this may lead to troublesome condensation within the exchanger.

By means of a by-pass from the heat exchanger it is possible to control the temperatures of oxidation by the above modified method.

A continuous 24-hr.-per-day test was conducted upon this modified converter before its upper working capacities had been established. A total of 121 efficiency determinations were taken over the whole period of the test. A 4-layer platinum gauze of 0.003 in. diameter wire and 80 mesh, in the same type of cylindrical multi-layer converters as used on the previous-mentioned test, gave a test average of 95.1 per cent oxidation efficiency on 9.88 per cent $NH_3$ gas mixtures at a rate of 2.1 cu. ft. of $NH_3$ per min. per sq. ft. of exposed gauze surface. There were no preliminary arrangements for the above-mentioned test, since it was conducted at an unexpectedly early time due to a rapidly diminishing supply of Grade B aqua. The gauze had been in continuous service prior to the test. The 121 efficiency determinations exhibited consistent agreements and the whole plant operation was practically automatic. Since this test chanced to be carried out on an 0.003 in. diameter wire and 80-mesh gauze, with a total exposed surface in the four layers of 8.6 sq. ft. (*i. e.*, 2.3 sq. ft. per layer), only 60.0 lbs. $NH_3$ per oz. of platinum per day were oxidized. It does not seem necessary to give a tabulation of these 121 efficiency determinations. It is interesting to note that the first operations on the heat interchanger for the air intake utilized a platinum catalyst of four layers of 0.0025 in. diameter wire at 80 mesh. Equally as high conversions were obtained with the same rate of gas flow as when using 0.003 in. diameter wire gauze. The yield per ounce of platinum is thus considerably increased over any previously obtained in the United States.

The use of the heated gas mixture on a 10 per cent $NH_3$ gas increased the 4-layer cylindrical gauze catalyst temperature a total of approximately 250° C. The speed of the NO formation reaction is thus greatly accelerated, and with much less contact time of the gas molecules with the platinum surface the period for the nitrogen formation reaction is not sufficient. By decreasing the contact time of the gas with the catalyzer surface and through a proper proportioning of temperature, the time for the preferential oxidation of ammonia to the oxides of nitrogen, rather than to the ultimate nitrogen, is secured. The heat is obtained from the gases produced in the reaction, and hence no external energy is utilized. It had always been necessary to cool these gases prior to their absorption in water, hence the auxiliary hot nitric oxide to air exchanger served a double purpose. By mixing the heated air with the cold ammonia gas, or rich ammonia-air mixture, just prior to the catalyst entrance and within an aluminum, or preferably silica-lined iron pipe, no decomposition or pre-catalysis to nitrogen results.

A U. S. Patent, 987,375, by Kaiser covers the use of externally heated air in connection with this work. Dr. Landis[1] has written of the Kaiser method as follows: "The direct heating scheme used by Kaiser required the combustion of additional fuel and seemed to have no apparent advantages of any sort over the Ostwald system." The commercial developments at the Oxidation Unit of U. S. Nitrate Plant No. 1 worked up to the use of the air exchanger on the catalyst chamber step by step. The improvements over the work of Kaiser consisted not only in utilizing the exchange of heat from the hot gaseous products of the oxidation reaction, but the conditions to prevent predecomposition of the resultant hot ammonia-air mixture were established. The previous failure of the former heat exchangers have been due to the necessarily long contact of the heated ammonia-air mixture with the heat-exchanging surface. A resultant decomposition of a certain amount of the ammonia prior to its entrance to the gauze must follow

An increased gauze temperature can be secured for low ammonia concentrations by the above methods. This permits the use of sufficient oxygen, from air alone, to yield much more efficient oxidation. Not only does the higher temperature increase the velocity of the oxidation reactions, but the increased oxygen content of the lower ammonia mixtures favors the nitrogen oxide formation reaction. Thus, we observe the tremendous interdependence of oxygen, temperature, and contact surface upon the speeds of the reactions under consideration. The importance of this extra amount of oxygen is particularly great for gas mixtures containing impurities in the form of complex molecules which are easily oxidized, such as naphthalene, soluble tars, phosphine, etc.

The work mentioned above demonstrated that a high efficiency of oxidation of ammonia could be secured by the use of a multi-layer type of gauze for poorer grades of ammonia. It has been possible to oxidize a good quality of Grade B coke oven ammonia with from 88 to 89 per cent conversions, when using a 12 per cent (by vol.) $NH_3$ mixture at the rate of 50 lbs. of $NH_3$ per oz. of platinum per day. The methods were so improved at the first tests as to secure 95 to 96 per cent oxidation with a minimum capacity of 60 lbs. of $NH_3$ per oz. of platinum.

### CAPACITY TESTS WITH AUXILIARY AIR EXCHANGER

It seemed advisable to attempt capacity tests upon the modified form of oxidation equipment. The supply of coke oven aqua at U. S. Nitrate Plant No. 1 was nearly exhausted, but the operations were sufficient to give an estimate as to the value of the improvements. Greater gas flows than given in the data of Table 11 could not be secured from the available equipment at the time of the tests. The data of Table 11 merely show that even to-day we have no information as to the upper capacity limit of the modified type of converter. The improvements are a distinct advantage as far as the conservation of platinum is concerned, for the platinum depreciation,

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[1] *Loc. cit.*, p. 474.

as compared to other operating costs, is an important item in the total operating charges. Not only have high commercial oxidation efficiencies been secured, but a great saving in platinum depreciation has resulted.

TABLE 11

OPERATION—At Oxidation Unit of U. S. N. P. No. 1
SOURCE OF $NH_3$—Grade B coke oven aqua
DATE—May 1, 1919
CATALYST—Cylindrical 4-layer gauze with heat exchanger
ANALYSTS—Montillon, Newton, Kennedy, and Coe

| | Cu. Ft. per Min. | | | | | |
|---|---|---|---|---|---|---|
| HOUR | AIR | Air-$NH_3$ Mix. | Total | Vol. $NH_3$ Per cent | Gauze Temp. ° C. | Conversion Per cent |
| 1.10 | 158 | 88 | 246 | 10.27 | 1005 | 95.5 |
| 1.15 | 166 | 89 | 255 | 9.90 | 995 | 95.5 |
| 1.25 | 166 | 90 | 256 | 10.20 | 1005 | 93.6 |
| 2.00 | 166 | 89 | 255 | 9.94 | 1010 | 94.6 |
| 2.20 | 166 | 91 | 257 | 10.33 | 1018 | 93.5 |
| 3.00 | 166 | 73 | 239 | 9.48 | 1025 | 97.5 |
| 3.30 | 171 | 79 | 250 | 10.15 | 1035 | 96.2 |
| 4.15 | 195 | 80 | 275 | 8.60 | 980 | 95.0 |
| 4.30 | 197 | 81 | 278 | 8.65 | 990 | 96.4 |
| 5.00 | 168 | 87 | 255 | 10.33 | 1050 | 94.4 |
| 5.30 | 171 | 90 | 261 | 10.31 | 1075 | 95.8 |

The data of Table 11 are averages of two determinations on simultaneous samples.

There was no assurance but that much greater gas flows could be oxidized. The highest capacities of Table 11 as applied to the oxidation of a Grade B coke oven ammonia by means of a 4-layer cylindrical gauze of 0.0026 in. wire and 80 mesh, show that a conversion of 95 per cent can be secured at the rate of 100 lbs. $NH_3$ per oz. of platinum per day, and a catalyst temperature of over 1000° C. This is essentially double the capacity and with 4 per cent higher conversions than secured on the tests of the single-layer electrically heated Landis type of converters at Plant No. 2.

As applied to the oxidation of ammonia for the 33,000 lb. $NH_3$ oxidation units at U. S. Nitrate Plant No. 1 it means a yearly saving of 481,800 lbs. of $NH_3$, provided high-grade $NH_3$ could be secured. Fifty per cent of the platinum requirements is also eliminated by the use of the heat exchanger. There would also have been an additional yearly saving of 5,694,000 k. w. h. alone in case the electrically heated, single-gauze type of converter had been adopted for use at U. S. Nitrate Plant No. 1. A figure for the saving on this size of plant, expressed in dollars and cents, when using the modified type of converter over the electrically heated form depends much upon the value of $NH_3$ and the cost of electrical energy. As a minimum, it represents a yearly operating saving of $100,000, and this can make or break the application of such a plant to ordinary commercial competition.

### REQUISITES AND LIMITATIONS OF A MODERN CATALYST

An outline of the development of the processes for the oxidation of ammonia by means of the oxygen of the air has been given step by step. While this article has been unduly long it must be admitted that many rather important details have still been omitted. Success with the cylindrical multi-layer gauze type of catalyst was not obtained until methods of mounting the four layers upon the cylindrical holder had been solved. While in theory a silica cylindrical holder may seem to prevent undue decomposition, and have all the other ideal characteristics, still in practice such a form of catalyst holder is very unpractical. A nickel holder, which is shown in Figs. 4 and 5, was developed at U. S. Nitrate Plant No. 1. Prior to the use of this type of holder serious troubles were encountered from the influence of the relative expansion effects of the platinum wire gauze, the clamping wire and the cylindrical gauze holder frame. Silica cylindrical holders with either platinum wire or Invar clamps failed to satisfy the demands for making a tight connection, at all temperatures, between the gauze catalyst and holder. When using the improved double ring clamp on the nickel cylinder and base, all the failures due to the gauze mounting were eliminated. A nickel-steel cylinder, which is protected by means of a silica tube of very slightly smaller outside diameter than the inside steel cylinder diameter, will make a better and more economical gauze holder than one of pure nickel. The protecting silica tube is to be recommended for all installations utilizing a preheated ammonia-air mixture, since nickel promotes a certain amount of predecomposition.

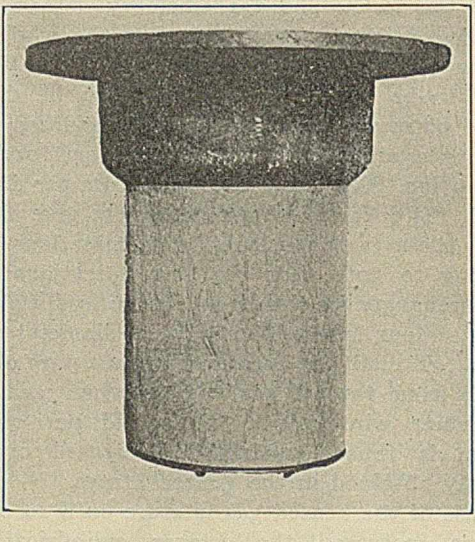

FIG. 4

While the cylindrical form of a 4-layer gauze catalyst was used in the commercial tests on heated intake mixtures with excellent success, nevertheless, the cylindrical form of platinum gauze as used to-day has certain limitations. The real feature of the gauze cylinder consists in the stability of the gauze temperature conditions which result from the radiations from the catalyst surfaces within the intake side of the platinum cylinder. This effect becomes clearly illustrated if a solid nickel cone is suspended within the inner zone of the cylinder. A series of tests was carried out at U. S. Nitrate Plant No. 1 as to the influence of various methods of gas distribution to the non-preheated cylindrical type of gauze. It was interesting to note when using a special tangential aluminum nozzle to deliver the oncoming gas, with a high velocity, tangentially to the surface of the gauze, that absolutely every trace of vibration on the gauze was eliminated. The same effect was produced when using preheated mixtures. When using the nonheated original type of cylindrical gauze catalyst, or a flat catalyst, it is very easy to observe waves and flickerings upon the gauze. The introduction of a nickel cone within the inner section of the cylinder caused a drop in the gauze temperature which could be detected by the eye. This was very obvious when a cone only half the total height of the gauze was employed. This served best to show the function of the radiations within the nonheated cylindrical gauze. Good oxidation results may be obtained upon most any form (flat, etc.) of platinum gauze catalyst on Grade A ammonia, provided it is installed within a nonconducting casing. However, the greater the uniformity of the gauze physical conditions, temperature, etc., the less the catalyst responds to occasional variations in operations.

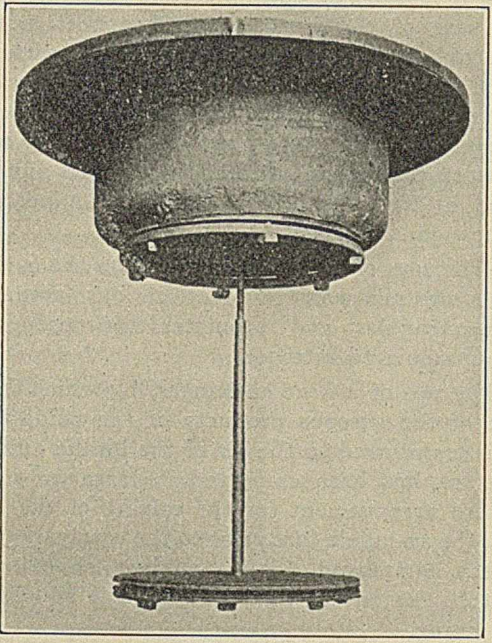

Fig. 5

The writer does not believe any catalyst can operate day in and day out with high commercial conversions without a flexible control of the catalyst temperature. This statement does not apply to C. P. ammonia-air mixtures. Yet it is more logical to oxidize commercial ammonia with a catalyst equipment which insures freedom from variations. The use of an electrically heated catalyst, or a heat exchanger of proper design, will solve the problem for the average grades of commercial ammonia. In view of the recent work it seems ridiculous to use electrical energy. As a matter of fact, the writer believes that the use of electrical energy as a means of securing gauze temperature should not be considered even if it could be secured gratis. The reasons for this opinion are based upon the conclusions derived from the series of commercial studies of the past year. The major functions of a preheated intake air mixture in the oxidation of ammonia are:

(1) The establishing of a high catalyst temperature in the presence of a distinct excess of oxygen. This means a high catalyst temperature for a low ammonia concentration.

(2) The correct proportioning of the gas velocity before and after the catalyst. The effect of a preheated gas mixture as a physical stabilizer to the catalyst is certainly an important feature. It is making enormous demands upon a gauze when a cold ammonia-air mixture is delivered to a thin layer of catalyst surface, which is heated to about 900° C. by the exothermic character of a reaction, to expect a high temperature in the gas phase and perfect gas distribution. The best results in this oxidation reaction are obtained when the temperature gradient is carefully adjusted. The preheated gas mixture should be delivered to the gauze at as high a temperature as possible and thereby decrease the otherwise abrupt volume expansion effects which are caused by the decided changes in temperature. It is the temperature of the gas phase which governs the reaction velocity.

The method of accomplishing these desirable features, without the pre-catalysis or decomposition of the ammonia prior to its entrance to the catalyst, was worked out in the commercial size units at U. S. Nitrate Plant No. 1. Nernst has studied the displacement of the equilibrium of the arc nitric oxide formation reaction along a temperature gradient. It is perhaps possible that the cooling may be in the order of 1000° per millimeter, and that the equilibrium corresponding to the temperature of each thin layer is rapidly adjusted. However, the interesting relationships were those existing between diffusion forces and reaction velocity. While the ammonia oxidation reaction may not be of the same magnitude, yet the relative effects of diffusion and reaction velocity must affect the stability conditions to a distinctly different degree, when a heated intake gas is delivered to the heated catalyst, than when a cold gas is used.

When using the cylindrical form of catalyst, it will be observed that there must be a definite ratio of diameter to height in order to secure the best gas distribution to the gauze. This is of particular importance when utilizing nonheated gas mixtures. These ratios have not as yet been well established. When using the preheated mixture the matter of distribution at the gauze does not become so important.

Unless the bottom section of the cylinder is protected with a silica cover there is an opportunity for a certain amount of decomposition. This bottom metallic plate also exerts a slight cooling effect upon the extreme edge of the gauze. In an effort to eliminate these objections the writer has made a mantle of a small platinum gauze similar to the familiar Welsbach gas mantle. A very good mantle can be formed by adjusting the height of the gauze to the diameter in such a manner as to enable the edges of one side to be doubled over and sewed together with a platinum wire. This form of platinum mantle exhibits a particularly delightful effect and there is also a distinct platinum saving over the cylindrical type. It will be very clear that in the use of a platinum mantle catalyst only one edge of a gauze is utilized in clamping it to the holder. With a flat gauze the four edges must be retained by a proper flange or clamping device. When using a 9-in. diameter cylinder with even the improved closed bottom plate and four layers of gauze, there is a protected surface of 113 sq. in. out of the total 1470 under the edges of the clamps. Thus, there is a platinum surface loss of practically 8 per cent, even when using a cylinder where only two edges of the gauze are covered with the clamps of the gauze holder. This loss is still greater in a flat installed gauze where four edges must be clamped.

The work which was conducted on a plant-size scale at U. S. Nitrate Plant No. 1 certainly has increased the working knowledge along the lines of ammonia oxidation. The general limitations of many designs of catalyzers have been determined and the relative importance of the large number of variables has been studied. The above paragraphs will serve to indicate only the more important features of the work. A form of platinum catalyst converter has been developed which will greatly excel all other present existing types, yet even this type can be excelled when an exact working theory of the true nature of the reaction has been established.

### SUMMARY

I—The influence of the more important factors involved in the oxidation of ammonia have been discussed.

II—It has been shown that the coördination of catalyst temperature, gas-phase temperature, oxygen concentration and catalyst contact time must be made with great care. The interdependence of these factors, when dealing with commercial grades of ammonia, has been briefly discussed. An expression of one factor in the absence of the others is meaningless.

III—The importance of the use of some form of controlled temperature regulation for the catalyst and intake gas mixture has been demonstrated. This may be accomplished in part by means of outside electrical energy, or in whole by a proper utilization of the heat of the oxidation reaction.

IV—The use of a nonexternally heated multi-layer platinum gauze catalyst results in a decided decrease in capacity and NO conversion efficiency over that obtained when using preheated air mixtures.

V—The use of electrical energy as a source of heat for the catalyst is not only extravagant, but it also does not satisfy the demands for sufficient gas temperature and distribution to the catalyst.

VI—A single-layer gauze catalyst is distinctly impractical.

VII—A decided economy of platinum will result by using the smallest area of space between the wires (large mesh) and the smallest diameter of wire consistent with fabrication costs. An iridium alloy with platinum can be used to secure sufficient ductility and tensile strength in the finer diameter wires. It is probably impractical to employ wires of much less than 0.0026 in. diameter. A mesh of at least 120 should be employed for a single-layer catalyst. The various layers of a multi-layer catalyst should not utilize the same diameter of wire and mesh of gauze. The use of a 0.0026-in. diameter wire and 120-mesh platinum (with small amounts of iridium) gauze in the form of a gas mantle has been recommended as a desirable catalyst. The minimum economical size of wire is limited by the sprouting effect and recrystallization of the platinum during catalysis and the resultant decrease in tensile strength. The use of a heat-conducting coarse mesh separator, such as a $^1/_4$-mesh, $^1/_{16}$-in. diameter platinum gauze, enables the utilization of far greater surfaces of platinum per unit height of a multi-layer gauze catalyst.

VIII—A method of platinum gauze activation without the use of electrical energy has been outlined. The use of a separated gauze layer and a coarse mesh platinum wire separator enables the activation of a new gauze when it is placed as the second layer of a multi-layer catalyst. Any form of conducting separator between the layers can be used to good advantage provided it does not protect too large a percentage of the new gauze surface.

IX—The use of a heat exchanger on the combined ammonia-air mixtures involves serious commercial operating troubles and promotes the pre-catalysis of the ammonia to nitrogen.

X—The use of a heat exchanger, by which the heat content of the gaseous products of the oxidation reaction is transferred to the air of the intake ammonia-air mixture, has been employed in large-scale operations. An arrangement for the mixing of the heated air with the ammonia just prior to the catalyst entrance has been employed. This mixing chamber and catalyst holder on the ammonia-air side should have a silica lining.

XI—The advantages in the use of the above described heat exchanger as employed in the oxidation of ammonia consist in:

(*a*) The preheating of the intake ammonia-air mixture without the decomposition of the intake gas constituents through pre-catalysis to nitrogen.

(*b*) A sufficiently increased catalyst temperature is secured whereby it becomes only slightly affected by commercial operating variations, or periodic poisons.

(*c*) A sufficiently high temperature in the gas phase cannot be obtained with the normal high gas velocities and resultant short periods of catalyst contact even when using electrically heated catalysts. The desirable feature of the whole oxidation reaction is the production of high reaction speeds or velocities for the short period of contact. The preheating of the ammonia-air mixture accomplishes this better than any other method. The waste heat of the oxidation reaction should be employed since the gaseous products have to be cooled prior to their absorption.

(*d*) The physical instability of the gauze is reduced to a minimum by the use of preheated mixtures. The sudden volume expansion changes caused by an excessive instantaneous temperature rise are prevented by the use of preheated mixtures. The catalyst holder design should be so made as to deliver the gases to the catalyst at as nearly the catalyst temperature as possible.

(*e*) The extending of the catalyst holder proper to a decided distance within the nonconducting chamber makes it possible to utilize the maximum radiation and conduction effects. This design applies to flat as well as cylindrical gauze installations.

XII—A form of commercial catalyst has been described which will oxidize at least 100 lbs. of $NH_3$ per day per ounce of 0.0026-in. diameter wire and 80-mesh platinum gauze at 95 to 96 per cent conversion to NO. It is probable that the capacity is even greater than these figures.

XIII—The influence of such poisons as naphthalene, soluble tar, phosphine, etc., have been studied. The action of the above-mentioned poisons can be minimized by the use of high oxygen concentrations with simultaneous high gas and catalyst temperatures and minimum times of catalyst contact. The poisoning by phosphine is of quite a different character than that of naphthalene. It appears that the one forms definite platinum compounds, while the other depletes the oxygen concentration. When using ordinary air as the source of oxygen it is accordingly essential to employ low ammonia concentrations with air mixtures.

XIV—The following facts have been considered in reference to the comparative estimates of the various factors:

| | |
|---|---|
| Cost of electrical energy at $0.004/k. w. h. per lb. $HNO_3$ (100 per cent) | $0.00071 |
| Cost of platinum loss by dusting of sprouts at $115.00 per oz. $HNO_3$ (100 per cent) | $0.00031 |
| Cost of 1 per cent drop in efficiency for $NH_3$ at $0.10 per lb. $HNO_3$ (100 per cent) | $0.0003 |

Average complete nitric acid charges for a whole oxidation plant:

| | |
|---|---|
| Power, steam, etc., per lb. $HNO_3$ (100 per cent) | $0.0013 |
| Operating labor, per lb. $HNO_3$ (100 per cent) | $0.0011 |
| Repairs, labor, per lb. $HNO_3$ (100 per cent) | $0.00036 |

XV—That type of appliance which meets with the greatest success commercially is the one which is most nearly automatic and foolproof. If a given type of converter, with or without a multi-layer gauze, and without a suitable heat exchanger, is susceptible to poisons, variations in operation, etc., it is destined to be surpassed. The work at the U. S. Nitrate Plant No. 1 has been conducted in an effort to meet the commercial conditions. The enthusiasm and hard work of all the men associated with the project has greatly aided in the excellent results that were obtained.

XVI—The most essential factors involved in the choice of a commercial catalyst for use in the oxidation of ammonia are:

(1) High temperature of the intake gas phase.
(2) High catalyst temperature.
(3) High oxygen concentration.
(4) Controlled contact time with catalyst.

These are all interdependent. It is also desirable to have:

(5) Maximum oxidation with minimum weight of platinum.
(6) Utilization of the heat of reaction.
(7) Minimum catalyst free space with maximum catalyst surface per unit weight.
(8) Elimination of sudden expansion effects from abrupt excessive temperature changes from gas to catalyst.

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# THE INFLUENCE OF ESTER TRANSPOSITION IN THE DETERMINATION OF SAPONIFICATION NUMBERS

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## INTRODUCTION

The following directions for obtaining the saponification value of an oil are taken from "The Volatile Oils" by Gildemeister and Hoffmann, second edition, translated by Kremers, Vol. 1, p. 572: "The saponification is conducted in a wide-necked flask of potash glass of 100 cc. capacity. A glass tube about 1 m. in length and passing through a stopper serves as a reflux condenser." As this book is published under the auspices of one of the large manufacturers of essential oils, it may be taken that this description represents the usual practice in the determination of saponification numbers and ester values. As the ester is frequently the valuable constituent in an essential oil, the saponification number or ester value is a matter of importance. It should be further noted that in actual practice a tube less than 1 m. long is frequently used as an air condenser.

Redfield[2] has made a study of the effect of the use of various forms of condensers in the assay of peppermint oil. He says, "One possible source of error that seems to have received no attention is the low efficiency of the reflux condenser that is employed. Any oil lost through incomplete condensation would, obviously, cause low results." He used three different condensers and six different peppermint oils and obtained striking results. Using a sample containing 8.01 per cent of ester, the poorest condenser gave 0.33 per cent low with a maximum variation from 0.20 per cent to 0.40 per cent. This 0.33 per cent is an error of 4.20 per cent on the total of 8.01 per cent. Using the acetylated oil, in which the ester amounted to 65.08 per cent, the poorest condenser gave results averaging 4.87 per cent low, varying from 3.54 per cent to 6.92 per cent in individual analyses. This last result with its variation of 6.92 per cent low shows an error of 10.6 per cent figured on the amount present. Redfield does not go into the reasons for this great loss further than the statement above quoted, but

[1] The experimental work except the preparation of some of the samples of esters was carried out at Tarkio College by A. M. Pardee.

[2] This Journal, 6 (1914), 401.

his results are important. Menthol commands a high price, and peppermint oil is valuable on account of its menthol content. Therefore an error of 10 per cent in the estimation of this constituent is serious. The poorest condenser that Redfield used is probably as good as those frequently employed. Redfield's work has an important bearing on the estimation of esters in general, which is a scientific problem as well as a practical one.

As Redfield says, "Any oil lost through incomplete condensation would, obviously, cause low results." In the oil with which Redfield worked the ester present was menthyl acetate, which boils at 222.4° according to Oppenheim,[1] or 227.8°, according to Kishner.[2] It does not seem probable that any appreciable amount of a substance of such a high boiling point, certainly not 5 per cent or 10 per cent of it, would be likely to escape through even a poor condenser. Some other explanation must be sought. It has been shown by Bertoni,[3] Saloman,[4] Kossel and Kruger,[5] Henriques,[6] Bacon,[7] Kreman,[8] Sudborough,[9] Bruni and Contardi,[10] Haller,[11] Berthelot,[12] Komnenos,[13] Pfannl,[14] Reid,[15] Madinaveitia,[16] Kolhatkar,[17] Qua and McLaren,[18] Wren and Still,[19] Wilcox and Brunel,[20] and others, that when an ester derived from one alcohol is dissolved in another alcohol, the second alcohol replaces the first in part, the reaction coming to equilibrium when certain concentrations are reached. Bertoni found this reaction to be extremely rapid with nitrites, but with ordinary esters, in the absence of catalysts, it is extremely slow, probably as slow as the esterification of an alcohol by an organic acid, but like esterification it is enormously accelerated by relatively small amounts of strong acids. Reid[21] has shown that sodium alcoholates are some 4,000 times more effective than an equivalent amount of hydrochloric acid. In a roughly quantitative experiment he found that methyl benzoate is transformed in ethyl alcohol solution by one per cent of its equivalent of sodium ethylate at the rate of 3 per cent per minute at 25°. Anderson and Pierce[22] find for the same temperature that methyl benzoate is 25 per cent saponified in 90 per cent ethyl alcohol in 108 min. by 111 per cent of its equivalent of sodium alcoholate. As the alcohol contained 10 per cent of water in this case the velocities are not strictly comparable, but it appears that the transformation of methyl benzoate into ethyl benzoate is some 1500 times as rapid as is its saponification. While the saponification is half complete in 4 hrs., the alcoholysis is probably nearly complete in several minutes. Anderson and Pierce find the saponification of acetates to be six or seven times as rapid as that of the benzoates and we may assume that, correspondingly, the alcoholysis of acetates is considerably more rapid than that of benzoates.

Henriques[1] many years ago concluded that in the saponification of glycerides, etc., by alcoholic potash the transformation of the glyceride into the ethyl ester is the first reaction, which is followed by the saponification of the ethyl ester. The results of Anderson and Pierce[2] beautifully confirm this conclusion. They find that methyl, ethyl, normal propyl, isobutyl, isoamyl, and benzyl acetates are saponified at exactly the same rate in methyl alcohol. As all of these esters must have been transformed into methyl acetate almost completely, within a few seconds, in the large excess of methyl alcohol used as solvent, they were actually measuring the rate of saponification of methyl acetate in each case and should have obtained the same velocity as they did. They obtained exactly similar results with these esters in ethyl and also in amyl alcohol; also with methyl and ethyl benzoates. With phenyl acetate, which is an ester of a different class, different results were obtained. On the other hand they find very different rates of saponification with methyl, ethyl, and propyl acetates, 0.1136, 0.0639, and 0.0435, respectively, in water solution.

Returning to the usual method of quantitative saponification of ethereal oils in which 0.2 g. of, say, menthyl acetate is added to 10 cc. alcoholic potash, there are 150 times as many molecules of ethyl alcohol present as of the menthyl acetate and we may expect its transformation into ethyl acetate to be practically complete within a few seconds. Now we have an entirely different problem; we have to provide such a condensing arrangement as will prevent the escape of ethyl acetate. As this ester boils at 77.4° and has a molecular weight of only 88, we can see that there would be danger of loss by its escape unless an efficient condenser is used.

A simple qualitative experiment, which is readily tried and which will convince anyone of ester transformation, is to add a few drops of odorless tri-acetin, b. p. 258°, to 10 cc. of 2 *N* alcoholic potash or soda in a dish. A strong odor of ethyl acetate is at once apparent.

It may seem remarkable that more difficulty has not been encountered with saponification work. In the case of linalyl acetate, terpinyl acetate, and acetates of other tertiary alcohols, this transformation does not seem to take place with anything like such rapidity. In many oils the acid is some other than acetic and the ethyl esters of such acids do not boil at such low temperatures as ethyl acetate and con-

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[1] *Ann.*, **120** (1861), 351.

[2] *J. Russ. Soc.*, **27**, 480.

[3] *Gazz. ital.*, **12** (1882), 435.

[4] *Ber.*, **8** (1875), 1509.

[5] *J. prakt. Chem.*, [2] **39** (1889), 157.

[6] *Z. angew. Chem.*, **1898**, 338.

[7] *Am. Chem. J.*, **33** (1905), 79.

[8] *Monatsh.*, **26** (1905), 783; **27** (1906), 410; **29** (1908), 23.

[9] *Proc. Chem. Soc.*, **21**, 87; *Centbl.*, **1** (1905), 1234.

[10] *Gazz. ital.*, **36** (1906), 356.

[11] *Compt. rend.*, **143** (1907), 657.

[12] *Ibid.*, **143** (1907), 717.

[13] *Monatsh.*, **31** (1910), 687; **32** (1911), 77.

[14] *Ibid.*, **31** (1910), 301.

[15] *Am. Chem. J.*, **45** (1911), 479.

[16] *Ann. soc. españ. fis. quim.*, **12** (1914), 426; *Chem. Abs.*, **9**, 2643.

[17] *J. Indian Inst. Sci.*, **1** (1915), 107; *Chem. Abs.*, **9**, 2762.

[18] THIS JOURNAL, **38** (1916), 1905.

[19] *Ibid.*, **38** (1916), 1821.

[20] *J. Chem. Soc.*, **111** (1917), 1019.

[21] *Am. Chem. J.*, **45** (1911), 506.

[22] *J. Phys. Chem.*, **22** (1918), 44.

[1] *Z. angew. Chem.*, **1898**, 344.

[2] *J. Phys. Chem.*, **22** (1918), 55.

sequently are not so liable to escape through the condenser. Thus the methyl salicylate or oil of wintergreen would, by such transformation, give ethyl salicylate which is even less volatile than the original ester and would be in no danger of escaping.

Rupp and Lehmann[1] recommend the use of glass-stoppered flasks in saponification instead of flasks with reflux condensers.

Winkler[2] has advised the use of propyl alcohol instead of ethyl alcohol in saponification work. He notes that it is a better solvent for fats than ethyl alcohol and has a higher boiling point so that no reflux condenser is required. He worked only with fats and waxes. Had he used acetic esters he might have obtained higher values on account of the less volatility of propyl esters as compared with ethyl.

To test this point two esters were chosen, benzyl acetate boiling at 206°, and methyl benzoate boiling at 198.6°. If the low results with poor condensation are due to a loss of the original ester, there should be nearly the same loss with these two esters, since their volatility is nearly the same; but if, by ester transposition, the one gives ethyl acetate, greatly increasing the volatility, while the other yields ethyl benzoate, decreasing the volatility somewhat, the acetate only should show loss with poor condensers. The experiments justified this expectation.

If instead of ethyl alcohol we use methyl alcohol as the medium, far greater losses are to be expected with the benzyl acetate, since methyl acetate boils at 54° and would, if formed, escape rapidly, while there would be no change in the volatility of the methyl benzoate. With alcohols of higher molecular weight, less volatile esters will be formed by alcoholysis and the losses should be still less. Accordingly comparative runs were made with isobutyl, normal butyl, and isoamyl alcohols. Experiments were made also with benzyl formate, b. p. 202°, since methyl formate, b. p. 32°, is still more volatile than the acetate.

### APPARATUS AND MATERIALS

The apparatus for saponification was as simple as possible, duplicating the description quoted as standard. Resistance-glass flasks, round bottom, 100 cc. capacity, with 18 mm. ring neck, were connected by corks to pieces of thin-walled glass tubing, 12 mm. in diameter and a meter in length, which served as reflux condensers. Five such flasks used in each series were fitted into 87 mm. openings on the cover of a large water bath. All could be raised and lowered simultaneously, thus making the heating uniform.

The alcohols used, methyl, ethyl, isobutyl, normal butyl, and isoamyl, were of commercial purity. Each was treated with potassium hydroxide for 24 hrs. and distilled before use. The first two of these alcohols thus purified contained 5 per cent water, which was necessary for the saponification. Sufficient water was added to the other alcoholate solutions at the time of saponification to insure complete reaction between the alcoholic alkali solution and the ester.

The standard alcoholic alkali solutions were prepared by adding sufficient sodium metal to the various alcohols to make approximately *N*/5 strength. These solutions were allowed to stand 24 hrs. before standardizing against *N*/10 hydrochloric acid, which was in turn standardized by the silver chloride gravimetric method. The same 10 cc. pipette was used for measuring out the alcoholates for standardization and for the saponifications.

Of the esters used some of the samples were good commercial products and some were prepared by the usual methods. Only the formate calls for special attention.

One sample of benzyl formate, H, was made according to the method of Behal,[1] except that as anhydrous formic acid was not at hand, a 90 per cent acid was used with a corresponding excess of acetic anhydride. On account of the nearness of the boiling points of benzyl formate, 203°, and benzyl alcohol, 206°, fractionation is of little use for purification. The main fraction of the product, boiling between 199° and 202°, was used without further purification. From the analysis below it appears that it contained about 87 per cent ester.

The other sample, I, was made by ester transposition, and as this reaction has been but little studied with formates, this experiment is of some interest. In 40 g. benzyl alcohol, 0.15 g. sodium was dissolved and 50 g. methyl formate added. A considerable precipitate was formed. The mixture stood for three days at room temperature.

Water was added, the oil washed four times with water, dried, and distilled, 29 g. of it passing over between 197° and 200°, leaving 2 g. of residue. Analysis showed about 52 per cent ester in the product, proving that the reaction had taken place as expected.

### PROCEDURE

Samples of the esters, 0.2 to 0.3 g., were weighed into the flasks, and 10 cc. of the alcoholate added to each. The flasks were put on the steam bath for exactly 1 hr., after which 50 cc. of carbon dioxide-free water were added to each and the excess of alkali titrated, using phenolphthalein as indicator. Care was taken throughout the work to make the results comparable.

### RESULTS

The results are given in Tables I to V, inclusive, all of one run being in a single line, the average of the run being in the last column. The averages were taken before discarding the second decimals of the individual results. The results in a single run are more strictly comparable than those from different runs which were made at different times and with different standard alcoholate solutions.

### DISCUSSION OF RESULTS

The results with isobutyl alcohol are high and unreliable. The end-points in the titrations of its solutions were difficult to obtain and the isobutyl alcoholic alkali changed strength from day to day. The

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[1] *Apoth.-Ztg.*, **24**, 972; *Chem. Abs.*, **4** (1910), 1910.

[2] *Z. angew. Chem.*, **24** (1911), 636.

[1] *Ann. chim. phys.*, [7] **20** (1900), 421.

isoamyl solution did not titrate well and saponification was in some cases evidently incomplete. The results with these two alcohols may be left out of the discussion.

TABLE I—METHYL BENZOATE—SAMPLE A, 98.51 PER CENT; SAMPLE B, 99.25 PER CENT

| No. | Sample | Per cent Ester Found | | | | | Average |
|---|---|---|---|---|---|---|---|
| | | Methyl Alcohol Solution | | | | | |
| 1 | A | 94.7 | 97.0 | 94.4 | 93.7 | 94.2 | 94.80 |
| 2 | B | 95.6 | 96.2 | 96.0 | 95.6 | 95.1 | 95.68 |
| 3 | B | 95.5 | 94.7 | 96.6 | 95.3 | 95.3 | 95.48 |
| 4 | B | 95.5 | 95.8 | 95.8 | 95.3 | .... | 95.63 |
| 5 | B | 98.8 | 97.8 | 96.0 | 97.6 | 97.3 | 97.58 |
| | | Ethyl Alcohol Solution | | | | | |
| 6 | A | 99.3 | 98.7 | 98.2 | 98.3 | .... | 98.64 |
| 7 | A | 97.7 | 98.5 | 98.3 | 97.9 | .... | 98.10 |
| 8 | A | 98.2 | 98.2 | 98.7 | 97.9 | 98.9 | 98.38 |
| 9 | B | 99.1 | 98.4 | 98.7 | 99.0 | 99.5 | 98.93 |
| 10 | B | 99.5 | 98.8 | 99.5 | 100.2 | 99.9 | 99.80 |
| 11 | B | 99.5 | 99.3 | 99.7 | 99.3 | 99.5 | 99.45 |
| 12 | B | 99.6 | 98.8 | 98.3 | 99.2 | .... | 98.96 |
| 13 | B | 99.4 | 98.7 | 98.9 | 99.0 | 98.9 | 99.00 |
| | | Isobutyl Alcohol Solution | | | | | |
| 14 | B | 100.6 | 102.0 | 100.2 | ..... | .... | 100.9 |
| 15 | B | 100.6 | 102.1 | 102.4 | 100.1 | .... | 101.3 |
| 16 | B | 99.8 | 100.8 | 101.2 | 101.3 | .... | 100.6 |
| 17 | A | .... | ..... | ..... | ..... | .... | ..... |
| | | Normal Butyl Alcohol Solution | | | | | |
| 17 | A | 99.3 | 98.3 | 99.0 | .... | .... | 98.91 |
| 18 | B | 98.5 | 98.9 | 99.3 | 100.4 | .... | 99.38 |
| 19 | B | 98.7 | 99.3 | 99.4 | 99.8 | .... | 99.30 |
| | | Isoamyl Alcohol Solution | | | | | |
| 20 | B | 96.1 | 95.4 | 95.4 | 98.8 | 93.3 | 95.79 |

Considering Table I, we find the average result in methyl alcohol solution to be 3.27 per cent low, the highest figure being only 0.41 per cent low. The vigorous boiling of the methyl alcohol may have driven out some of the methyl benzoate vapor, or the saponification may have been incomplete, since Anderson and Pierce found saponification in methyl alcohol seven times as slow as in ethyl alcohol.

In ethyl alcohol solution the average variation from the accepted values is 0.39 per cent, the average divergence of a single determination from the mean of its own series is 0.26 per cent. Comparing the average results on Sample B in ethyl alcohol, 99.25 per cent, with 99.34 per cent found in normal butyl alcohol, we find that there has been no appreciable loss of ester. Excellent results were obtained in both ethyl and normal butyl alcohols.

TABLE II—BENZYL ACETATE—SAMPLES C, D, AND E, 99.58 PER CENT

| No. | Sample | Per cent Ester Found | | | | | Average |
|---|---|---|---|---|---|---|---|
| | | Methyl Alcohol Solution | | | | | |
| 21 | C | 25.4 | 26.4 | 22.1 | 24.9 | 26.9 | 25.1 |
| 22 | C | 19.3 | 21.2 | 20.2 | 21.2 | 22.4 | 20.9 |
| 23 | C | 14.6 | 27.0 | 15.7 | 18.1 | 18.7 | 18.8 |
| 24 | C[1] | 71.8 | 61.1 | 65.6 | 62.5 | 61.2 | 64.4 |
| 25 | D | 51.3 | 52.2 | 48.7 | 49.6 | 48.5 | 50.1 |
| 26 | D | 27.4 | 26.6 | 33.0 | 30.7 | 27.7 | 29.1 |
| 27 | E | 30.0 | 22.0 | 25.6 | 29.8 | 27.1 | 26.7 |
| 28 | E | 15.4 | 28.3 | 38.10 | 49.9 | 21.6 | 30.6 |
| | | Ethyl Alcohol Solution | | | | | |
| 29 | C | 92.5 | 93.3 | 93.3 | 93.4 | 94.2 | 93.33 |
| 30 | C | 91.5 | 92.1 | 92.0 | 92.1 | 92.7 | 92.08 |
| 31 | C | 90.3 | 90.3 | 90.4 | 91.6 | .... | 90.65 |
| 32 | C | 90.6 | 93.1 | 92.0 | 93.2 | .... | 92.22 |
| 33 | C | 91.6 | 90.0 | 91.2 | 90.1 | 90.8 | 90.99 |
| 34 | D | 95.0 | 93.6 | 93.5 | 94.1 | 94.5 | 94.13 |
| 35 | D | 94.8 | 95.1 | 96.8 | 96.1 | 95.0 | 95.23 |
| 36 | E | 97.6 | 97.3 | 97.7 | 97.8 | 98.3 | 97.71 |
| 37 | E | 98.2 | 97.4 | 97.3 | 98.5 | 99.4 | 97.87 |
| | | Isobutyl Alcohol Solution | | | | | |
| 38 | E | 101.6 | 101.2 | 101.2 | 102.3 | 101.2 | 101.48 |
| 39 | E | 98.8 | 101.5 | 100.6 | 100.7 | .... | 100.6 |
| | | Normal Butyl Alcohol Solution | | | | | |
| 40 | E | 99.3 | 99.1 | 99.1 | 99.4 | 99.5 | 99.30 |
| 41 | E | 99.5 | 100.4 | 99.2 | 100.0 | 100.3 | 99.86 |
| | | Isoamyl Alcohol Solution | | | | | |
| 42 | C | 89.9 | 90.2 | 89.6 | 86.0 | 89.8 | 89.86 |
| 43 | C | 89.4 | 90.0 | 89.5 | 90.2 | 90.5 | 89.91 |
| 44 | D | 92.6 | 93.1 | 85.1 | 78.9 | 91.4 | 87.14 |
| 45 | D | 87.1 | 87.7 | 91.7 | 92.3 | 93.1 | 92.37 |

[1] Water-cooled coil condenser.

TABLE III—ETHYL BENZOATE

| No. | Per cent Ester Found | | | | | Average |
|---|---|---|---|---|---|---|
| | Methyl Alcohol Solution | | | | | |
| 46 | 98.1 | 98.3 | 99.2 | 99.1 | .... | 98.70 |
| 47 | 98.8 | 97.9 | 98.5 | 98.0 | .... | 98.32 |
| | Ethyl Alcohol Solution | | | | | |
| 48 | 99.0 | 98.1 | 98.9 | 98.8 | 99.5 | 98.88 |
| | Normal Butyl Alcohol Solution | | | | | |
| 49 | 99.1 | 99.6 | 99.3 | 99.6 | 99.7 | 99.48 |
| 50 | 99.6 | 98.8 | 98.9 | 98.4 | 97.5 | 98.64 |
| | Isobutyl Alcohol Solution | | | | | |
| 51 | 98.9 | 99.5 | 99.7 | 99.6 | 100.8 | 99.69 |
| 52 | 97.8 | 98.7 | 97.9 | 98.8 | .... | 98.31 |

TABLE IV—BENZOYL BENZOATE

| No. | Per cent Ester Found | | | | | Average |
|---|---|---|---|---|---|---|
| | Methyl Alcohol Solution | | | | | |
| 53 | 98.7 | 98.4 | 99.1 | 98.6 | 98.6 | 97.72 |
| | Ethyl Alcohol Solution | | | | | |
| 54 | 97.9 | 98.2 | 98.2 | 98.7 | 98.0 | 98.19 |
| | Normal Butyl Alcohol Solution | | | | | |
| 55 | 98.1 | 97.8 | 98.5 | 97.8 | 98.5 | 98.14 |
| 56 | 98.8 | 98.3 | 97.4 | 98.5 | 98.9 | 98.40 |
| | Isobutyl Alcohol Solution | | | | | |
| 57 | 98.9 | 99.1 | 98.8 | 99.2 | 99.1 | 99.01 |

Turning to Table II we find just what was expected. The results in methyl alcohol solution except those of Runs 24 and 25 are extremely low, averaging only 25 per cent of the ester present. They are also very irregular, varying all the way from 15.4 per cent to 49.9 per cent in a haphazard fashion. No explanation can be given for the comparatively high results in Run 25. It is possible that saponification had largely taken place before the heating began. In Run 24, water-cooled coil condensers were used and even here the figures obtained are only two-thirds of what they should be.

With ethyl alcohol the results are more irregular than they should be. A close comparison can be made of Runs 36 and 37 with Sample E, which average 1.89 per cent lower than the average value found in normal butyl alcohol solution. There has been a slight loss of ethyl acetate.

The results in normal butyl alcohol are entirely satisfactory.

From Tables III and IV we find that satisfactory results are obtained in all of the alcohols, those in methyl alcohol being only a trifle low.

TABLE V—BENZYL FORMATE—SAMPLE H, 86.92 PER CENT; SAMPLE I 52.63 PER CENT

| No. | Sample | Per cent Ester Found | | | | | Average |
|---|---|---|---|---|---|---|---|
| | | Methyl Alcohol Solution | | | | | |
| 52 | H | 68.1 | 68.3 | 68.1 | 66.2 | 64.4 | 67.02 |
| 53 | I | 49.8 | 50.4 | 48.5 | 49.5 | 48.3 | 49.51 |
| | | Ethyl Alcohol Solution | | | | | |
| 54 | H | 85.1 | 84.8 | 84.5 | 84.7 | 84.5 | 84.70 |
| 55 | I | 48.5 | 51.7 | 51.4 | 51.4 | 51.5 | 51.52 |
| | | Normal Butyl Alcohol Solution | | | | | |
| 56 | H | 87.2 | 86.7 | 86.8 | 87.0 | 87.1 | 86.92 |
| 57 | I | 52.4 | 53.0 | 52.8 | 52.6 | 52.4 | 52.63 |
| | | Isobutyl Alcohol Solution | | | | | |
| 58 | H | 87.4 | 88.1 | 87.5 | 87.7 | 88.1 | 87.77 |
| 59 | I | 52.3 | 52.3 | 52.2 | 52.3 | 52.4 | 52.31 |

The results of Table V, at first sight, are surprising, those in methyl alcohol with Sample H being 20 per cent low and with Sample I only 2 per cent low. In ethyl alcohol they are 2 per cent and 1 per cent low.

The explanation is furnished by the work of Anderson and Pierce.[1] They find that methyl formate, in methyl alcohol solution, at 25°, is 54 per cent saponified in 1.68 min. Under the same conditions methyl acetate requires 245 min. for 50 per cent saponification. Or taking the average values of their velocity

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[1] *J. Phys. Chem.*, **22** (1918), 55.

constants, the formate is saponified 350 times as rapidly as the acetate. It is probable that the methyl formate formed was nearly all saponified before the flasks could be put on the steam bath.

It appears that normal butyl alcohol, which can now be obtained in great purity at a moderate price, offers many advantages as a medium in which to carry on saponification. We have found this alcohol particularly suited for the quantitative saponification of fats, waxes, etc., results on which will be published shortly.

### CONCLUSIONS

1—The alcoholysis of esters is to be taken into account in quantitative saponification.

2—Low results are to be expected when acetates are saponified in ethyl alcohol solution unless good condensers are used.

3—Normal butyl alcohol appears to be the best medium in which to carry on saponifications.

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## OIL-FIELD EMULSIONS

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### PROPERTIES AND TREATMENT OF OIL-FIELD EMULSIONS FROM THE GOOSE CREEK (TEXAS) FIELD

The infiltration of water into the oil sands in drilling operations has been the source of much trouble and expense to the oil producer and refiner and there have been various methods advocated for shutting off water from wells.[2] Not only does the inflow of water decrease the productivity of the oil-bearing sands, but there is increased cost of production due to the expense of pumping water and replacing corroded tubing, casing pumps, and other fixtures.

From still another standpoint, also, the water has a detrimental effect in oil production. This arises from the fact that the water, mixing with the oil under the conditions of production, forms emulsions with the oil. The stability of the emulsions so formed varies considerably, not only for different fields and different wells in the same field but even for the same well during different periods of productivity. From certain emulsions the water separates upon standing; others are decidedly permanent in nature and show no tendency to separate, and it is these more stable ones which give the most trouble to the producer and refiner.

The amount of water varies from traces up to 60 per cent or more, but the majority of emulsions contain about 25 per cent. It has been assumed by many workers in the oil fields that all these will separate either oil or water, leaving an emulsion that is an exactly equal mixture of oil and water and to this they have given the name of "B. S." The term originated in the fact that when oil containing water, even a trace, is stored in large tanks, such as are in use at the pipe line pumping stations, there gradually accumulates a sediment known as "bottom settlings." These bottom settlings usually contain about 50 per cent water and considerable asphalt. It is very doubtful, however, whether all the emulsions will have this ratio as their settling end-point. By adding water to some of the more stable oil-field emulsions and agitating the mixture, it has been found possible to prepare emulsions containing as high as 90 per cent water which were quite stable and showed no appreciable separation after months of standing.

In order to be salable, or classed as "pipe line" oil and accepted by the transporting companies, a crude oil must contain no more than 2 per cent water. This is a purely arbitrary limit that has been fixed by the operating companies in accordance with their experience in refining. This necessitates, however, some treatment of the emulsions in the field.

### PROCESSES FOR SEPARATION OF WATER

(1) FILTRATION PROCESS—The process of filtration has very little bearing on the treatment of oil-field emulsions, since it would not be possible to handle large quantities of oil economically, even if it were otherwise feasible. These filtering devices have been applied mainly to the separation of lubricating oils from water. The filtering medium is wetted initially with the external or dispersing phase and hence is not wetted during the filtration by the internal or dispersed phase. The tendency, however, is to cause a clogging of the filter. The filtering process has been improved somewhat by combining it with a certain electrical treatment.[1]

(2) EVAPORATION PROCESS—This method consists in heating the emulsion in open tanks or pits by means of coils containing superheated steam. It is uneconomical from the standpoint of fuel consumption and oil-evaporation loss, but oil production has been notorious for its wasteful methods and, until recent years, possibly even to this day, most of the dehydration of emulsions has been accomplished in this way. The fuel consumption is roughly 25 barrels of fuel oil per 1000 barrels of oil recovered. The oil-evaporation loss is about 5 per cent, depending upon the nature of the oil treated as regards the percentage of low boiling constituents. The heating of emulsions preparatory to other treatment is advantageous, but this heating is usually limited to a temperature of from 150° to 180° F. and is carried out in closed systems.

(3a) ELECTRICAL PROCESS. ALTERNATING CURRENT —The pioneer patent in the electrical treatment of oil-field emulsions was taken out by F. G. Cottrell.[2] This process depends for the demulsification upon the action of high potential alternating current electricity. The water is dispersed as finely divided globules throughout the oil and these are caused to coalesce by the action of the electrostatic forces. Quoting from the patent:

> These globules are thereby subject to electrostatic forces dependent upon the relative potentials and dielectric constants

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[1] Read at a meeting of the Southeast Texas Section of the American Chemical Society, at Houston, Texas, May 31, 1919.

[2] F. B. Tough, "Methods of Shutting Off Water in Oil and Gas Wells," Bureau of Mines *Bulletin* 163.

[1] Cottrell, U. S. Patent 987,114 (1911).

[2] Cottrell and Speed, U. S. Patent 987,115 (March 21, 1911).

of the materials in contact, and caused to coalesce into masses which may be readily removed from the body of the oil by well-known processes, such as settling.

The Petroleum Rectifying Company, of California, operating under this and other patents, has installed a number of plants in California, Oklahoma and Kansas.

(3*b*) ELECTRICAL PROCESS. DIRECT CURRENT—This process consists in passing the emulsion between electrodes connected to a source of direct current electricity with a potential of from 250 to 400 volts, with a current varying from a few milli-amperes to 10 amperes. The patent[1] under which the direct-current electrical treatment is operated claims that the process depends upon cataphoresis or electrical migration. The original experiments which served as a starting point for the development of this patented process were performed by the author with the help of Mr. G. W. Jones in May 1917, and the idea was based upon the known migration of colloidal particles when subjected to electrical stress.[2] We will see later, in the consideration of our experimental data, that this migration of particles must be a factor. Some electrolysis doubtless takes place since the electrodes are only about $^1/_8$ in. apart and at times a considerable current passes.

(4) CENTRIFUGAL PROCESS—The application of the centrifuge to the separation of water from these emulsions is rather limited. It is mainly useful in separating the last traces of water which have been discharged by other means. Thus it is used in the final step of the electrical treatment.

(5) CHEMICAL PROCESSES—The possibilities along the line of chemical treatment will be apparent from a consideration of our results and from the discussion of the action of certain treating compounds already on the market.

(6) GENERAL PROCESSES—Very often a number of the different methods are applied so that one supplements the others. The treatment of oil-field emulsions practiced by the Gulf Production Company in the Goose Creek (Texas) field consists of a combination of closed heating, settling, direct current electrical treatment and final separation of the remaining portions of the water by means of the centrifuge. Settling may be resorted to between the various stages of the treatment and the oil may be subjected to more than one electrical treatment, if necessary. In this combined process there is very little loss of the lighter fractions through evaporation and the fuel consumption is only about 10 barrels of fuel oil per 1000 barrels of oil recovered.

## THEORETICAL CONSIDERATION OF THE MECHANISM OF COLLOIDAL SOLUTION AND EMULSIONS

The stability of colloidal solutions has been explained as due to the formation of surface films on the dispersed particles, preventing them from coalescing. These films may be either electrical or nonelectrical, or both, and when they are destroyed, agglomeration and precipitation of the particles occur. That electrical films may function in preventing coalescence, due to the repulsion of like charges, has been recognized for a long time. The fact that there was a movement of colloidal particles when subjected to electrical stress was recognized by Linder and Picton,[1] and this migration could only be indicative of the existence of charge of definite polarity on the particles themselves. In line with the general theory of the protecting action of surface films, it is assumed that these electrical films are formed by the preferential adsorption of an ion of an electrolyte. The fact that charged colloidal particles are discharged by solutions of electrolytes, due to the adsorption of an ion carrying a charge opposite to that already on the particles, is in accord with this surface condensation of ions. It was shown by Picton and Linder[2] that the precipitated material was contaminated by the electrolyte, and particularly by that ion of the electrolyte which, due to its charge being opposite to that of the colloidal particle, functioned as the effective precipitating agent. Hardy's[3] assumption that the ion of the electrolyte, having the same charge as that of the particles, had no effect in the precipitation is probably unreliable and it has also been shown that the point of coagulation does not always correspond to the point of electrical neutrality. It is clearly recognized, however, that ion adsorption plays a rôle.

It is usually assumed that emulsions are a special type of colloidal solution and that they differ from ordinary liquid-solid colloidal systems to a greater extent than could be explained, by the fact that the disperse phase is a liquid instead of a solid.

That ions may function as emulsifying agents, analogous to their action of forming protective films on colloidal particles, seems entirely possible and the work of certain investigators seems to indicate that they do so. Thus, the investigations of Wilson[4] and of von Lerch[5] on the curvature of the interfaces between nonmiscible liquids, point, according to Bancroft,[6] to ion adsorption. Ellis[7] has even prepared emulsions which owe their stability to ion adsorption. In working with phenol-water mixtures it was noticed that the "cloud" formed upon the separation of the second liquid layer from a saturated solution of phenol in water persisted for hours. It is not unlikely that any slight stability which this phenol water emulsion has is due to hydrogen ion adsorption. Work is in progress on the three-component system, phenol–water–acetic acid, and the preliminary results indicate that the clouds formed in this system are more permanent than in the two-component system, phenol–water.

With a liquid as the disperse phase, however, it is not surprising that in general it should require a rather tough coherent film such as could be obtained only from solid particles. The ordinary emulsifying agents are themselves colloids and the conditions for regu-

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[1] Seibert and Brady, U. S. Patent 1,290,369 (January 7, 1919).

[2] *J. Chem. Soc.*, **67** (1895), 63.

[1] *J. Chem. Soc.*, **67** (1895), 63.

[2] *Loc. cit.*

[3] *Z. phys. Chem.*, **33** (1900), 385.

[4] *J. Chem. Soc.*, **1** (1848), 174.

[5] Drude's *Ann.*, **9** (1902), 434.

[6] *J. Phys. Chem.*, **19** (1915), 276, 280.

[7] *Z. phys. Chem.*, **80** (1912), 597.

lating which liquid shall function as the disperse phase have been very well defined. Thus, according to Bancroft,[1] "A hydrophile colloid will tend to make water the dispersing phase, while a hydrophobe colloid will tend to make water the disperse phase." Even in such cases, where the films protecting the disperse phase are colloids, we have charges upon the particles in so far as the colloids themselves carried charges.

### EXPERIMENTAL

The emulsions studied were obtained in the Goose Creek (Texas) field and, although they may or may not be representative of oil-field emulsions in general, the results are interesting, nevertheless, from the standpoint of the general theory of emulsification. As they are representative of the more stable of the Goose Creek emulsions, the results are applicable to the general treatment of the product of this region.

These emulsions are systems of water dispersed in oil as an external phase. This is clearly shown by the ordinary tests applied in the identification of phases in such systems.[2] One of the most satisfactory tests in such cases is the treatment of the emulsion with some component of one of the two phases. If the emulsion spreads in or mixes with the added component or phase, that phase is evidently the external or dispersing phase. It was found that these emulsions mixed readily with dry crude oil in all proportions but did not mix with water or salt solutions. The emulsified water contains salt (sodium chloride, etc.), sometimes up to 10 per cent, and if such aqueous solution was the external phase the emulsions would conduct the current readily. As a matter of fact, with electrodes 2 in. apart and with a potential difference of 250 volts impressed, it is not possible to notice any deflection of the needle of a sensitive milliammeter placed in the circuit. Clearly, then, the oil is the external phase.

The particles of water forming the disperse or internal phase are very finely divided and are apparent as a "fuzziness" in thin layers of the oil. Practical oil-field men identify the presence of water in an oil by placing a few drops on a piece of glass and holding vertically so as to allow drainage and form a thin film of oil on the surface of the glass. A dry oil will appear as a clear, amber colored film, while an oil containing water will appear "fuzzy."

THE CHARGE ON THE PARTICLES—The attempt was made to get some information as to whether or not the particles were charged and, if so, the nature of that charge. A drop of the emulsion was placed on the slide of a microscope and two small platinum wires, connected into a 70-volt direct current circuit, were brought into contact with the drop of oil. It was impossible to get any results in this way, due to the capillary effects, since the oil flowed from the center and collected about both wires. Some of the emulsion was then placed in a cell, Fig. 1, and a potential of 70 volts was impressed after connecting the electrodes to a direct-current circuit. It was thought that it might be possible to get an indication of migration and hence of the charges on the particles by measuring the percentage of water in the two sides of the cell after the experiment had run for some time. The cell was left connected for 22 hrs. and at the end of that time considerable change in outward appearances had taken place in the two sides. The color of the original emulsion was a yellow-brown. After the 22-hr. run the oil in the positive side of the cell was much darker than the original emulsion and the oil in the negative side much lighter. The presence of more water particles would cause a lighter appearance, and the less the number of particles the nearer would the color approach the dark green-black of dry oil. This would seem to indicate that water particles had migrated from the positive to the negative side, and that there was a positive charge on the particles. In neither side was there any discharged free water in the bottom of the cell. When determinations of the water content on the two sides of the cell were made, no difference was found, all the oil in each side of the cell being tested. This result was rather surprising in view of the quite evident color changes that had taken place. After running a number of these tests, however, it was noticed that upon withdrawing the electrodes from the oil a mass of water particles adhered to the positive electrode, and upon examination it was found that the water particles in the negative side had been driven to the outside against the side of the vessel. This clearly pointed to a negative charge on the particles. In that case they would be attracted to the positive electrode and collect around it, causing a darkening in the outside layer of the oil as they migrated to the center. On the negative side they would be repelled by the electrode and forced to the outside layers near the glass, causing a lighter color. It was therefore decided that the particles were negatively charged.

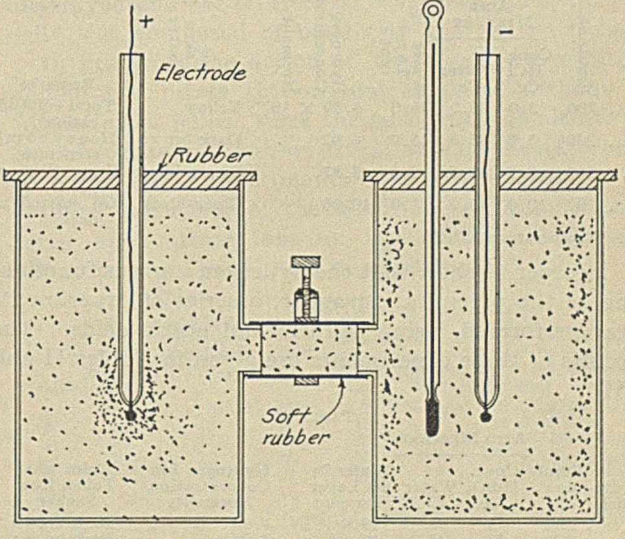

Fig. 1—Migration of Particles

PRECIPITATION BY ELECTROLYTES—If the particles were negatively charged, this charge might be neutralized by some readily adsorbed cation, and pre-

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[1] *J. Phys. Chem.*, **19** (1915), 275. Note—The term hydrophobe colloid is applied to a substance forming a colloidal solution in some nonaqueous solvent and not doing so in water; the term hydrophile colloid to a substance forming a colloidal solution in water but not in the nonaqueous liquids considered.

[2] *J. Phys. Chem.*, **18** (1914), 34.

cipitation brought about. Hydrogen ion is more strongly adsorbed than most ions, as a rule, and it was therefore decided to try the effect of various concentrations of different acids. The experiments were carried out as follows: 200 cc. of the emulsion containing 25 per cent water were placed in a 500 cc. ground-glass-stoppered graduate and 50 cc. of the acid added. The mixture was then shaken on an electrically driven shaking machine for 20 min. in order to insure intimate contact. It was then allowed to stand for 22 hrs., after which the percentage water in the oil layer was determined.

When more water was added and the mixture agitated, it was possible to incorporate this added water with the emulsion, the color becoming lighter with increasing proportions of water. In the case of the addition of hydrochloric acid solution, a change was quickly apparent as the emulsion became darker colored almost immediately. The notes in connection with Table I, where the results with hydrochloric acid are tabulated, refer to this color change.

TABLE I

| Number | Emulsion. Cc. | Acid Mixture<br>Conc. HCl Cc. | <br>Water Cc. | Water in Oil Layer. Per cent | Hydrogen Ion Concentration Normality | Color when Taken from Shaker | Remarks |
|---|---|---|---|---|---|---|---|
| 1... | 200 | 2.0 | 48.0 | 36.0 | $4.89 \times 10^{-1}$ | Yellow | Total emulsification |
| 2... | 200 | 5.0 | 45.0 | 15.0 | 6.02 | Dark brown | Honeycomb structure |
| 3... | 200 | 7.5 | 42.5 | 7.0 | 8.87 | Brown-black | Separation of good |
| 4... | 200 | 10.0 | 40.0 | 1.0 | 10.00 | Green-black | Oil started at once |

Temperature 25° C.

In order to show that the hydrogen ion was functioning as the precipitating agent, a series of experiments was performed, using sulfuric and acetic acids. The results of these experiments are given in Tables II and III.

TABLE II

| Number | Emulsion Cc. | Acid Mixture<br>Conc. $H_2SO_4$ Cc. | <br>Water Cc. | Water in Oil Layer Per cent | Hydrogen Ion Concentration Normality | Color when Taken from Shaker |
|---|---|---|---|---|---|---|
| 1..... | 200 | 5 | 45 | 19.0 | $1.88 \times 10^{-1}$ | Dark brown |
| 2..... | 200 | 10 | 40 | 12.0 | 3.04 | Dark brown |
| 3..... | 200 | 20 | 30 | 2.5 | 3.86 | Black-green |
| 4..... | 200 | 30 | 20 | 1.75 | 10.00 | Black-green |

Temperature 25° C.

TABLE III

| Number | Emulsion Cc. | Acid Mixture<br>Glacial Acetic Cc. | <br>Water Cc. | Water in Oil Layer Per cent | Hydrogen Ion Concentration Normality | Color when Taken from Shaker |
|---|---|---|---|---|---|---|
| 1..... | 200 | 2 | 48 | 40.0 | ...... | Yellow-brown |
| 2..... | 200 | 5 | 45 | 38.0 | $0.45 \times 10^{-1}$ | Dark yellow-brown |
| 3..... | 200 | 10 | 40 | 30.0 | 0.86 | Brown-black |
| 4..... | 200 | 20 | 30 | 30.0 | 2.51 | Dark brown-black |
| 5..... | 200 | 35 | 15 | 5.0 | 8.53 | Green-black |

Temperature 25° C.

The hydrogen ion concentrations, expressed in Tables I to III, were determined by means of the hydrogen electrode. In our experiments we had added 50 cc. of an acid mixture to 200 cc. of the emulsion and, as the emulsion was 25 per cent water, we always had 100 cc. of acid solution in the system. For the hydrogen ion concentration measurements the quantities of acid used in the various experiments to make up the 50 cc. of added mixture were diluted to 100 cc. The e. m. f. of the cell (normal calomel electrode–hydrogen electrode in the given acid solution) was balanced against a known e. m. f. and the hydrogen ion concentration computed according to the following equation:[1]

$$E = 0.058 \log 1/c + 0.28$$

When the H ion concentrations are plotted against the water percentage in the separated oil layer the curves as given in Fig. 2 are obtained.

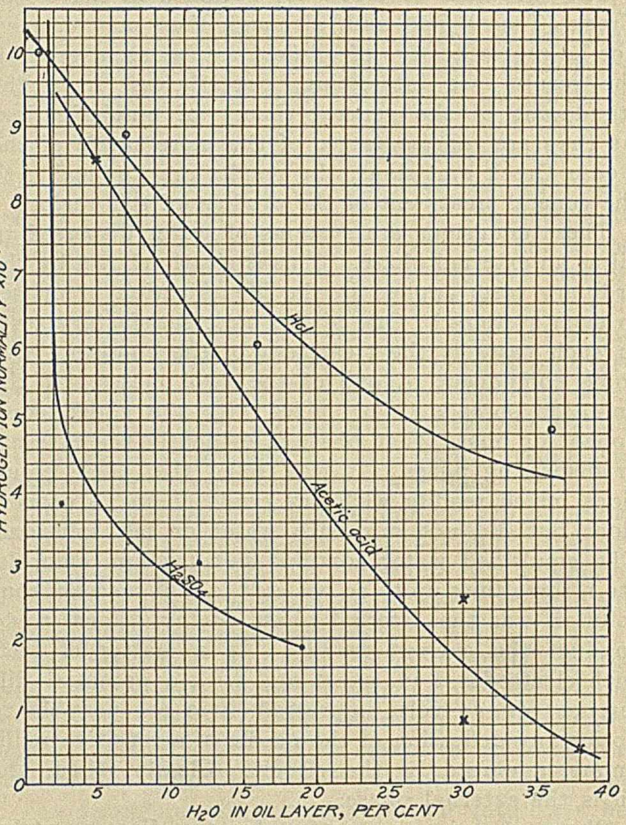

FIG. 2—PRECIPITATION OF WATER PARTICLES BY HYDROGEN ION

Since it is not safe to follow Hardy[2] and assume that the ion carrying a charge opposite to that of the colloidal particles is the only effective ion, we would expect the hydrogen ion concentration necessary for complete discharge to vary somewhat; and particularly, on account of the preferential adsorption of ions, we would not expect the curves to coincide. Since, however, the hydrogen ion concentration necessary for the complete discharge of the water from the oil ranges around the value $10.0 \times 10^{-1}$ normal, we can safely ascribe the precipitation to the effect of hydrogen ion, and our previous conclusions regarding the existence of a negative charge on the particles are substantiated.

Since the hydrogen ion neutralized the charge on the particles and precipitated the emulsion, it ought to be possible to discharge them in a similar manner by means of other strongly adsorbed cations. In line with the generally strong adsorption of ferric ion by various substances, and from the general consideration of the stronger precipitating power of polyvalent ions over that of ions of less valency, it was of interest to

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[1] Hildebrand, *J. Am. Chem. Soc.*, **35** (1913), 847.

[2] *Z. phys. Chem.*, **33** (1900), 385.

see what effect ferric ion would have. 200 cc. of the emulsion were treated with ferric chloride solution, as in the previous experiments with acids. Table IV gives the results of these tests.

TABLE IV

| | ADDED MIXTURE | | | |
|---|---|---|---|---|
| Number | $FeCl_3$[1] Solution Cc. | Water Cc. | Sp. Gr. of Added Mixture | Water in Oil Layer Per cent |
| 1........ | 2.0 | 48.0 | ...... | 22.0 |
| 2........ | 5.0 | 45.0 | ...... | 8.0 |
| 3........ | 7.5 | 42.5 | ...... | 2.0 |
| 4........ | 10.0 | 40.0 | 1.0610 | 1.5 |
| 5........ | 20.0 | 30.0 | 1.1213 | 1.5 |
| 6........ | 35.0 | 15.0 | 1.2050 | 0.5 |
| 7........ | 50.0 | 0.0 | 1.2878 | 0.5 |

Temperature 25° C.

[1] Ferric chloride solution used in making up added mixture contained 66.24 g. of $FeCl_3$ per 100 cc.

REMARKS

Sample 4, after 22 hrs., contained 150 cc. of a black jelly with a layer of good oil above it. This jelly flowed easily and upon being disturbed broke up, depositing most of its water phase.

Sample 5, after 22 hrs., contained 125 cc. of black jelly very similar in action to that of Sample 4.

Samples 6 and 7, after 22 hrs., contained 180 cc. of stiff black jelly which was very stable. Good oil on top.

As in the case of hydrogen ion, we found that ferric ion discharged the emulsions. In lower concentrations the action was perfectly regular, but in the higher concentrations as in Expts. 4 to 7, we did not get a separation of the water phase itself, but obtained jellies of varying stability. The jellies obtained in Expts. 6 and 7 were very stable indeed; the cylinders containing them could be turned over and the supernatant oil drained off without disturbing or displacing them. Upon removing some of these jellies with a spatula they were found to be of the consistency of a very stiff apple butter, and transference or manipulation did not destroy them. Jelly 6 contained 60 per cent by volume of ferric chloride solution, and Jelly 7 contained 56 per cent. Jellies 4 and 5 were very unstable.

Although hydrogen ion resulting from the hydrolysis of the ferric chloride might have had some effect, particularly in Expts. 1 to 5, nevertheless the results of Expts. 6 and 7 clearly show the influence of the ferric ion. It might seem, since the jellies contained from 56 to 60 per cent of the water phase, that they resulted from a partial precipitation or insufficient positive ion adsorption. If this were the case, hydrogen ion should cause the discharge of these jellies into their separate phases. Samples of the two stiff jellies were treated with varying concentrations of hydrogen ion but in no case were the jellies destroyed. Evidently the particles of which the jellies were composed were no longer negatively charged or they would have been discharged by the hydrogen ion of the acid.

It is a well-known fact that certain colloids are positively or negatively charged, depending upon the character of the dispersing phase. Thus albumin is positively charged in acid solution[1] and negatively charged in alkaline solution.[2] Since the jellies we obtained were evidently not negatively charged it seems possible that the adsorption of ferric ions had carried the particles past the neutral or isoelectric point and that they were now positively charged. Since a stiff jelly of this character does not lend itself to measurement of migration in an electric field, the only other way seemed to lie in testing the effect of strongly adsorbed anions upon the jelly.

Just as hydrogen ion is one of the most strongly adsorbed cations, so hydroxyl ion is one of the most strongly adsorbed anions. It was not possible, however, to use hydroxyl ion to identify the charge on the jelly because of the ferric ion present. In a study of the order of adsorption of anions by precipitated barium sulfate the following order was found:[1]

Ferrocyanide> nitrate> nitrite> chlorate> permanganate> ferricyanide> chloride> bromide> cyanide> sulfocyanate> iodide.

Since nitrate ion is strongly adsorbed and there is no interfering action between it and the ions already present, it was selected as being suitable for our purpose. Sodium ion is known to be very little adsorbed, hence we used sodium nitrate in these experiments. When the gel obtained from the original treatment of the emulsion with ferric chloride was treated with a saturated solution (25° C.) of sodium nitrate, it was destroyed and the oil freed. It seemed, then, that the jelly was composed of positively charged particles.

In line with the action of these gels, ferric nitrate should precipitate the original emulsion without the formation of jellies, since the adsorption of nitrate ion would counteract to some extent at least the adsorption of ferric ion. Experiments were carried out to determine the effect of the simultaneous adsorption of ferric and nitrate ions on the emulsion. Table V shows the results of these determinations.

TABLE V

| | | ADDED MIXTURE | | SEPARATED | | | |
|---|---|---|---|---|---|---|---|
| Number | Emulsion Cc. | $Fe(NO_3)_3$ Solution Cc. | Water Cc. | Solution Cc. | Sponge Cc. | Water in Oil Layer Per cent | Color after Standing 22 hrs. |
| 1... | 200 | 5 | 45 | 5 | None | 32.0 | Light brown |
| 2... | 200 | 10 | 40 | 15 | 70 | 16.0 | Brown |
| 3... | 200 | 15 | 35 | 25 | 80 | 5.0 | Dark brown |
| 4... | 200 | 25 | 25 | 65 | 35 | 1.0 | Dark brown |
| 5... | 200 | 50 | 0 | 65 | 35 | 0.5 | Green-black |

The temperature of liquids during these experiments was 25° C. The sponge obtained in these experiments was very mobile and broke up upon the slightest agitation. Ferric nitrate solution used in making up the added mixtures contained 67.32 g. $Fe(NO_{33})$ per 100 cc.

These results with ferric nitrate clearly show that both ions have an effect in the precipitation and bear out our previous conclusions as to the strong adsorption of nitrate ion.

In order to see to what extent the increase in the density of the water phase influenced these precipitation results, a number of experiments were run, using saturated solutions (25° C.) of sodium sulfate, sodium chloride, sodium carbonate and sodium bicarbonate, but in no case did we obtain a discharge of the water particles.

EFFECT OF ORGANIC SOLVENTS—There are a number of methods in use for determining the percentage of water in an emulsion. Most books on petroleum analysis recommend the distillation method. This

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[1] Hofmeister's *Beitr. chem. Physiol.*, **5** (1904), 27.

[2] Pflüger's *Archiv.*, **24** (1887), 247; cf. Bancroft, *J. Phys. Chem.*, **19** (1915), 350.

[1] Weiser and Sherrick, *J. Phys. Chem.*, **23** (1919), 205.

consists in adding toluene to a sample of the emulsion and distilling. The added toluene keeps down the troublesome frothing that usually occurs when undiluted emulsions are distilled. The water, toluene, and certain light portions of the oil come over, and as they separate into layers without emulsifying the percentage of water can be computed. The method most in vogue in the oil fields, on account of its simplicity, is to add a high-grade gasoline to a sample and centrifuge it. The volume percentage of water can then be read off directly on the graduated centrifuge glass. Usually the results obtained by these two methods will check, but occasionally the emulsions will not respond to this gasoline treatment. It has been found that ether is even better than gasoline for this centrifuge method. The explanation usually offered for this method is that the addition augments the difference in density of the two phases, causing a greater tendency to settle. This may be true to some extent but it cannot be the only effect, as will be shown.

The existence of negative charges on the water particles has been shown, but it is doubtful whether the ions alone function as the emulsifying agent. It seems probable that the ions which are responsible for the charge are condensed on solid particles which in turn form the protecting films. In many of these emulsions there is considerable earthy material and it may be possible that this material serves as the emulsifying agent, being itself peptized by ion adsorption.

On the other hand, the asphalt in these oils may be responsible for the formation of the films. Some slight amount of asphalt is present in colloidal solution in these crude petroleums, as a hydrophobe colloid, and would cause the formation of an emulsion with water as the disperse phase. It was found to be possible to prepare an emulsion of salt solution in pure white paraffin oil by using 0.5 per cent of asphalt. The emulsion so formed was not as stable as the natural oil-field emulsions and no definite charge on the particles could be identified; nevertheless it was much more stable than the suspension made by shaking the pure oil with the salt solution.

It is entirely possible that this system is even more complicated than the previous assumptions would indicate. Thus we might have the earthy material adsorbing asphalt or other heavy hydrocarbons from the crude oil, and these in turn forming protective films about the water particles, with the consequent adsorption of ions to impart a charge to the particles.

Richardson[1] found that the earthy matter in Trinidad asphalt had a high adsorption capacity for the bitumen of the asphalt.

Now in so far as the asphalt, either alone or condensed upon earthy matter, acted as the emulsifying agent, it would seem that the action of the ether in facilitating a separation of the two liquid phases might be due to the solvent action of the ether on the asphalt rather than to any augmentation of the difference in density of the two phases. If this were so, a liquid, miscible with the oil phase and having a high solvent action on the asphalt, should discharge the emulsion even if it had the same density as the emulsion itself. In order to test this point the specific gravity of the emulsion was determined and a mixture of ether and carbon disulfide having this same specific gravity was made. When this solvent mixture was added to a sample of the emulsion it discharged the water even more readily than ether alone. It would seem then that the action of these organic solvents was due to solvent effects rather than to differences in density.

## COMMERCIAL COMPOUNDS AND CHEMICALS FOR TREATING OIL-FIELD EMULSIONS

There are on the market certain compounds for the treatment of oil-field emulsions. These compounds are usually crude soaps or sodium salts of sulfonic acids, obtained by sulfonating either a coal-tar oil or a petroleum.[1] All of such compounds examined were hydrophile colloids, which seems to be the explanation for their action in discharging these oil-field emulsions.

Just as there is selective adsorption of ions, so there is selective adsorption of colloids, and certain hydrophile colloids might have a much greater tendency than others to destroy an emulsion formed by means of a given hydrophobe colloid. Just as precipitation of colloidal particles is due to the adsorption of an ion with a charge opposite to that upon the particles, so colloids of opposite charges precipitate one another. But in the destruction of an emulsion formed by a hydrophobe colloid it is not necessary that the hydrophile colloid be of an opposite charge. Thus we have negatively charged soap particles precipitating the negatively charged water particles of these emulsions.

These properties and actions of oil-field emulsions would indicate in a general way the methods for their efficient treatment. It must be borne in mind, however, that the emulsions from different fields may differ markedly in properties and therefore might require entirely different treatment. In so far as they do differ, each field would have to be investigated in order to indicate the best method of treatment. In any case, it may be advantageous to combine a number of processes to supplement one another.

The author hopes to be able to procure samples so that representative emulsions from the other oil fields of the country may be examined.

## SUMMARY

The results of this investigation are summarized as follows:

1—The emulsions occurring in the Goose Creek (Texas) oil fields have been studied.

2—These emulsions consist of salt solution as disperse phase and oil containing asphalt as the dispersing phase.

3—The water particles migrate to the anode under electrical stress and are therefore negatively charged.

4—Strongly adsorbed cations neutralize the negative charge on the particles and precipitate the water.

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[1] *J. Phys. Chem.*, **19** (1915), 245–6.

[1] Francis and Rogers, U. S. Patent 1,299,385 (1919).

5—Ferric ion is adsorbed to such an extent that it will carry the particles over from a negative charge through the isoelectric point to a condition of positive charge in a manner analogous to the reversal of charge on albumin particles.

6—From the experiments with ferric chloride and ferric nitrate it is apparent that both ions of an added electrolyte are effective in precipitation of the charged particles.

7—The decrease in stability of these emulsions upon the addition of ether is probably due to the solvent action of the ether on the asphalt rather than to any increase in the difference in density of the two liquid phases. An ether-carbon disulfide mixture of the same gravity as the emulsion will discharge the water.

8—The action of certain commercial treating compounds is probably due to the fact that they are hydrophile colloids. A hydrophile colloid should discharge an emulsion formed by the use of a hydrophobe colloid, while a hydrophobe colloid should discharge an emulsion formed by the use of a hydrophile colloid.

### ACKNOWLEDGMENT

In conclusion, the author wishes to thank Mr. E. T. Gregg for aid and helpful suggestions, and Dr. F. M. Seibert and Mr. J. Van der Henst for procuring samples.

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## TESTING THE MILDEW RESISTANCE OF TEXTILES[1]

By B. S. Levine and F. P. Veitch

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A study of the fundamental factors determining the effectiveness and durability of processes of waterproofing and mildewproofing textile fabrics, such as cotton duck and cotton canvas, was undertaken with the primary object of finding simple formulas and methods for treating cloth which are applicable for small-scale use on the farm and also suitable for use by commercial treating plants. Prerequisites for successful work on the main problem are, of course, suitable methods for determining water and mildew resistance. The method here described, which is not regarded as final but subject to improvement with experience and greater knowledge of the problems involved, has been used for the past two years and has proved to be useful in judging the probable serviceability of mildew-resistant treatments. The methods used for testing the water resistance of fabrics are described in a separate paper.[2]

Mildewing is due to the development of various mold growths on and in the fabrics. The number of species responsible for the deterioration is large, but chief among them are species of *Alternaria*, of *Cladosporium*, and some *Mucors*. The simultaneous occurrence of different kinds of molds seems to play an important part, and the production of pink and yellowish discolorations is probably due, at least in some cases, to the growth of both a *Mucor* and a mold producing a substance having a pink appearance in alkaline or neutral reaction and a yellow one in an acid reaction.

Gueguen[1] is of the opinion that the spores causing the mildewing of fabrics are usually introduced into the fibers by the dead parts of the parent cotton plant, where they have been either in a dormant or germinating state, and concludes that mildew is hardly ever due to contamination of the fabric after weaving.

The presence in the air of spores of cellulose-destroying fungi has been demonstrated by McBeth and Scales,[2] who have isolated from plates exposed to air contamination over a dozen cellulose-destroying organisms, among which *Cladosporium herbarum* has been identified. Davis, Dreyfus and Holland[3] have shown that astonishingly large numbers of mold spores rain into the mill vats containing sizing materials used on the component threads, thereby becoming introduced into the woven fabric.

We have repeatedly mildewed pieces of treated and untreated fabrics by inoculating their surfaces with pure cultures of *Cladosporium*, *Alternaria*, and other molds, and have found that, under laboratory conditions, converted canvas may be completely destroyed by several species of *Aspergillus*.

Sterilized duck inoculated with spores and mycelial fragments of species of *Alternaria* and of *Cladosporium* and incubated for two weeks, developed mold growth which, at the end of another two weeks, entered deeply into the fabric. Furthermore, heavy fabrics, subjected to certain finishing processes having a sterilizing effect on the preëxisting mold spores and mycelial fragments, readily mildew under favorable field conditions. It is clear, therefore, that even canvas apparently free from original mold impregnation will mildew if exposed to air contamination and to conditions encouraging mold growth.

### METHODS USED TO DETERMINE MILDEW RESISTANCE

Tests for mildew resistance of fabrics have been in use heretofore. One, occasionally followed, is, briefly, to bury a sample of the cloth under ground at a depth of 12 to 15 in. for a period extending over one month. The ground is kept moist by occasional watering. The condition of the fabric at the end of the test period is considered to indicate the degree of mildew resistance.

This method may give valuable information regarding the resistance of fabrics to bacterial action, but its value for determining mildew resistance is questionable. Waksman[4] found that soil samples taken from a depth of 12 to 30 in. on plating out developed only *Zygorhynchus*, and that *Aspergillus*, *Alternaria*, *Cladosporium*, *Penicullium*, and other organisms commonly present in the soil had not appeared in the plates in 24 hrs.; while in the upper soil strata there may be 1,000,000 fungi per gram of soil. This, really, is a small number of organisms,

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[1] Read at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

[2] This Journal, **12** (1920), 26.

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[1] *Compt. rend.*, **159** (1914), 781.

[2] U. S. Dept. of Agr., Bureau of Plant Industry, *Bulletin* **266**, pp. 24–25.

[3] "Sizing and Mildew in Cotton Cloth," **1880**, Palmer and Howe, Manchester.

[4] *Science*, N. S., **44** (1916), 320–23.

as compared with the many millions of bacteria usually present. Canvas buried under ground would, therefore, be subject to bacterial rather than to fungus attack. That this is so, is indicated by the fact that cotton duck coated with a thin layer of paraffin remained practically unattacked when buried under ground for nearly a month, whereas mildew developed in less than a month when inoculated in the laboratory.

Furthermore, since it is generally recognized that different soils have different microbial flora, that species present under one combination of conditions may be absent under others even in the same soil, it is not practicable to standardize this method of testing.

Another method is to roll together several samples of the cloth to be tested with layers of fresh horse manure and of sawdust and keep for about a month in a moist condition. At the end of the period the condition of the cloth is observed, and if no deterioration is evident, the samples are again rolled up and left for another month or two.

Haubner,[1] Henneberg and Stohmann,[2] Knieriem,[3] Choukevitch[4] and others have shown that cellulose is fermented by bacteria in the intestinal tract of practically all animals, man included. It is reasonable to think, therefore, that cellulose-destroying bacteria abound in fresh feces, but that molds are practically absent. This statement has been confirmed in this laboratory. Finally, this procedure obviously cannot be standardized, and, because of its offensive character, is not suited for laboratory work.

The simplest and most useful method heretofore used is that of suspending the test sample in a closed jar containing some water. The jar is kept in a dark, preferably warm, room for 5 to 7 days. At the end of this period, the test is discontinued. This test, though subject to some criticism, is better than those previously described, since it can be easily conducted under standard conditions. The period of incubation usually employed, however, is entirely too short. We have found that certain fabrics, which have remained unattacked by molds for over a week, have proved to be susceptible to mildew and were completely overgrown in three weeks to one month of incubation. Davis, Dreyfus and Holland[5] have employed a procedure for testing the mildew resistance of cotton goods similar to the one just described, with a period of incubation from 40 to 50 days. In experiments on mildewing "pure cloth" the following results, among others, are given:

> "Seventh day.—Damp but nothing visible. Twelfth day.—Visible only under the microscope. Twentieth day.—Slight fructification. Twenty-eighth day.—Badly mildewed, brown spots, etc."

Their results, together with our observations, have convinced us that 30 days is the shortest allowable period of incubation when testing fabrics for mildew resistance.

A serviceable test for mildew resistance of textiles should include the following factors:

1—Aërobic conditions of growth.
2—Proper humidity.
3—Proper temperature.
4—Subdued light.
5—Sufficient period of incubation.
6—Standard conditions with regard to the controllable factors involved in the test.
7—Simplicity of procedure.

To meet these conditions the following procedure has been adopted. Cut six discs about $3^{1}/_{2}$ in. in diameter from the sample to be tested and place in running water at room temperature for at least 2 days. In the absence of running water place the discs in a beaker of water and change the water several times during the day. This soaking and washing is for the purpose of removing from the fabric as much of the water-soluble, germicidal and fungicidal substances as possible and also the fermentable material. If these are left in the fabric, they may suspend or hasten the development of the mildew spores, making it appear that the fabric is highly mildew-resistant or highly susceptible, whereas in practice the substances may be almost completely washed out by the first rain, and the resistance of the fabric become markedly different.

At the end of the period of soaking, place the discs between clean blotting papers or towels and remove excess of water by pressure. Place the discs in six bacteriological Petri plates containing 10 to 15 cc. of plain agar jelly free from nutrient matter, being careful that the plates do not become air-tight. The plates with the discs are incubated in a closed chamber at a temperature of 20° to 25° C. for 7 to 10 days. If they show a heavy and well-developed growth, the test is discontinued. If, however, the growth of mold is entirely absent or is merely starting, the discs are inoculated with stock cultures of *Alternaria*, *Cladosporium*, and a pink *Mucor*, and further incubated for from 3 to 4 weeks. The first period of incubation is designated for convenience as the "pre-inoculation period."

During the second period of incubation weekly examinations of the plates are made macroscopically and with the aid of the binocular microscope whenever necessary. The factors observed and taken into consideration, are:

1—Extent of contamination or so-called spontaneous growth.
2—Extent of inoculation growth.
3—Discoloration.
4—Strength of the fabric.
5—Nature of the predominating growth.

A rating on the basis of ten has been worked out which is, of course, arbitrary, and subject to future modification. Where results cannot be measured and expressed mathematically, precision cannot be expected. The definitions and ratings are based upon observable factors which do not lend themselves to definite measurement. They are, therefore, subject to errors introduced by the so-called individual equa-

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[1] *Amst-und Anzeigeblatt für die Landwirtschaftlichen Vereine der Königliche*, Sachson, **1854**.

[2] *Beitrage zur Begrundung einer rationellen Futterung der Wiederkauer*, Braunschweig, **1860-4**, 2 pts.

[3] *Z. biol.*, **21** (N. S. **3**) (1885), 67–139.

[4] *Ann. Inst. Pasteur*, **25** (1911), 247–276.

[5] *Loc. cit.*, p. 205.

tion. However, after some experience, the worker obtains a concrete understanding of the terms "very heavy," "heavy," "considerable," "fair," and "negligible."

The rating is based on one month's incubation.

| Observations | | | | |
|---|---|---|---|---|
| Contamination Growth | Inoculation Growth | Other Characteristics | Rating | Nomenclature |
| Very heavy[1] | ........ | Tendering of cloth | 0 | Mildew - susceptible |
| Very heavy[1] | ........ | Tendering not readily observable | 1 | Not mildew-resistant |
| Heavy[1] | ........ | Marked discoloration | 2 | |
| Heavy[1] | ........ | Visible discoloration | 3 | |
| Considerable | Fair | Slight discoloration | 4 | Negligibly mildew-resistant |
| Considerable | Negligible | No visible discoloration | 5 | Slightly mildew-resistant |
| Fair | Negligible | No visible discoloration | 6 | Considerably mildew-resistant |
| Negligible | Negligible | No visible discoloration | 7 | Mildew-resistant |
| Negligible | Visible only through binocular microscope | No discoloration | 8 | Highly mildew-resistant |
| Negligible | None | No discoloration | 9 | Very highly mildew-resistant |
| No | None | No discoloration | 10 | Mildew-proof |

[1] Where the contamination growth is heavy the condition of the inoculation growth may be overlooked. In fact it is frequently overgrown by the spread of contamination molds.

Data permitting the comparison of the results of laboratory tests of the mildew resistance of textile fabrics by the above method with field exposures have been obtained, and, though at present still meager, are indicative of the value of the test. Pieces of treated and untreated cloth were stretched over frames in the form of tents and exposed to weather conditions in the vicinity of Washington for nearly a year. The samples were then brought into the laboratory and examined for mildew. The table shows the results of the laboratory test and outdoor exposure of some of the samples.

| | Laboratory Test | | | | |
|---|---|---|---|---|---|
| Number | Contamination Growth | Inoculation Growth | Other Characteristics | Rating | Exposure Test |
| 34791[1] | Very heavy | ........ | No readily observable tendering of cloth | 1 | Heavily mildewed |
| 34792[1] | Heavy | ........ | Marked discoloration | 2 | Black mildew |
| 34780[1] | Heavy | ........ | Marked discoloration | 2 | Black and yellow mildew |
| 34772 | Heavy | ........ | Marked discoloration | 2 | Black and green mildew |
| 34797 | Heavy | ........ | Marked discoloration | 2 | Considerably mildewed |
| 34856 | Heavy | ........ | Marked discoloration | 2 | Black mildew |
| 33309 | Considerable | Fair | Slight discoloration | 4 | Some black mildew |
| 34828 | Considerable | Fair | Slight discoloration | 4 | Heavily mildewed |
| 34832 | Considerable | Fair | Slight discoloration | 4 | Mildewed |
| 34834 | Considerable | Fair | Slight discoloration | 4 | Mildewed |
| 32409 | Considerable | Negligible | No visible discoloration | 5 | Some black mildew |
| 34826 | Considerable | Negligible | No visible discoloration | 5 | Slightly mildewed |
| 34748 | Considerable | Negligible | No visible discoloration | 5 | Mildewed |
| 33331 | Fair | Negligible | No visible discoloration | 6 | No mildew |
| 33460 | Fair | Negligible | No visible discoloration | 6 | No mildew |
| 32388 | Negligible | Negligible | No visible discoloration | 7 | No mildew |
| 33434 | Negligible | Negligible | No visible discoloration | 7 | No mildew |
| 32383 | Negligible | Visible only through binocular microscope | No visible discoloration | 8 | No mildew |
| 33017 | Negligible | ........ | No visible discoloration | 9 | No mildew |
| 33001 | None | None | No visible discoloration | 10 | No mildew |
| 33003 | None | None | No visible discoloration | 10 | No mildew |

[1] The first three samples were of untreated gray duck—the remainder were from treated material.

It will be seen from these preliminary results that samples which by the laboratory method give a resistance of six or better withstood exposure for a whole year under normal weather conditions near Washington, D. C. How much longer these fabrics will withstand exposure without mildewing is now being determined. The procedure can apparently be relied upon, especially in distinguishing between resistant and nonresistant treatments.

### SUMMARY

I—The methods heretofore usually employed for testing mildew resistance of fabrics are outlined and their disadvantages pointed out.

II—A laboratory method is described which is simple in execution and the details of which have been standardized.

III—A rating on the scale of 10 and a system of nomenclature have been developed on the basis of laboratory observations. The practical significance of these underexposure conditions will be further studied and reported.

IV—A comparison has been made of the results of the laboratory test with results of exposure tests.

## THE INFLUENCE OF THE METHOD OF MANUFACTURE ON THE USE OF CASEIN IN GLUE MAKING

By Samuel Butterman

Forest Products Laboratory, Madison, Wisconsin

Received August 20, 1919

The urgent necessity for a water-resistant glue for use in aircraft construction was realized immediately upon our entry into the war, but at that time, in this country, relatively little was known regarding its preparation. The severe weather conditions to which airplanes are subjected and the impracticability of covering all glued joints in a machine with a waterproof coating, led the Air Service of the War Department and the Bureau of Construction and Repair of the Navy Department to adopt very exacting requirements as to water resistance for all glue used in the manufacture of certain aircraft parts. The U. S. Forest Products Laboratory, Madison, Wis., was called upon to investigate this subject in order to obtain definite information as to the properties of, and methods of obtaining water-resistant glue.

Two types of water-resistant[1] glue have been successfully developed, one based on soluble blood albumin and the other on casein. Casein is practically insoluble in water, but in the presence of alkaline substances it forms solutions which are highly viscous and possessed of marked mucilaginous properties. If lime is present, these solutions soon "set," and on drying form a hard mass which does not redissolve in water. Such a mixture of casein, lime and other alkaline substance, to which certain other ingredients may be added to confer additional desirable properties, forms the so-called "waterproof" casein glues which are commercially available at the present time.

In the early work at this laboratory in the development of casein glue formulas it was found that shipments of casein from different sources, or often two shipments from the same maker, exhibited such marked

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[1] F. L. Browne, "Water-resistant Glues," *Chem. & Met. Eng.*, **21** (1919), 136.

differences in behavior that the glue formula had to be seriously altered for each sample of casein. This made it necessary to extend our study to cover the influence of the method of manufacturing casein on its use in glue.

### MANUFACTURE OF CASEIN

Casein occurs as the principal protein of milk, closely associated with lime and calcium phosphate in a form generally designated as calcium caseinate. The casein is obtained as a precipitate by freeing it more or less completely from this combination. The methods of doing this may be divided into two classes:

1—Acidification of milk. The acids commonly used are lactic, hydrochloric, and sulfuric.

2—Coagulation of milk by rennet.

For the sake of economy, casein is not made from whole milk. The milk is first passed through a cream separator to obtain butter-fat and the skimmed milk is used for the manufacture of casein. Although it is also possible to obtain casein from buttermilk, very little is made from it at the present time, and we shall therefore confine our discussion to skim-milk casein.

LACTIC ACID OR NATURAL-SOUR METHOD—In this method the necessary acidification is produced by the fermentation of the lactose of milk. The milk is allowed to stand at room temperature until the amount of lactic acid produced is almost enough to cause separation of the curd from the whey, and then warmed to about 130° F., whereupon the curd separates. The whey is drained off and the curd is sometimes washed with cold water. The curd is wrapped in cloth and pressed to remove the remaining whey or wash-water as far as possible, and dried by spreading it on trays in a drying tunnel through which air, at a temperature not over 130° F., circulates. This method of procedure is sometimes spoken of as the "vat" or "cottage cheese" method.

In order to avoid loss of time fresh skim milk is sometimes warmed and allowed to flow out of a pipe. From a neighboring vat a stream of warm, sour whey is allowed to flow in such a way that it mixes with the stream of skim milk, and the liquid falls into a third vat from which the whey is finally drained and the curd washed, pressed, and dried as before.

An excellent grade of natural-sour casein is made by the "ejector" method developed by the Bureau of Animal Industry.[1] The skim milk (or buttermilk) is allowed to sour until its acidity, as determined by titration with a standard alkali solution, using phenolphthalein as indicator, is 0.8 to 0.9 per cent, expressed as lactic acid. It is then allowed to run out of the tank through an ejector where it is rapidly heated by introducing steam, and to fall into a second tank where the curd collects on top. The whey is drained off and the curd washed, pressed, and dried.

METHOD OF COAGULATION WITH ACIDS—In this method the necessary acidification is produced by adding acid directly to the milk. This saves the time required for the production of lactic acid by natural souring.

The fresh skim milk is placed in a vat and heated with steam to about 120° F. About one pint of sulfuric acid (sp. gr. 1.84) for every 1,000 lbs. of milk is diluted with a gallon of water and added to the milk, which is gently stirred until the curd separates. The whey is drained off and the curd washed. It may then be pressed and dried, as in the case of natural-sour casein, or it may be "cooked." This process consists in covering the curd with water and heating to 170° to 175° F., when the curd collects in a semi-fluid, plastic, tough mass. The water is drained off, and the soft curd barreled and shipped.

By far the greater part of the commercial casein made in the United States is produced by the sulfuric acid method. In some creameries where the whey is later used for recovering lactose, hydrochloric acid is substituted, to avoid certain mechanical difficulties at a later point in the process.

J. L. Sammis, of the Dairy Department of the University of Wisconsin, has shown that by proper manipulation sulfuric acid curd can be made with as low ash content as natural-sour casein.[1]

THE GRAIN-CURD METHOD—The Bureau of Animal Industry has developed a method for making commercial casein by the hydrochloric acid method which gives a product of exceptional purity. This method has been successfully put into practice by at least one large creamery.

The method takes its name from the character of the curd when obtained from milk in which the hydrogen ion concentration is approximately that of the isoelectric point of casein, $P_H = 4.6$. This is easily controlled in practice by adding the dilute acid to the milk and testing small samples by means of methyl red, comparing the color with that of a stock solution of known hydrogen ion concentration. By the careful regulation of temperature and acidity the curd is easily freed from impurities.

METHOD OF COAGULATION WITH RENNET—Rennet casein is obtained by treating milk with rennet. Since no acid is formed during the process, the ash content of the caesin thus produced is very high.

### CHARACTER OF COMMERCIAL CASEIN

Commercially available caseins are of the most diverse character. They range in quality from practically white, sweet smelling products relatively low in impurities, through light yellow to dark brown material with sour and highly offensive odors. The marked variation in behavior of caseins in various applications is shown by the specific preferences of different consumers for one type or another. Thus one manufacturer maintains that natural-sour casein alone is satisfactory for his purpose, whereas another stipulates that only mineral acid casein is to be furnished. In many instances scientific supervision is lacking; no explanation for this preference is given beyond some reason expressed in the vernacular of the trade and hence devoid of any significance to one not familiar with the particular application under consideration.

In our work in developing casein glue formulas, this wide dissimilarity in the caseins was a source of much difficulty because a formula which gave satisfactory results with one casein might fail completely with another. With any casein of reasonably good quality, however, it was possible by an alteration in the proportions of the ingredients of the formula to obtain a satisfactory glue. Investigations were therefore made into the causes of variation in commercial casein made by different methods and their effect upon the use of casein in glue.

The results of the first part of this work have already been published.[2] Over 300 samples of commercial casein, made by different methods and different makers, were analyzed for moisture, fat, ash, "acidity," and nitrogen, the last giving a measure of the organic impurities other than fat present. In

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[1] A. O. Dahlberg, "The Manufacture of Casein from Buttermilk or Skim Milk," U. S. Dept. of Agr., *Bulletin* **661**.

[1] Work about to be published.

[2] F. L. Browne, "The Proximate Analysis of Casein," THIS JOURNAL, **11** (1919), 1019.

Table I are given the results of the analyses of samples of casein made at a large creamery by different methods. These results are typical of the casein produced at the present time by each of these methods:

TABLE I—RESULTS OF ANALYSES OF CASEIN MADE BY DIFFERENT METHODS

| METHOD | Av. No. of Samples | Moisture Per cent | Fat (Moisture-free Basis) Per cent | Ash (Moisture-free Basis) Per cent | | | Nitrogen (Moisture Fat-Ash-free Basis) Per cent | Acidity[1] Cc. |
|---|---|---|---|---|---|---|---|---|
| | | | | Max. | Min. | Av. | | |
| Buttermilk | 9 | 6.97 | 9.56 | 2.18 | 0.88 | 1.36 | 14.77 | 9.2 |
| Grain curd | 11 | 9.48 | 0.33 | 3.76 | 1.08 | 1.65 | 14.84 | 9.9 |
| Natural sour | 18 | 7.87 | 0.27 | 2.62 | 1.33 | 2.16 | 14.84 | 8.7 |
| Sulfuric acid | 34 | 7.81 | 0.35 | 5.36 | 3.02 | 4.05 | 14.46 | 7.6 |
| Sulfuric cooked | 8 | 8.89 | 0.12 | 5.58 | 3.92 | 4.25 | 15.04 | 5.9 |
| Hydrochloric cooked | 8 | 9.44 | 0.18 | 5.09 | 4.14 | 4.71 | 15.03 | 5.2 |
| Hydrochloric acid | 6 | 7.10 | 0.16 | 6.03 | 5.51 | 5.74 | 14.32 | 6.7 |
| Rennet | 3 | 8.29 | 0.63 | 8.39 | 7.18 | 7.97 | 14.41 | 7.9 |

[1] Acidity is expressed as cc. of $N/10$ sodium hydroxide solution required to dissolve 1 g. of moisture-, fat- and ash-free casein and give a solution neutral to phenolphthalein.

For skim-milk casein the moisture and fat contents are independent of the method of precipitating the curd, although the nitrogen content varies considerably. None of these seems to have much influence on the behavior of casein in glue. Further discussion will therefore be limited to the effect of ash content and "acidity."

## INFLUENCE OF IMPURITIES ON USE OF CASEIN IN GLUE

It was early observed that caseins prepared by the three commercial methods—lactic acid, mineral acid, and rennet—show marked differences with respect to the quantity of water required to reduce the glue prepared from them to the same viscosity. In general, caseins of the same type require a quantity of water which varies within a definite range and is somewhat sharply differentiated from the quantity required by other types. Indeed, in most cases,[1] it is possible to name the method of manufacture by a mere observation of the relative amount of water required by the casein under investigation. From Table II it will be seen that this property closely parallels the ash content of the casein.

Since this variation in water requirement is by far the most serious one encountered in using any casein for glue making, a thorough study was made of the relation between water requirement and ash content of commercial caseins. For this purpose casein glue Formula 4 of this laboratory[2] was selected, and glues were made from a large number of commercial caseins of different kinds, the amount of water used in each case being varied until the desired viscosity was obtained. A similar study was made later with three entirely different glue formulas. The results obtained were similar in all cases; therefore the data given below seem to have general application to casein glues.

The method of procedure was as follows: 100 to 200 g. of dry, powdered casein were weighed and mixed with *x* parts of water. After soaking a few minutes until the casein was thoroughly wet, a suspension of lime containing one part of hydrated lime to 6 parts of water was stirred in. The amount of lime used in this suspension was equivalent to 15 per cent of the weight of casein used. Finally an amount of sodium silicate solution (sp. gr. 1.4) equal to 0.7 of the weight of casein was added, and the mixture was then vigorously stirred until all particles of casein had dissolved, giving a homogeneous mass. (In the following tables the "water-casein" ratio means the ratio of the total weight of water used to that of casein.) Among the characteristics observed in these glues were the consistency and glue "life." If the glue exhibited, by simple observation, a viscosity intermediate between a thin, watery mixture and a thick, heavy mixture, its consistency was recorded as "medium." Similarly a very high viscosity was described as "stiff." By the term "life" is meant the period of time between the preparation of the glue and the point where it becomes too thick to spread properly.

Seventy-two different caseins were tested in this way. A few typical samples selected at random are given in Table II.

TABLE II—INFLUENCE OF ASH AND ACIDITY ON VISCOSITY AND LIFE OF GLUE

| TYPE OF CASEIN | Ash Per cent | Acidity Cc. | Ratio of Water to Casein | Consistency | Life Hrs. |
|---|---|---|---|---|---|
| Grain curd | 1.28 | ... | 2.3 | Medium — | 12.0 |
| Lactic acid | 1.43 | 7.4 | 2.4 | Medium — | 11.0 |
| Lactic acid | 1.43 | 7.6 | 2.4 | Medium — | 11.0 |
| Lactic acid | 1.44 | 9.0 | 2.4 | Medium — | 18.0 |
| Lactic acid | 1.49 | 7.9 | 2.5 | Medium — | 16.0 |
| Lactic acid | 1.62 | 8.8 | 2.4 | Medium | 8.5 |
| Lactic acid | 1.7 | 7.9 | 2.3 | Medium | 16.0 |
| Lactic acid | 1.81 | 8.6 | 2.5 | Medium — | 23.0 |
| Lactic acid | 1.81 | 8.5 | 2.4 | Medium | 12.0 |
| Lactic acid | 2.51 | 8.2 | 2.5 | Medium | 10.0 |
| Lactic acid | 2.62 | 10.6 | 2.5 | Medium + | 6.5 |
| Sulfuric acid | 2.64 | 7.0 | 2.5 | Medium — | 14.0 |
| Grain curd | 2.7 | ... | 2.5 | Medium | 9.0 |
| Sulfuric acid | 3.02 | 9.1 | 3.0 | Thin | 18.0 |
| Sulfuric acid | 4.29 | 6.0 | 2.7 | Medium | 6.5 |
| Sulfuric acid | 4.91 | 7.1 | 2.7 | Stiff — | 5.5 |
| Sulfuric acid | 4.96 | 8.1 | 2.7 | Medium + | 5.0 |
| Sulfuric acid | 4.96 | 6.0 | 2.7 | Stiff | 6.5 |
| Sulfuric acid | 4.93 | 8.5 | 2.9 | Medium + | 9.0 |
| Sulfuric acid | 5.06 | ... | 2.9 | Medium | 6.0 |
| Sulfuric acid | 5.08 | 8.2 | 2.9 | Medium + | 6.5 |
| Sulfuric acid | 5.10 | 8.4 | 3.1 | Stiff + | 3.0 |
| Sulfuric acid | 5.36 | 5.8 | 2.8 | Stiff | 6.0 |
| Sulfuric acid | 5.58 | 5.7 | 2.8 | Medium + | 7.0 |
| Sulfuric acid | 6.03 | 6.5 | 3.1 | Stiff — | 4.5 |
| Rennet | 8.59 | 5.5 | 3.7 | Medium + | 5.0 |

An examination of Table II will show the close relation between the ash content of casein and the water-casein ratio required to give a glue of medium consistency. This at once explains the variation in the behavior of casein made by different methods. It is to be noted that when a mineral acid casein is so made that its ash content lies in the same region as lactic acid casein, its water requirement approaches that of the latter. It should also be observed that there is no abrupt transition in the ash contents, and therefore in the water-casein ratios, of caseins made by different methods, but that they merge gradually into each other. The recent work of the Bureau of Animal Industry and of J. L. Sammis has shown that, under the proper conditions of manufacture, the ash content of mineral acid casein is as low as that of lactic acid casein, in which case there is no difference in the behavior of the products of the two methods.

It is interesting to note, as shown in Table III, the effect on the behavior of the casein after washing. Washing lowers the ash content and consequently the water-casein ratio required to produce a given

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[1] Caseins made by the method of Sammis or by the grain-curd method are exceptions to this rule.

[2] U. S. Patent 1,291,396, granted to S. Butterman, and assigned to the United States.

TABLE III—EFFECT OF WASHING THE CURD ON THE BEHAVIOR OF THE CASEIN

| TYPE OF CASEIN | Times Curd Washed | Ash Per cent | Acidity Cc. | Ratio of Water to Casein | Consistency | Life Hrs. |
|---|---|---|---|---|---|---|
| Lactic acid | 0 | 2.51 | 8.2 | 2.5 | Medium | 10.0 |
| Lactic acid | 3 | 1.44 | 9.0 | 2.4 | Medium — | 18.0 |
| Lactic acid | 0 | 2.46 | 8.5 | 2.3 | Medium + | 7.5 |
| Lactic acid | 3 | 1.93 | 7.4 | 2.4 | Medium — | 11.0 |
| Lactic acid | 0 | 2.20 | 8.9 | 2.5 | Medium | 11.0 |
| Lactic acid | 3 | 1.49 | 7.9 | 2.5 | Medium — | 16.0 |
| Lactic acid | 0 | 2.62 | 10.6 | 2.5 | Medium + | 6.5 |
| Lactic acid | 3 | 1.33 | 9.0 | 2.4 | Medium — | 13.0 |
| Sulfuric acid | 1 | 5.58 | 5.7 | 2.8 | Medium + | 7.0 |
| Sulfuric acid | 2 | 3.55 | 6.2 | 2.8 | Medium — | 12.0 |
| Sulfuric acid | 0 | 4.40 | 6.5 | 2.8 | Medium | 6.5 |
| Sulfuric acid | 2 | 4.15 | 6.3 | 2.8 | Medium — | 9.0 |
| Sulfuric acid | 0 | 3.94 | 8.2 | 2.6 | Medium | 9.0 |
| Sulfuric acid | Several | 2.64 | 7.0 | 2.5 | Medium — | 14.0 |

viscosity. This is shown in the table either by the lower water-casein ratio or by the lower viscosity or longer life exhibited by the glues made from the lower ash caseins.

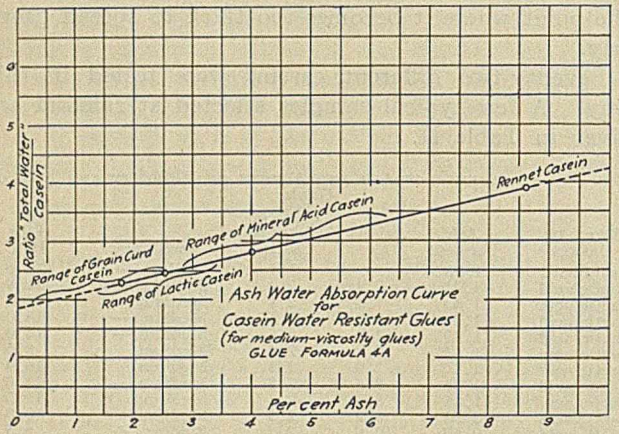

FIG. 1

### CASEIN GLUE—CHARACTERISTIC CURVE

The general relations just discussed are presented in a very striking manner if a casein glue characteristic curve is constructed by plotting ash content against water-casein ratio. In Fig. 1 four typical points are plotted—one for each type discussed. The properties of each point have been selected to represent the average characteristics observed for these types. The data used for this curve are given in Table IV. The water-casein ratio in each case is such as to produce a glue of medium viscosity.

TABLE IV

| TYPE OF CASEIN | Ash Per cent | Water Casein |
|---|---|---|
| Grain curd | 1.8 | 2.3 |
| Lactic acid | 2.5 | 2.4 |
| Mineral acid | 4.0 | 2.8 |
| Rennet | 8.6 | 3.9 |

In Fig. 2 the values of ash and water-casein ratio necessary to give a glue of medium viscosity are plotted for 72 different samples of casein. The curve drawn coincides with Fig. 1. The average deviation from the straight line approaches 0.2 part of water. This is practically negligible because the water was not measured more closely than 0.1 part and the observation of viscosity is only approximate, so that the experimental error is at least 0.3 part; yet but two of the 72 points plotted exceed this experimental error.

In checking the data of Table II against this curve, it must be remembered that the curve is drawn for medium viscosity glues, and therefore it is necessary to correct roughly the water-casein ratio to conform to this viscosity wherever it was not actually observed. Table V illustrates such a correction in the case of two glues.

TABLE V

| Ash Per cent | Water Casein Observed | Consistency | Water Casein Corrected | Consistency |
|---|---|---|---|---|
| 6.03 | 3.1 | Stiff — | 3.3 | Medium |
| 1.43 | 2.40 | Medium — | 2.2 | Medium |

By extrapolation it can be predicted that an ash-free casein would require 1.85 parts of water. A sample of casein, made by the Van Slyke[1] method, was available whose ash content was 0.38 per cent. According to the graph such a casein should require 1.95 parts of water to make a glue of given viscosity. Investigation showed that 2.15 parts were actually required, which is well within the experimental error.

The curve in Fig. 1 represents an equation of the type

$$y = mx + c.$$

Hence if A is the ash content of the casein, and W the water-casein ratio required to give a glue of medium viscosity,

$$W = 0.24A + 1.85$$[2].

By making a determination of the ash content of a given sample of casein, it is therefore possible to tell at once the proper proportion of the ingredients required to mix it into a satisfactory glue, regardless of the method by which the casein has been prepared. It is therefore possible to use casein made by any of the commercial methods for making casein water-resistant glue and still obtain uniform results.

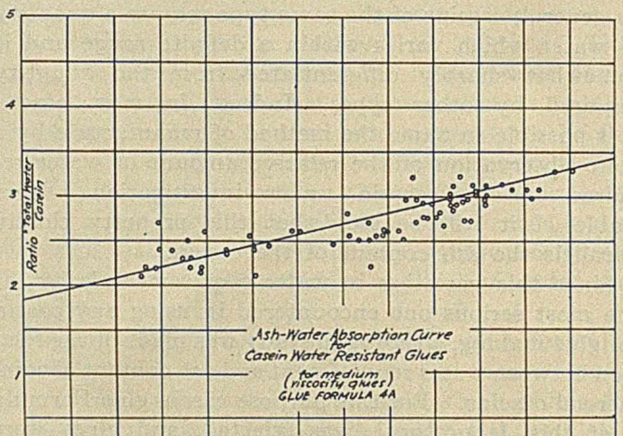

FIG. 2

### SUMMARY

1—A brief description of the commercial methods of manufacturing casein is given.

2—The variation in the behavior of casein made by different methods when used in water-resistant glue is due to the variation in ash content.

3—Since the amount of water required to give a glue of medium viscosity is a linear function of the ash content, it is possible to plot a "glue characteristic curve" for any casein glue formula by means of which a uniform production of glue from casein made by any of the commercial methods can be insured.

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[1] *J. Biol. Chem.*, [1] **35** (1918).

[2] These constants apply to Formula 4 only.

# ALKALI FUSIONS. I—THE FUSION OF SODIUM *p*-CYMENE SULFONATE WITH SODIUM HYDROXIDE FOR THE PRODUCTION OF CARVACROL[1]

By H. D. Gibbs and Max Phillips

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## INTRODUCTION

The study of a number of commercially important alkali fusions is under way in this laboratory. The investigation of the reaction between sodium *p*-cymene sulfonate and sodium hydroxide, involved in the production of carvacrol, is published at this time, not for the reason of its commercial importance, but because other work on cymene has been in progress in this laboratory for some time[2] and also because the work of Hixson and McKee[3] on the commercial manufacture of carvacrol which has appeared so recently describes a commercial procedure that appears to be open to improvement.

The usual method of conducting fusions in a fire-heated open kettle, with stirrer, is open to serious objections in many manufacturing operations, and is especially undesirable in laboratory studies for many reasons, among which may be mentioned local overheating, the change in the composition of the melt due to evaporation, the action of air which in some cases causes undesirable oxidation, and the fact that this method of studying reaction rates and conditions is very slow, because a number of hours are usually required for the determination of each point on the various curves involved.

We have devised an apparatus permitting of the determination of six points on a curve in a period of time only a little greater than that usually required for one point, and at the same time avoiding the other disadvantages above enumerated.

The results show that the fusions made in an autoclave give greatly increased yields, and a saving in chemicals and ease of operation over the open-kettle method.[4] The results differ materially from those of Hixson and McKee.

## MATERIALS

SODIUM *p*-CYMENE SULFONATE—Cymene was obtained by purifying the crude "spruce turpentine" from a sulfite pulp mill by digesting with lime for several days, and distilling at a pressure of 5 mm. The distillate and about $^1/_5$ of its volume of 95 per cent sulfuric acid were placed in a vessel provided with a mechanical stirrer and agitated together for several hours at room temperature. After separating off the acid and washing the oil with water, fresh acid was added and the stirring continued until a portion of the oil after being washed with water, gave, at most, a very light yellow color when shaken with sulfuric acid. A total of 15 hrs. stirring with acid usually sufficed to give the desired product. The oil, washed free from sulfuric acid and dried over calcium chloride, was fractionated over sodium using a Glinsky still head. Practically all distilled over from 176.5° to 177.5°, leaving only a small amount of viscid material in the flask. 1000 cc. of the cymene fraction and 1600 cc. sulfuric acid (sp. gr. 1.84) were heated together on a water bath with constant mechanical stirring. This was continued until a test portion was completely soluble in water. The sulfonated product was treated with barium carbonate and the barium sulfonate obtained in the usual way. The solution of this salt was then carefully treated with a sodium carbonate solution, the barium carbonate filtered off, and the filtrate evaporated to dryness on the steam bath. The colorless residue was finely powdered and dried in a vacuum oven at 120°. This material was used in all of our fusion experiments. A sulfur analysis made on this product gave the following results:

Calc. for $C_{10}H_{13}.SO_3Na$: S, 13.55. Found: 13.51, 13.42

SODIUM HYDROXIDE—This was the "C. P." article purified with alcohol and assaying 98 per cent NaOH.

## APPARATUS

The apparatus[1] used in our fusion experiments is shown in Fig. 1. It consists of a sheet iron tank, B, filled with solder to the level C, and insulated by means of asbestos walls H. The bath is heated with gas burners, D, and the temperature regulated by proper adjustment of the gas supply by means of valves F. The temperature is indicated by a thermometer inserted in well X. With careful attention the temperature of the bath may be maintained practically constant. The six tubes N, in which the fusion mixture is placed, are provided with screw caps and copper gaskets and may be screwed down so that they are gas-tight. The tubes are held in the carrier M by means of clamp O and screws P. The carrier may be raised or lowered by means of racks U and gears T operated through crank S. It is held in position when either raised or lowered by means of a ratchet gear V and stop W. The carrier is so constructed that it revolves in bearing Q moving on guides R, and driven by the motor J through the spur gear K, shafts Z and bevel gears L, the tumbling motion thus imparted to the tubes N insuring the complete and constant mixing of the contents. The whole is mounted on angle iron frame A supplied with suitable castors to make the apparatus portable.

## EXPERIMENTAL METHODS

ALKALI FUSIONS—In ascertaining the conditions for obtaining the highest yield of carvacrol it was neces-

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[1] Presented at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] This Journal, 10 (1918), 453; 11 (1919), 455, 1130.

[3] *Ibid.*, 10 (1918), 982; McKee, U. S. Patent 1,265,800 (1918).

[4] Although Hixson and McKee employed a cylindrical steel vessel which could be tightly closed, fitted with a stirrer and thermometer, and heated in a eutectic mixture of sodium and potassium nitrates with accurate temperature control, they record no experiments in which the vessel was closed to prevent escape of gases.

A covered fusion vessel was employed in order that a condenser could be attached to recover considerable quantities of cymene formed during the reaction. Taking this recovered cymene into consideration their best yield was 64.65 per cent [52.31 (carvacrol) + 12.34 (cymene calc. as carvacrol) = 64.65], except in one large-scale operation when it figured 66.4 per cent [57.2 (carvacrol) + 9.2 (cymene calc. as carvacrol) = 66.4].

They state: "Without a cover the fusion mass thickens, due to reaction with oxygen of the air, and the volatile oil which distils off is lost."

[1] The apparatus was constructed by R. Hellbach and G. Orange, of the mechanical staff of this laboratory.

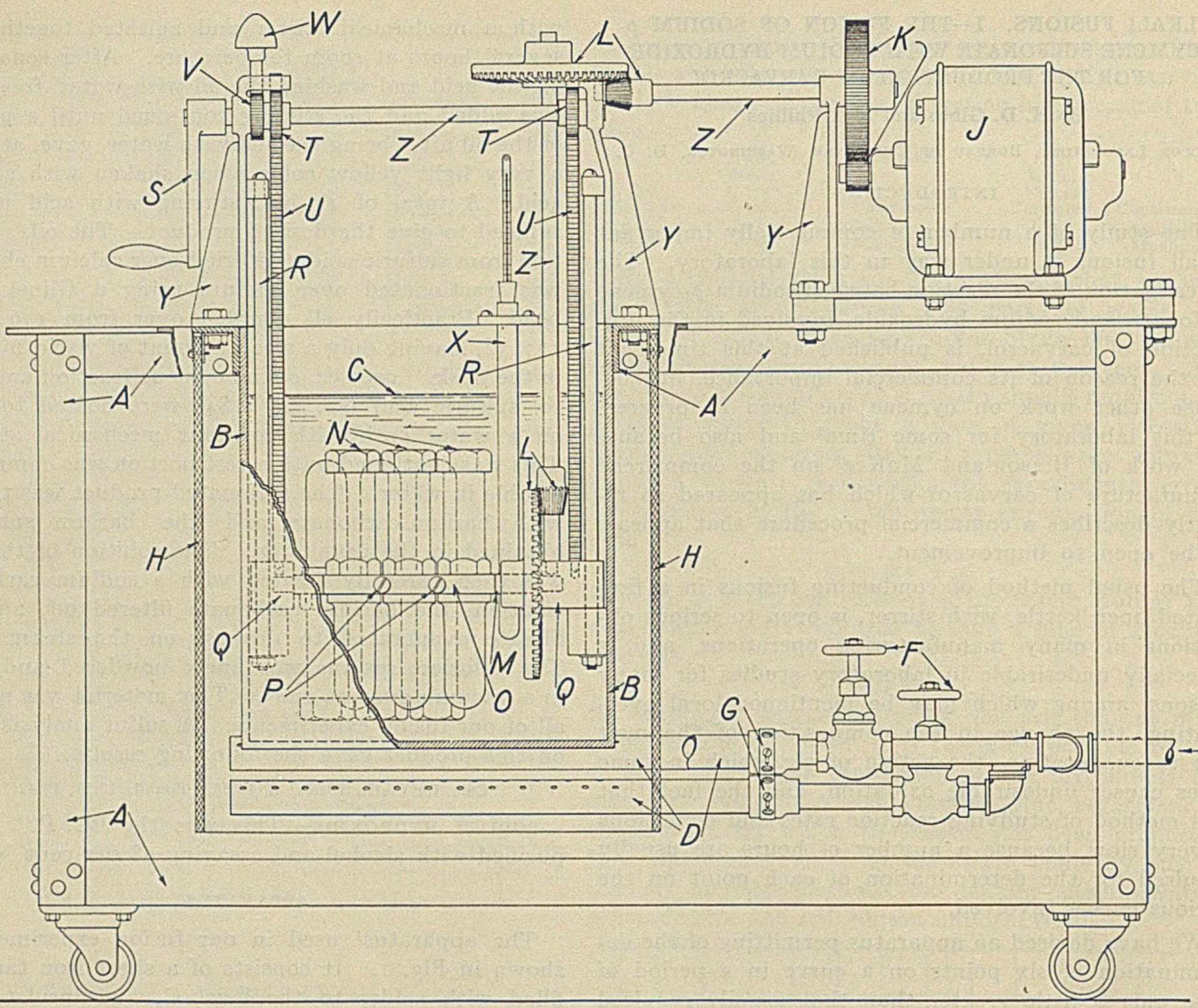

FIG. 1—APPARATUS FOR ALKALI FUSION

sary to determine experimentally the four following factors:

1—Proper fusion temperature.
2—Proper fusion period.
3—Ratio of sodium hydroxide to the sodium cymene sulfonate.
4—Relation between the carvacrol yield and the percentage of water in the charge.

Accordingly, 0.1 mole of the sulfonate mixed with the theoretical amount of alkali (0.2 mole) was placed in each one of the six tubes and the latter rotated in the metal bath kept at a constant temperature. At certain intervals of time, namely, 1, 2, 4, 6, 8, and 10 hrs., a tube was removed, suddenly chilled with cold water and analyzed for its carvacrol content. Experiments were conducted at 280°, 325°, 350°, and 360°, and from the data thus obtained, the proper fusion period and temperature were deduced. Having determined this, an experiment was then carried out using the same amount of sulfonate but different amounts of sodium hydroxide for each tube, the fusion being conducted at the optimum temperature and fusion period determined by the previous experiments. In the same manner, the effect of the addition of water to the fusion mixture was determined by adding a known amount of water to each tube, using the optimum conditions of the other factors previously determined experimentally.

ISOLATION OF THE CARVACROL—The fused mass was removed from the tubes by means of hot water, filtered, acidulated with dilute sulfuric acid, and extracted with ether. On evaporating the solvent, a residue consisting of crude carvacrol was obtained.

METHOD OF ANALYSIS—The amount of total carvacrol obtained from the evaporation of the ether was determined and a weighed sample analyzed for its carvacrol content by means of the Messinger and Vortman[1] method, as subsequently modified by Kremers and Schreiner.[2] Instead, however, of using an iodine solution of known normality, standardization was made against pure carvacrol, employing conditions identical in all analyses. This we consider the only satisfactory method for determining the yields of carvacrol. A criticism of the methods employed by other workers is to be found under the heading "Discussion."

### EXPERIMENTAL DATA

EFFECT OF THE TIME AND TEMPERATURE OF THE FUSION ON THE CARVACROL YIELD—Using the same amount of sulfonate in each case ($^1/_{10}$ mole) and the theoretical amount of sodium hydroxide (0.2 mole) four fusion experiments were carried out at different

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[1] *Ber.*, **23** (1890), 2753.

[2] *Pharm. Rev.*, **14** (1896), 221; Allen's "Commercial Organic Analysis," 4th Ed., **4**, 399.

temperatures, namely, 280°, 325°, 350°, and 360°. The results obtained are recorded in Table I, and graphically in Fig. 2, Curves 1, 4 and 5.

TABLE I—TIME AND TEMPERATURE OF FUSION

CONSTANTS—Ratio of sodium *p*-cymene sulfonate to sodium hydroxide

VARIABLES—Temperature and time

| Number | Fusion Period Hrs. | Carvacrol Yield Expressed as Per cent of Theoretical 280° | 325° | 350° |
|---|---|---|---|---|
| 1 | 1 | 1.2 | 25.0 | 37.5 |
| 2 | 2 | 2.8 | 39.8 | 60.6 |
| 3 | 4 | 5.2 | 56.1 | 71.6 |
| 4 | 6 | 9.2 | 59.3 | 74.1 |
| 5 | 8 | 11.7 | 62.3 | 72.8 |
| 6 | 10 | 15.6 | 64.2 | 74.7 |

This table indicates that the best temperature is 350°, and the proper time 6 hrs.

To further substantiate this a fusion at 350° was attempted, with other factors constant. Low and irregular yields of carvacrol resulted. The destruction of the carvacrol at 360° was considerably reduced by incorporating water in the reaction mixture. Data from this experiment are found in Table V and the graphic representation in Curve 3, Fig. 2.

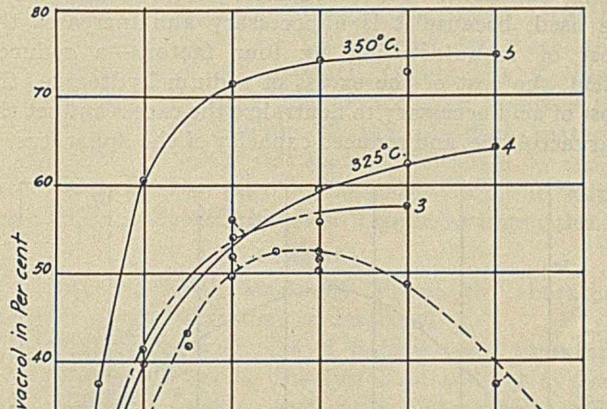

FIG. 2—FUSION PERIOD-YIELD CURVES

Curves 1, 4, and 5 are the graphic representations of the data in Table I; Curve 3 that of Table V; and the dash, Curve 2, is reproduced from the work of Hixson and McKee showing the yield by the open pot fusion at 360°, 1 mole sodium cymene sulfonate to 18 moles sodium hydroxide

EFFECT OF THE AMOUNT OF SODIUM HYDROXIDE UPON THE CARVACROL YIELD—A fusion experiment was carried out using 0.1 mole sodium cymene sulfonate with various amounts of sodium hydroxide in each tube. The fusion was carried out for 6 hrs. and at 350°, that is, at the optimum fusion temperature and period as previously determined. The results obtained are recorded in Table II, and graphically in Fig. 3.

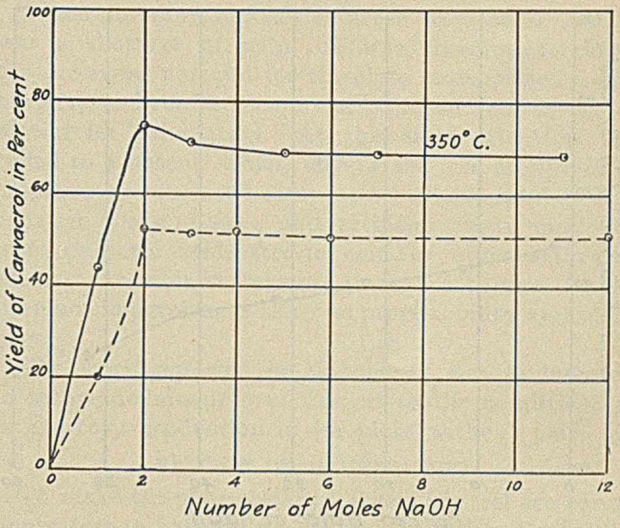

FIG. 3—CONCENTRATION-YIELD CURVES

The full curve plots the data found in Table II, and the dash curve is taken from the work of Hixson and McKee showing the yield by the open pot fusion at 360° for 6 hrs. with varying amounts of sodium hydroxide

TABLE II—FUSION MIXTURE

CONSTANTS—Temperature, 350°; time, 6 hrs.

VARIABLE—Ratio of sodium *p*-cymene sulfonate to sodium hydroxide

| Number | Number of Moles Sodium Hydroxide to 1 Mole of Salt | Carvacrol Yield Expressed as Per cent of the Theoretical |
|---|---|---|
| 1 | 1 | 43.4 |
| 2 | 2 | 74.4 |
| 3 | 3 | 70.8 |
| 4 | 5 | 68.3 |
| 5 | 7 | 68.5 |
| 6 | 11 | 68.1 |

This table indicates that a slight excess over the theoretical amount of sodium hydroxide should be employed, about 2.2 moles to 1 mole of sodium *p*-cymene sulfonate.

EFFECT OF WATER UPON CARVACROL YIELD—Since a charge consisting only of sodium cymene sulfonate and sodium hydroxide is apt to be too viscid to pour readily even at the temperature of 350° and since in large-scale productions it is very desirable to have the fusion mixture flow readily so that the fusion kettles can be emptied without difficulty, experiments were carried out for the purpose of determining the effect of water upon the carvacrol yield. The results obtained with varying quantities of water are shown in Table III and graphically in Fig. 4.

TABLE III—EFFECT OF WATER

CONSTANTS—Temperature, 350°; time, 6 hrs.; 1 mole of sodium cymene sulfonate to 2.2 moles of sodium hydroxide

Variable—Amount of water

| Number | Per cent Water in Charge Calculated on the Total Amount of NaOH Present | Carvacrol Yield Expressed as Per cent of the Theoretical |
|---|---|---|
| 1 | 2 | 74.7 |
| 2 | 12 | 72.0 |
| 3 | 22 | 70.5 |
| 4 | 32 | 68.4 |
| 5 | 42 | 66.8 |
| 6 | 52 | 62.1 |

The data in Table III show that water in the charge tends to decrease somewhat the carvacrol yield when the fusion period is 6 hrs. Data were next obtained

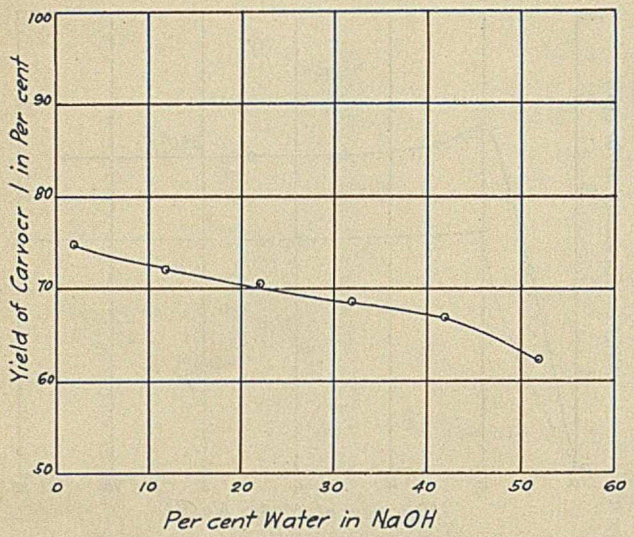

FIG. 4—CONCENTRATION OF WATER AS RELATED TO CARVACROL YIELD. GRAPHIC REPRESENTATION OF DATA FROM TABLE III

to show the effect of increased time of fusion with constant amounts of water. The six tubes were filled with a mixture consisting of 0.1 mole of the sulfonate, 0.22 mole sodium hydroxide and 50 per cent water (calculated as per cent of total amount of sodium hydroxide added) and heated for varying periods of time, from 2 to 22 hrs. The results are given in Table IV and in Fig. 5.

TABLE IV—TIME OF FUSION

CONSTANTS—Temperature, 350°; 1 mole sodium cymene sulfonate to 2.2 moles sodium hydroxide and an amount of water equal to 50 per cent of the weight of the sodium hydroxide

VARIABLE—Time

| NUMBER | Fusion Period in Hrs. | Carvacrol Yield Expressed as Per cent of the Theoretical |
|---|---|---|
| 1 | 2 | 54.2 |
| 2 | 6 | 63.6 |
| 3 | 10 | 68.0 |
| 4 | 14 | 65.1 |
| 5 | 18 | 62.2 |
| 6 | 22 | 49.5 |

This table indicates that a slightly increased fusion period is necessary when the fusion mixture is diluted with water.

It is to be noted from the data of Tables III and IV and Figs. 4 and 5 that the optimum yields of carvacrol were not obtained when water was incorporated in the reaction mixture, and since experiments carried out at 360° without water in the charge showed a decided lowering of the yield, the effect of water in the mixture fused at 360° was studied. The results are recorded in Table V, and graphically in Curve 3, Fig. 2.

TABLE V—FUSION PERIOD YIELD

CONSTANTS—Temperature, 360°; mixture, 1 mole sodium cymene sulfonate to 2.2 moles sodium hydroxide and an amount of water equal to 50 per cent of the weight of the sodium hydroxide

VARIABLE—Time

| NUMBER | Fusion Period in Hrs. | Carvacrol Yield Expressed as Per cent of the Theoretical |
|---|---|---|
| 1 | 1 | 29.8 |
| 2 | 2 | 41.3 |
| 3 | 4 | 54.0 |
| 4 | 6 | 55.7 |
| 5 | 8 | 57.5 |

This table shows that the destruction at high temperatures is much reduced by the presence of water and that the time of fusion must be increased.

## DISCUSSION OF RESULTS

From these experiments it appears that the highest yield of carvacrol is obtained when the fusion is conducted at 350° in an autoclave. When fused at this temperature with sodium hydroxide containing about 2 per cent of water, 6 hrs. seems to be the optimum fusion period. Fusions conducted for longer than 6 hrs. do not seem to affect the carvacrol yield either way. If, beside the sodium cymene sulfonate and sodium hydroxide, water is also added to the charge to the extent of 50 per cent of the sodium hydroxide used, the fusion period should be increased to 10 hrs., and under these conditions higher temperatures may be employed, thus increasing the speed of the reaction without materially affecting the yield. Small quantities of water, 10 to 20 per cent, have one beneficial effect in that the fusion mixture is more fluid, and the mass can, therefore, be readily removed from the kettle, a fact which is of considerable practical importance. So far as the sodium hydroxide is concerned, a little more than the theoretical amount should be used, 2.2 moles to 1 mole of the sodium cymene sulfonate being sufficient. More sodium hydroxide should not be used, because it is unnecessary and increases the cost of manufacturing by four factors—a reduced yield, the cost of the excess of sodium hydroxide, the cost of acid necessary to neutralize the excess and set the carvacrol free, and reduced capacity of the apparatus.

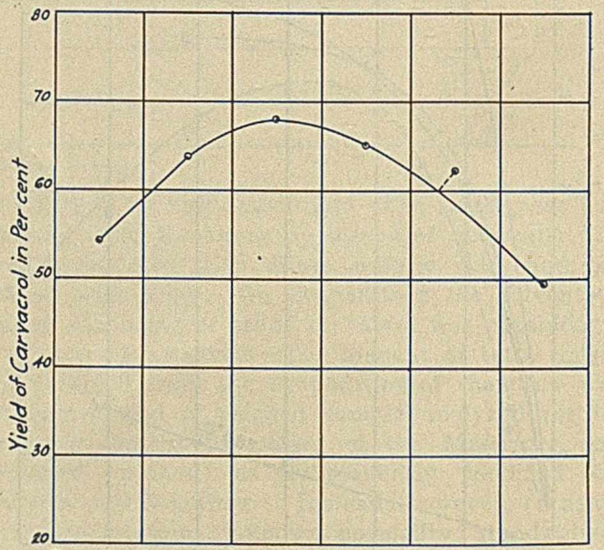

FIG. 5—FUSION PERIOD-YIELD CURVE WITH WATER IN MIXTURE. GRAPHIC REPRESENTATION OF DATA IN TABLE IV

The advantages of working in an autoclave are summarized as follows:

1—The very deleterious action of the oxygen of the air is reduced to a minimum.

2—No products distil during fusion and the reaction mixture remains constant in respect to water. A certain amount of water gives a cleaner product and permits easier emptying of the autoclave.

3—The contents of the autoclave are easily discharged through a valve at the end of the fusion, due to pressure generated within.

4—An increase of about 23 per cent in the yield is obtained by the laboratory investigations over the best laboratory yield obtained by Hixson and McKee,[1] that is, 75 per cent instead of 52 per cent. Under large-scale working conditions the presence of the necessary small amount of water in the melt may reduce the yield slightly, although it is possible that this may not be the case.

We wish to call attention to the accuracy of the method employed for determining the carvacrol in all of this work. By extracting with ether the acidified solution after fusion, a crude carvacrol is obtained that is contaminated by other extractive matter. The purity of the carvacrol extract varied from 75 to 99 per cent, and depended upon the conditions of the fusion and the care employed in drying the ether extract.

Schorger[2] weighed the ether extract and considered it as carvacrol. There is no doubt that his best yield of 52.9 per cent is for this reason too high. He employed potassium hydroxide for his open-pot laboratory fusions and states that the yields are very poor and hard to duplicate.

Hixson and McKee[1] extracted the crude carvacrol with benzene, removed the solvent by distillation and fractionated the product, taking the distillate between 227° and 245° as carvacrol; or removed the carvacrol by distillation of the acidified material with steam. Even if this material obtained by either method is further purified, as they state,[3] it seems reasonable to expect that it still contains impurities.

### SUMMARY

I—An apparatus especially suited to laboratory studies of caustic fusions is described.

II—The various factors of temperature, time, and concentration affecting the fusion of sodium cymene sulfonate with sodium hydroxide have been studied, and it is shown that by conducting the fusion in an autoclave yields of carvacrol as high as 75 per cent are readily obtained, as compared with less than 60 per cent by fusion in an open pot.

III—The fusions of other sulfonic acids are being studied.

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## THE USE OF HYDROGENATED OILS IN THE MANUFACTURE OF TIN PLATE

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The manufacture of tin plate in the United States consumes from 5,000 to 10,000 tons of palm oil per year. Many substitutes have been tried without success, and there has developed in the industry a general belief that no satisfactory substitute exists. Tallow was used in the early manufacture of tin plate, but for many years palm oil has been the only oil used in tin pots.

When shipping difficulties arose on account of the war a shortage of palm oil was threatened. With the increased demand for tin plate some pressure was brought to bear to secure the palm oil said to be essential for production. At this time attention was called to a patent[1] which covers the use of glycerides or esters of saturated fatty acids, all kinds of hydrogenated oils and fats, and artificial esters produced from palmitic acid, stearic acid, or other saturated acids. Available statements in regard to this process were not in agreement as to its practicability and economy.

The work reported in this paper was undertaken to secure definite information as to the conditions of satisfactory production of tin plate without palm oil.

### PROCESS OF MANUFACTURE

To make tin plate, cleaned sheets of steel are thrust singly into a bath of molten tin, entering through a layer of zinc chloride flux which covers part of the surface of the tin bath. The sheets are carried by rolls up out of the tin through oil which floats to a depth of about 15 in. over the tin. The oil serves to prevent oxidation of the surface of the tin bath, and to dissolve tin oxide which may be formed. The temperature of the tin is around 315° C. (600° F.), and that of the oil near the surface about 240° to 250° C. It is evident that oil for this purpose must stand a high temperature without undue volatilization or decomposition. With palm oil care must be taken that the temperature does not become too high, since at higher temperatures the oil polymerizes, loses its power to keep the plate clean, and is carried out on the plate in excessive amount.

### PRELIMINARY LABORATORY EXPERIMENTS

Before attempting a practical test a few experiments were made to observe the effect of heat on different oils. The vegetable oils obtained in the United States are all too volatile to be worth considering for continuous heating at 250° C. The only easily available hard oil is cottonseed oil hydrogenated to different degrees of hardness. For preliminary heating experiments there was at hand a lard substitute consisting of cottonseed oil hardened to an iodine number of 97 and some cottonseed oil hardened to an iodine number of about 19.

Lots of about 100 g. of oil were heated in porcelain crucibles which were set in holes in asbestos board over Bunsen burner flames. The temperatures were not regulated very closely and varied from 200° to 300° C. at different times.[2] Buttons of tin weighing about 50 g. and oxidized by previous heating in the air were placed in the bottoms of the crucibles. The oils were heated seven times, usually 5 or 6 hrs. at a time. The weights of oil and of tin were obtained after each heating. The tin was oxidized each time by heating in the air, and fresh oil was added to replace the loss during heating. At the end of the seventh heating the palm oil and the lard substitute

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[1] *Loc. cit.*

[2] This Journal, **10** (1918), 260.

[3] "This was done by redistilling the product obtained from the fusion liquor by either of the two methods mentioned. No difficulty was experienced in getting a product with a fairly constant boiling point."

[1] U. S. Patent 1,242,532 (October 9, 1917).

[2] Temperature readings in the laboratory heating tests were taken with thermometers not wholly immersed and were not corrected. They are, therefore, all low, but comparable for the different oils.

had polymerized to such an extent that they would have been entirely useless in a tin pot, so they were rejected and a fresh lot of palm oil was compared with the same hard oil and another material which had been offered as an improvement over the very hard oil. This material, a by-product fat, was more like palm oil in its physical properties and enough cheaper than the hardened cottonseed oil to make it more economical if it could be used. The lots were heated eight times more, when the palm oil and the by-product fat were so polymerized as to be useless. The very hard product was still in fair condition.

The behavior of palm oil in the crucibles resembled its behavior in a tin pot, that is, with successive heatings it became more viscous when hot, and harder when cold; the loss from fresh oil was more rapid than after it had been heated for some time; and it brightened the oxidized tin.

The lard substitute resembled palm oil, but it polymerized somewhat more easily. The by-product fat, which contained more free fatty acids than any of the other samples, attacked the oxidized tin much more vigorously. It lost more weight than palm oil at lower temperatures, and polymerized in about the same time. The heating tests indicated, on the whole, that the lard substitute and the by-product material would not give as good service as palm oil in a tin pot.

The very hard oil did not clean up the oxidized tin well during the first few heatings, but as the heatings continued, it became softer when cold than it was when fresh, and cleaned the oxidized tin well. At first the hard oil was much more fluid than palm oil when melted, but after several heatings it became somewhat thicker when melted. It lost much less weight than palm oil during the heating.

These experiments indicated that a very hard hydrogenated cottonseed oil might be expected to stand the heating in a tin pot without any disagreeable consequences in the way of unpleasant odors, excessive loss from volatilization or from polymerization with consequent carrying out of oil on the plate leaving the bath.

### COMMERCIAL TEST

In order to learn how the hardened oil would work in a tin pot, arrangements were made for an operating test. Through the kindness of Dr. David Wesson enough hardened cottonseed oil was secured to make a fairly thorough test. The first lot obtained had an iodine number of about 3. A second lot had an iodine number of about 17. This latter was the hardest oil which could be secured at the time without having a special run made, as was done for the first lot. There was no detectable difference in operation between the two lots.

The experiment was carried on at a tin plate plant which had been in operation less than a year. The equipment was therefore new and uniform throughout the plant, but had been operating long enough to be broken in and running normally. The tin pots were of the type most widely used in this country, with 84-in. rolls. The plate was cleaned by a machine of the usual type. Ground peanut hulls were used for cleaning.

At the start of the experiment all the oil was removed from one pot at the regular Saturday cleaning. Eight hundred and fifty pounds of hardened oil were added to the pot, and, on the basis of the preliminary heating experiments, the superintendent of the plant was urged to keep the oil as hot as possible over Sunday while the mill was not in operation. However, on account of unfortunate past experience with substitutes for palm oil, the foreman in charge kept the pot with hardened oil at a lower temperature than the pots with palm oil, which are normally kept much below the working temperature over Sunday.

When the plant started Sunday night very unsatisfactory plate was produced on Stack 9, where the hardened oil was in use. The plate continued poor for several turns after the other stacks began to produce satisfactory plate. It was not possible to clean the oil from the plate by one treatment, even when the pressure of the rolls in the cleaning machine was increased, and fresh peanut meal was added more often than usual. Recleaning removed all the surplus oil and gave a marketable plate, though the product of the first few turns was not up to the average quality of the plant.

The first plate made was not very bright. An average sheet selected from one of the other stacks by the manager appeared much better than an average sheet from Stack 9. Analysis of 12 samples from each of these two sheets showed an average of 1.33 lbs. of tin per base box for the sheet from Stack 9, and 1.72 for the other. Two sheets from Stack 9, taken during the second turn of its operation with hardened oil, carried 1.10 and 1.21 lbs. per base box. Five other sheets taken as representative sheets from Stack 9 during a period of 10 wks. carried 1.47, 1.33, 1.58, 1.58, and 1.55 lbs. of tin per base box.

After the first three days the plate from Stack 9 appeared to be in every way as good as the average product of the plant. At the beginning of the second week the first sheets made on all stacks in the plant were compared, and the plate made on Stack 9 was in no way different from that made on the other stacks.

The loss of oil by volatilization during the first week was much greater than the loss during subsequent weeks. The quantity added each day during any week was much less for Stack 9 than for those using palm oil.

After the first week no special attention was given to Stack 9, except to make sure that no palm oil was added. This was not difficult, as the tinners all preferred the hardened oil. It was operated with hardened oil alone for 12 wks. When the supply was used up additions of palm oil were made as required, with no effect on the operation of the machine.

The plate produced with hardened oil was not noticeably different from the rest of the plant product. Some observers thought that the front edges of the plate from Stack 9 were a little better than the average. The quantity of oil carried out on the plate appeared much less with the hardened oil.

TABLE I—LOSS OF WEIGHT ON HEATING 100 G. OF OIL FOR 5-HR. PERIODS AT THE TEMPERATURE INDICATED

| OIL | IODINE NUMBER | LOSS DURING EACH PERIOD | | | | | | TOTAL LOSS AT END OF EACH PERIOD | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 200° | 220° | 240° | 260° | 280° | 300° | 200° | 220° | 240° | 260° | 280° | 300° |
| Palm oil | 54 | 5.3 | 4.8 | 5.4 | 10.4 | 16.5 | .... | 5.3 | 10.1 | 15.5 | 25.9 | 42.4 | .... |
| Hardened cottonseed oil | 17 | 1.8 | 1.8 | 3.1 | 7.2 | 10.4 | 15.8 | 1.8 | 3.6 | 6.7 | 13.9 | 24.3 | 40.1 |
| Rendered tallow | 35 | 0.7 | 1.2 | 2.4 | 4.7 | 7.2 | 18.9 | 0.7 | 1.9 | 4.3 | 9.0 | 16.2 | 35.1 |
| Unrendered tallow | 32.5 | 2.0 | 1.3 | 2.7 | 1.1 | 5.2 | 11.6 | 2.0 | 3.3 | 6.0 | 7.1 | 12.3 | 23.9 |
| By-product fat | 32 | 11.3 | 16.9 | 15.8 | 5.5 | 9.2 | 7.4 | 11.3 | 28.2 | 44.0 | 49.5 | 58.7 | 66.1 |
| Hardened herring oil | 60 | 2.4 | 3.8 | 4.5 | 5.8 | 12.0 | 15.9 | 2.4 | 6.2 | 10.7 | 16.5 | 28.5 | 34.4 |

Although palm oil is not very disagreeable for the operator, the hardened oil was enough better in this respect to be noticeable.

The hardened oil in actual use did not show any tendency to polymerization, although at several times it was heated to temperatures much higher than would be safe with palm oil. There is also less danger of setting fire to the hardened oil when cleaning the tin pot.

There would seem to be no reason to expect economy in the consumption of tin with the use of hardened oil, unless the weight of coating on the plate should be decreased.

Six weeks after the hardened oil was used up the tin house records were examined by the superintendent of the plant and one of the authors of this paper. The production of plate and consumption of tin and oil on Stack 9 were compared with the values for the other stacks in the mill for several weeks preceding, for the 12 wks. of the test, and for the succeeding 6 wks. The following conclusions were reached: Over a considerable period Stack 9 does not differ materially from the average in performance. The tin consumption with hydrogenated oil was not appreciably different from that with palm oil. During the 12 wks. of the test the oil used per base box was not over $^3/_4$ of the average amount of palm oil used under similar conditions.

### IODINE NUMBERS OF OIL SAMPLES

No extensive analyses of oil samples were made. The first and second lots of hardened oil used had iodine numbers of 3.1 and 16.7, respectively.

At the end of the first week of use the hardened oil in the tin pot had an iodine number of 17.0. Samples on successive weeks gave values of 19.6, 21.2, 24.2, 25.3, 33.4. After the sixth week the values varied between 30.5 and 35.3 for the remaining 6 wks. of the test. Beginning at the thirteenth week, when palm oil was added, samples taken for 6 wks. had iodine numbers from 50.2 to 41.0, with no regularity in the variations. At about the middle of the period of use of hardened oil samples were taken on one day from 14 pots operating with palm oil. The iodine numbers varied from 41.7 to 53.6, the average being 45.0. Iodine numbers were obtained for several samples of beef tallow which had been heated in crucibles for different lengths of time. The original tallow had an iodine number of about 32. After heating for 5 hrs. at about 200° C., 6.5 hrs. at 220° C., and 7 hrs. at 240° C., the iodine number was 24.2. Further heating for 6-hr. periods at 260°, 280°, 290°, and 300° did not produce much change in the iodine number. It was from 22.3 to 24.5 for these samples.

These results indicate that palm oil in a tin pot will have an iodine number around 45, hydrogenated cottonseed oil about 32, and tallow about 23.

### HEATING TESTS

At the conclusion of the commercial test further experiments were conducted to determine losses on heating of the oils which had been used in the tin pots, together with some similar materials which were at hand. The palm oil and hardened cottonseed oil were from lots used in the experiment at the plant. Beef kidney fat, purchased at a local market, was used rendered and unrendered. The by-product fat has been described above. A sample of Alaskan herring oil which had been hydrogenated until it had an iodine number of 60 was obtained from the Oil, Fat and Wax Laboratory of the Bureau. Samples of about 100 g. of the oils were heated in crucibles for from 4 to 7 hrs. at each temperature from 200° to 300° C., inclusive, by 20° stages.

Table I shows the loss calculated on a basis of 100 g. original weight and a 5-hr. heating period at each temperature. The losses are given both for the individual periods and as total losses from the beginning of the heating to the end of each period.

The great loss of the by-product fat indicates clearly that there would be no advantage in using it when other materials were available. No values were obtained for palm oil above 280°, because at this temperature the oil polymerized to such an extent that it would be unfit for use in a tin pot. The behavior of the hardened cottonseed oil and of the palm oil is in agreement with their action in the tin pot. Tallow acts much like the hardened cottonseed oil in heating, and is said to resemble it in actual use. The chief objections to the use of tallow are said to be its unpleasant nature, as it decomposes in storage, and the greater difficulty in cleaning it from the plate, as compared with palm oil. The behavior of the hardened herring oil was very interesting. Although much softer than any of the other products except palm oil, having an iodine number of 60, it lost weight slowly on heating and showed very little tendency to polymerize on prolonged heating at 300°. It seems entirely probable that a more completely hardened oil of the nature of this sample of herring oil might prove superior to the hardened cottonseed oil for use in tin pots. It must be understood that these laboratory heating tests only indicate in a general way the probable relative losses in actual use.

### SUMMARY

Laboratory heating tests give useful indications of the relative values of different oils for use in tin pots.

During 12 wks. a tin pot using hydrogenated cottonseed oil operated somewhat better than with palm oil. The consumption of hardened oil was distinctly less than the consumption of palm oil. There was no appreciable saving of tin.

If palm oil should be unobtainable for the manufacture of tin plate, it could be replaced by hydrogenated cottonseed oil with no loss in operating efficiency.

With the industry adjusted to the use of palm oil, the higher cost of hardened oils probably balances the advantage to be obtained by their use, leaving little if any margin to pay for the privilege of using the hardened oils.

Heating experiments indicate that a hydrogenated fish oil might be obtained which would be satisfactory for use in tin pots, though hardened to a less degree than is necessary for the best results with cottonseed oil.

## LEAD COATED IRON[1,2]

### By Charles Baskerville

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Protective coatings for the prolongation of the life of iron and steel fall into three general classes, well described in a report from the Bureau of Standards (1919) as follows:

1—Metallic coatings.

2—Coatings in which the iron to be protected is itself converted at the surface into some less corrodible compound.

3—Organic coatings (varnishes, paints, enamels, etc.).

The present paper has to do with the first of the three classes and is especially concerned with the use of lead and lead-antimony alloy as protective agents.

If the iron be completely covered by another metal its life depends upon the ability of the covering metal to withstand the corrosive action of air and water to which it may be exposed. This is materially affected by the presence of various chemical fumes and gases such as sulfur dioxide, nitrogen oxides, chlorine, sulfuric acid, alkali-mists, etc. Mechanical strains, vibrations and the rough handling which usually obtains during packing, transportation, installation, etc., may bring about ruptures and scaling in the protective coating and thus expose the iron or steel which may have been originally perfectly covered.

The best manufacturing practice seeks a perfect coating initially but experience has shown the necessity for subsequent precautions because, where two metals, which always have a potential difference, are in juxtaposition in the presence of electrolytic water (acidulated, alkaline, or saline) electrolysis sets up with corrosion of one of them. If the iron be the electropositive member of the couple, it corrodes—the corrosion being activated by the presence of the other metal. Aluminum and zinc are electropositive to iron, and therefore are theoretically the best practical metallic protective coatings for iron, where the coating is broken, as they bear the burden of corrosion. Zinc forms several alloys with iron which are also electropositive to iron in a lesser degree. Tin, lead, copper, antimony and most of their alloys are electronegative, and hence facilitate the corrosion of the iron if it is incompletely covered or exposed by abrasion or other rough treatment. Practice has shown the importance of painting sheet tin and galvanized iron to fill in the broken coating.

Since lead is the cheapest of all the metals used for coating iron, and in addition gives the covered metal certain other desirable qualities, a commercial method of application has long been sought. It is hardly justifiable to incorporate here a bibliography on the subject. The most successful of the numerous efforts in this direction is the well-known terne plate, an alloy of about 75 per cent lead and 25 per cent tin, but this involves the use of costly tin. Lead has been successfully sprayed on iron by an atomizer (Schoop process) and the process is well suited for certain detailed protective work, but it is far too expensive in expert labor and time for tonnage production.

Modern interest in electronic conceptions and in the difference in properties of metallic allotropes caused us to investigate the processes covered by United States patents granted to Goodson,[1] which, briefly, consisted in subjecting a column of molten lead of small cross section in motion to the influence of an alternating current of low voltage and high current density for several hours, it being asserted that the lead thus became "activated," the molecular distribution effecting such change in physical condition that it would attach itself so firmly to iron that when the lead solidified it would not shrink away from the iron and leave exposed surfaces. Evidence of the production of an iron-lead alloy binder did not appear. The conditions detailed in the patents were carried out most conscientiously, with such additional advice and assistance as the inventor was able to give. It is hardly necessary to describe the apparatus used. Some promising results were obtained, but on checking up with metal not treated electrically the results were virtually duplicated.

Since it seemed that the problem of successfully and economically coating iron and steel with lead was not unsolvable, investigations were prosecuted along other lines and resulted in the production of products satisfactory for some purposes.

In working out a process for using lead and lead-antimony alloys as a protective coating on sheet iron and steel, the fundamental problem was to find a binder which would tie iron and lead firmly together. After much experimentation a preliminary coating of antimony proved to serve the purpose. Melted lead shrinks materially when it solidifies. Antimony tends to overcome this shrinkage, as is well known from the conduct and composition of type metal. Moreover, the alloy formed is harder than lead. With a preliminary coating of antimony followed by dipping in lead, the latter acquires an increasing percentage of antimony. This fact, together with the other observations, caused us to use a lead-antimony dip (eutectic of 12.5 per cent antimony) in the production of "protected iron" on a technical scale. Bending, twisting and hammering tests proved that the iron foundation would break before the coating. Photomicrographs clearly disclosed the antimony binder.

About 800 shingles, 9 × 16 in., of mild steel, of 24

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[1] Presented at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 11 to 13, 1919.

[2] Most of the experimental work described was done by Mr. V. A. Belcher.

[1] U. S. Patents 789,690; 789,215; 900,846; 900,847; 978,448; 1,061,066; other applications pending.

and 28 gauge, were made. Some of these sheets were subjected to aërated distilled water tests after having been pickled in sulfuric acid (6 : 1), washed with water, thoroughly blackened by an antimony chloride solution, again washed in water, and while still wet dipped through zinc chloride flux into molten lead-antimony (12 per cent), then into molten lead and finally quenched in oil. One series gave no iron rust indications during eleven days. In another series, aërated tap water tests brought out a few pinholes during the same period, but on the whole the condition of the samples was good. Allegheny iron, 26 gauge, showed some pinholes in both distilled and tap water aërated during 5 days. Rust usually showed first wherever there were sharp angles. In preliminary experiments many pinhole detection tests were made by the gelatin-ferricyanide method.

Two exposure tests of these shingles were made by the Research Laboratory of the National Lead Company, in Brooklyn, and are being continued. One test was with the coated shingles, packed and shipped in the same way as tin plate is, from the Maurer, N. J., plant of the United Lead Company. The other test was made with a smaller lot prepared at the same time, but painted on both sides. After an exposure to the weather for over three years, with all the varying conditions of temperature, rain, and snow of that period, both tests show 100 per cent efficiency, according to the reports from the director, Mr. G. W. Thompson. Another test was made by Mr. V. A. Belcher, on a roof in Michigan. After a considerable time the shingles were reported to be still in good condition. A test roof adjacent to a chamber sulfuric acid plant at Maurer, N. J., did not give satisfactory results. These shingles are not to be recommended, therefore, for use under the last-mentioned conditions, where considerable quantities of nitrogen oxides or sulfur dioxide may be in the air.

The weight of the protective coating was determined by cutting from shingles, test pieces presenting approximately 3 sq. in. of covered surface. After accurate measurement each piece was weighed. The metal was stripped with acid, washed, dried and again weighed. Iron, which had gone into solution by stripping, was separated and weighed as $Fe_2O_3$. The total iron thus determined, subtracted from the original weight of a piece, gave the amount of protective coating for the surface exposed. The average coating was 319.2 mg. per sq. in., or approximately 92 g. of coating per shingle. This was subsequently checked by weighing ten shingles before and after pickling, and before and after coating. The average proved to be 92 g. for 28 gauge and 93.5 g. for 24 gauge shingles, that is to say, 46 to 47 g. (about 1.5 oz.) per sq. ft.

Galvanized iron wire cloth was stripped with caustic soda. The wire was 23 gauge Trenton or 22 gauge B and S and corresponded to 4 mesh cloth. The amount of zinc per sq. in. averaged 438 mg. (63 g. or about 2 oz. zinc per sq. ft.). The nodules of zinc where the wires crossed varied in size. With wire gauze, 20 gauge Trenton or 19 B and S, 4 mesh, 12.5 per cent lead-antimony alloy gave 212 mg. coating per sq. in. (30 g. or about 1 oz. per sq. ft.). When first dipped in 12.5 per cent lead-antimony and afterwards in lead, the coating proved to be 270 mg. per sq. in. Cheap chicken wire and other netting may easily be coated with lead-antimony.

Several hundred feet of iron wire were coated, using an improvised outfit for moving the wire through the process. Smoothly drawn annealed wire took a good coating. Barbed wire was not successfully coated, for the points and sharp edges of the barbs were not covered, and quickly showed rust in the corrosion tests.

Extensive experiments were made in an effort to produce a satisfactory exterior coating on iron pipe to be used for petroleum pipe lines. Three-foot lengths of 8-in. pipe, some pieces being threaded at both ends, couplings for the same, and smaller pieces of 2-in. and 3-in. pipe, were used. All were obtained from the Pittsburgh plant of the American Tube Company. Suitable pickling vats, washers, antimonizers, and lead baths were devised, and a special mechanism designed and installed for dipping the pipe while in motion, the revolutions being controlled at will. Pipes were coated with lead and lead-antimony (12.5 per cent).

Corrosive experiments (aërated water tests, air exposure, burying in moist soil, etc.) showed a fairly good product, but not of sufficiently good grade to warrant production. The irregular surface of the pipe produced in milling interfered with perfect pickling and the subsequent necessary rough handling with pipe wrenches, etc., abraded the softer metal, thus exposing the iron.

At the request of the War Department, attempts were made to apply the process to produce a coating within shell to hold certain poison gases. Owing to the very irregular milled surface of the interior a perfect coating was not obtained.

The unusual recent interest in "passive" iron raised the question whether iron rendered passive might take a better coating of lead-antimony alloy. Two general methods of making iron "passive" were used; namely, treatment with aqueous solution of oxidizing agents (permanganates and dichromates) and with acid solutions. The final conclusion was that "passivity" did not improve the product.

A process was worked out for forming a binder on cast iron upon which pure lead could subsequently be cast and molded, especially for filter presses and filter frames. This involved the removal of silica (sand adhering from the mold), which prevented a uniform deposit of antimony and lead. The coating is successfully accomplished by introducing an extra step of pickling in hydrofluoric acid prior to treatment with the antimony salt solution. The coating thus produced is not sufficiently heavy and uniform to admit of practical use, but forms an excellent binder for casting thereon lead or lead alloy of any desired thickness.[1]

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[1] The process covering the treatment to secure the satisfactory binder is covered in application for U. S. Patent 847,323.

Sheet iron may be pressed into a variety of shapes without lubricants. If, however, the metal is subsequently to be plated (nickel, copper, etc.), the shaped articles (caps for automobile hubs, etc.) require pickling. Iron in sheets lends itself to pickling much more readily than when already shaped and formed. Moreover, in pressing, the scale is often forced into the metal, making pickling an even more difficult and expensive process. Lead is soft and, even though the deposit be not devoid of pinholes, serves as a lubricant in pressing. Processes have been worked out in this laboratory for plating lead-coated iron with copper or nickel or both.

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## SUGAR SIRUP FROM HOME-GROWN SUGAR BEETS[1]

By John M. Ort and James R. Withrow

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Sirup can be made from home-grown sugar beets for both culinary and table purposes. When made by published methods, this sirup is not always completely palatable and free from beet flavor. Experimental modifications of published processes gave a product leaving much to be desired, though it possessed no more objectionable flavor than the average sorghum sirup. The complete elimination of green portions greatly advanced the production of a highly satisfactory sirup flavor.

Interest in the subject among farmers is no new thing. Sugar beets are easily grown and a small plot would furnish the average rural household with ample sugar sirup. Beet sugar making would probably be a universal farm industry in many parts of the country if there were any simple way of consistently eliminating objectionable beet flavor from the sirup. The beets contain from 12 to 20 per cent sucrose, as high as 28 per cent having been observed. The yield of beet sugar per acre varies much, but averages from 0.8 to 1.8 tons, while sugar cane is stated to yield 4 to 5 tons per acre.

### DELETERIOUS SUGAR BEET FLAVORING CONSTITUENTS

In the manufacture of sugar from beet juice most of the salts and deleterious material are left behind in the residual sirup or molasses, which is salable only as a cattle food or fertilizer. The removal of the impurities of beet sirup has been the subject of experiment ever since beet sugar manufacture began. To obtain good sugar a complicated treatment of liming, carbonation, etc., must be followed and considerable sugar is left in the molasses. The sugars are believed to be held back by the albumins, alkalies, soluble nonprotein nitrogenous matters, potash, and other salts. These probably form a large portion of the undesirable flavoring material, and it is the opinion of beet sugar men generally that the sirup itself cannot be made suitable for human food. The *Sugar Beet*, October 1906, p. 124, states: "The simple concentration of beet juice would yield a sirup of very objectionable flavor and odor. To overcome this difficulty numerous laboratory experiments have been made during the last 50 years. None of the processes proposed had the slightest practical value, for all the products obtained were absolutely worthless." In the same publication it is stated that Salisbury and Kramper suggested that maple sirup be added to give the desired flavor.

C. O. Townsend and H. C. Gore[1] describe "a simple process of making from sugar beets a palatable and nutritious table sirup with a pleasant flavor. A patent for the process was issued to the authors of this bulletin for the benefit of the public so that any one is free to use it.[2] Tests by farmers as well as by the Department have proved the process to be practicable."

The authors give very complete directions in the Bulletin emphasizing especially the following points:

1—Cutting off the crowns of beets "at the point of the lowest leaf scar." The reason assigned is "that the crown or upper part of the beet contains a large part of the salts taken from the soil in the process of growth. It is desirable to have the sirup as free as possible from these mineral salts which, if present in too large quantities, would render the sirup unpalatable."[3]

2—Scrubbing free from dirt.

3—Skimming the boiling sirup. The authors state: "This operation removes the strong beet-like flavor and leaves a wholesome and palatable product."

4—Slow boiling.

5—Avoid scorching.

Although the method was simple, many reports of failure came to Ohio farm journals. Improper topping of beets was supposed to cause the difficulty.

References to the actual constituents causing taste and odor in the beet sirup are not plentiful. Classen[4] states that "the injurious nonsugars are defined as alkalies and soluble nonprotein nitrogenous matters." Leach and Winton[5] state that "beet sugar molasses is unfit for food, due to the presence of nitrogenous bodies which give it a very unpleasant taste and smell." Ware[6] gives "albumin amides" as an occurrence in the raw juice. Reference is also made to the presence of "alkalies, ammonia, and organic bases."

Of the substances identified as constituents of sugar beets, the nitrogen derivatives are apparently not the cause of the undesirable flavor. Trimethylamine is sometimes suggested as the offensive constituent, but it does not seem to exist in the sugar beet. The fact that it results as a destructive distillation product of the molasses does not prove that other processes

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

[1] "Sugar Beet Syrup," U. S. Dept. of Agr., *Farmers' Bulletin* **823** (1917), 2.

[2] U. S. Patent 1,155,806 (Oct. 5, 1915).

[3] See also G. L. Spencer, *Agricultural Yearbook*, **1898**, 313.

[4] "Beet Sugar Manufacture," Trans., Hall & Rolfe, 2nd Ed., p. 81, John Wiley & Sons, Inc., N. Y., 1910.

[5] "Food Inspection and Analysis," 3rd Ed., p. 570, John Wiley & Sons, Inc., N. Y.

[6] "Beet Sugar Manufacturing and Refining," 1st Ed., **1** (1905), 136, 346, J. Wiley & Sons, Inc., N. Y.

may lead to its formation. Betaine, which does occur, is described as sweet. Choline, whatever its taste, is toxic.

The object of the present investigation was to remove the undesirable flavor without injuring the sugar. The separation of the sugar as such would be wasteful and difficult in the kitchen or on the farm, and was not undertaken in the present work.

### EXPERIMENTAL

The beets used were grown in Ohio, near Toledo. Two bushels were received in November 1918, and 4 bushels in January 1919.

Details of the various methods of experiment need not be given further than to indicate results. While keeping strictly in mind the simplicity requirements of home treatment, a few experiments were added for broader insight into the behavior of the deleterious materials.

As the work resolved itself largely into a question of flavor, the preparation of large amounts of sirup by any one process was not necessary. Three to six beets (about 5 kilos) were ordinarily enough for an experiment. Following the directions of Townsend and Gore, the well-topped, unpared but sliced beets were just covered with boiling water, the temperature of which became thereby reduced to 70° to 80° C., as stated. They were occasionally shaken and unless otherwise indicated left to soak one hour. The temperature fell to 70° C. The juice was strained through cheese-cloth, evaporated over a low fire and skimmed from time to time. The thick sirup was very sweet but with a peculiar rubber- or beet-like flavor and odor. 450 cc. of sirup were obtained.

A long series of attempts was next made to eliminate or destroy the undesirable flavor. Among them may be mentioned clarification by milk, as in the case of maple sirup; preliminary desiccation, both atmospheric and vacuum, to coagulate albumins, etc.; liming, with subsequent precipitation by $(NH_4)_2CO_3$; peeling, decoring, dialysis; and treatment with such substances as fuller's earth, tannic acid, bleaching powder, basic magnesium carbonate, $Na_2SO_3$, $NH_4OH$ followed by $H_3PO_4$, and bone-black. Varying degrees of clarification were secured but no marked improvement in flavor. The use of Celite appeared to improve the flavor at times. Iron, like copper, left a metallic after-taste, less pronounced than when copper was used, and gave a darker sirup.

Variations of the temperature of extraction gave no improvement. A cold water extract had the same flavor as a hot one.

Experiments on the influence of the time of soaking the beets indicated that the greater part of the undesirable flavor was removed in the early part of the soaking period. The product of a 10-min. soaking was more bitter than that of the next 50 min., but the latter was not as much improved as was desirable. A process of peeling, decoring, slicing, and preliminary extraction for 10 min. gave an extract during the next 50 min. from which the peculiar flavor was not entirely eliminated, but it was not prohibitively prominent, and the sirup was light colored, nearly as bright as maple sirup, and by far the best tasting sirup produced in the early part of the investigation. Subsequent lime treatment gave a slight bitterness.

Salisbury and Kramper's method, using alum and $NaHCO_3$, gave a flavor differing from the usual one, possibly due to the alum. We agree with the authors that the product may have maple sirup added with advantage.

When samples of the sirup were boiled down, with stirring, to a white, dry, very light and fluffy powder, there appeared to be little objectionable flavor, but when dissolved in water to form a sirup, it was found to be unimproved. By aging sirup which had been sealed up while hot, good crystals of sugar could be obtained, but the bulk of the solid sugar separating had the usual beet flavor.

Toward the end of the work the beets began to soften and deteriorate from lack of proper care. It was concluded to investigate the influence of possible scorching from local superheating by direct fire evaporation. Previous work had been carried out in enamel ware dish pans. A steam-heated copper kettle was now used, treating the beets as in *Bulletin* 823. The product had a less objectionable flavor than any previous sirup made by this method and was probably as good as previous sirups made by any method. However, the after-taste of copper was left and it was ultimately concluded that, as in beet sugar manufacture, the nature of the juice renders copper vessels undesirable. To ascertain the reason for improvement in quality, a double run was made over a free flame in dish pans, using both the *Bulletin* 823 method and the method of careful decoring and peeling, which gave much better products than before with either method.

Further runs were made with both steam and flame evaporation to compare softened beets with hard beets to see if ripening processes had any part in the sudden ability to produce a good sirup, but no such distinction was found. It was noticed, however, that many of the beets had green shoulders, looking like sunburned potatoes, which develop an intensely bitter taste upon cooking. When this green portion was pared off a good sirup was produced, with but a trace of beet flavor, and even occasionally with no such flavor detectable. No extensive investigation of this point could be made on account of lack of material, but if it should be found that this method will give consistent results, it will be a simple matter to reduce the green portion by keeping the beet roots well covered with earth in the field. Sirup actually made from these green portions possessed the undesirable flavor to a very great degree, and was very dark colored. It is likely, therefore, that some, if not all, unsuccessful results bear a relation to this green portion of the beets. At sugar refineries beets are processed "as is" and no opportunity is given for selection, whereas we frequently used beets which (by accident) possessed little or no green portions. This doubtless explains the good results of Townsend and

Gore, and their failure to advise removal of the green portions.[1]

Ware calls attention[2] to the excessive amounts of albumin amides in unripe beets. Experiment showed that otherwise good sirup, if run down too far so as to really scorch, possessed an odor of urine or amines.

The color of the sirup from sugar beets was usually dark brown and turbid. Better filtration through felt or absorbent cotton, as in maple sirup production, will reduce turbidity and thereby reduce beet flavor. The beet slices after extraction rapidly became dark brown or black, as many vegetable materials do. A batch run down as rapidly as possible produced sirup many shades lighter than any previous product; in fact it was paler than many grades of maple sirup.

A single illustration of the quantitative results may be given. Seven beets were peeled and all rotten and green parts removed. The weight was 4.3 kilos. They were sliced, soaked in water as usual for an hour, the juice strained and the water extraction repeated. Results are shown as follows:

|  | Sirup Yield | Sp. Gr. at 15° C. | Sucrose by Sp. Gr. | Sucrose by Polariscope | Sucrose Recovered |
|---|---|---|---|---|---|
| First | 325 cc. | 1.400 | 77.5 per cent | 75 per cent | 252 g. (by sp. gr.) |
| Second | 175 cc. | 1.280 | 58.2 per cent | 54 per cent | 102 g. (by sp. gr.) |

The sucrose by specific gravity was taken from the usual tables. The polarimeter determination was by the method described in Leach, assuming that nothing optically active was present except sucrose. From these figures 9 beets would yield $^3/_4$ lb. of sugar equivalent, or 8.2 per cent of the weight of the peeled beets. The wastage from whole beets from paring may be as high as 20 per cent. Gore and Townsend state that 30 or 40 beets averaging from 1 to 2 lbs. make a bushel and give from 3 to 5 quarts of sirup.

It has been suggested that beet sirup might produce diarrheal effects, due to its salts, but such an effect has not been reported to us. It would appear that the salts of sorghum also have no such objectionable quality.

The statement has been made that the sirup does not keep well. In our work no attempt was made to preserve the product. Specimens which were opened but seldom remained in good condition. The sirup contains abundant material to support mold growth, and thorough sterilization is necessary. Maple sirup would also sour if it were thinner than 11 lbs. per gallon (65 per cent solids and 35 per cent water).

The cost of sugar beet sirup making will vary with the individual case. With proper care beets can be stored for months and manipulated as required, or the product made in equipment like that for maple sirup and canned for use. Maple sirup in Ohio cost 45 to 75 cents per gallon to produce before the war. Beet sugar sirup under the same conditions would probably cost about 75 cents, because of extra labor.

### CONCLUSIONS

1—The various published processes for making palatable sugar beet sirup do not consistently fulfil all claims made for them.

2—The use of copper kettles in beet sirup making is undesirable since it gives a metallic after-taste to the sirup. Enamel and aluminum ware are satisfactory.

3—The process of skimming will not in itself eliminate objectionable beet flavor.

4—The peculiar flavor can be practically eliminated from sugar beet sirup by proper attention to topping, paring off green portions, and brief preliminary extraction. The entire absence of green portions is necessary to good flavor.

5—The objectionable beet flavor may be due partly to immaturity. Preliminary storage of beets in this case will improve flavor.

### ACKNOWLEDGMENT

The thanks of the authors are due to Professor Vernon Davis, Ohio Director of Markets, for suggesting the problem and for furnishing beets, and to Prof. C. W. Foulk and Dean Clair Dye for suggestions.

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[1] When it was found that very unpalatable sirup was obtained by following the directions of *Bulletin* **823**, an inquiry was sent to the Department of Agriculture to ascertain the experiences of others. After this paper was read at the Buffalo meeting, a reply was received stating that varying results had been obtained. This was ascribed in some cases to the use of immature beets. It was also learned that the U. S. Dept. of Agriculture, Bureau of Plant Industry, Office of Sugar-Plant Investigations, in order to meet the difficulties encountered in following *Bulletin* **823**, now issue a mimeographed sheet calling attention to recent investigations advising additional precautions, inasmuch as air oxidation, the darkening of sliced beets, and failure to remove beet skin have "a marked effect on the color and flavor of the sirup." The statement is made that "the long continued boiling....results in an improvement of flavor," eliminating "much of the characteristic....objectionable beet-like flavor." The additional precautions recommended are:

1—Thorough ripeness of beets.

2—Peeling.

3—Immediate slicing into sufficient water to cover at least one inch to avoid darkening by air.

4—Raising temperature to 80° C., using wooden rack at bottom to avoid scorching.

Continued careful scum removal is again emphasized. The product is of the light improved quality obtained in the work herein reported. The new directions state that the sirups "possess little or none of the more or less objectionable flavor and unpleasant after-taste sometimes noted in sirups made according to the other method."

These precautions are similar to those used in the present investigation and should give better results than the original directions. No instructions are given or emphasis laid in either set of directions upon the importance of eliminating the green portion of the beet and it is probable that peeling would not entirely remove this part. The emphasis upon thorough ripeness does not cover the case, because green topped or shouldered beets may be otherwise thoroughly ripe and make good sirup if properly pared. The supplemental directions state that *Bulletin* **823** directs that: "The tops are removed, cutting them at the line of demarkation between the green and white skin," etc. No such direction was given in *Bulletin* **823**, the lowest leaf scar being the point designated, whereas on beets 12 in. long the green color on an otherwise good beet may go as low as 9 in. Such cutting would produce good sirup but waste much of the beet. In our experience the green outer part can be cut off, saving the inner part for sirup with little waste of beet.

[2] *Loc. cit.*, **1**, 348.

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## LIPOLYTIC ENZYMES IN OLIVE OIL

By Thos. M. Rector

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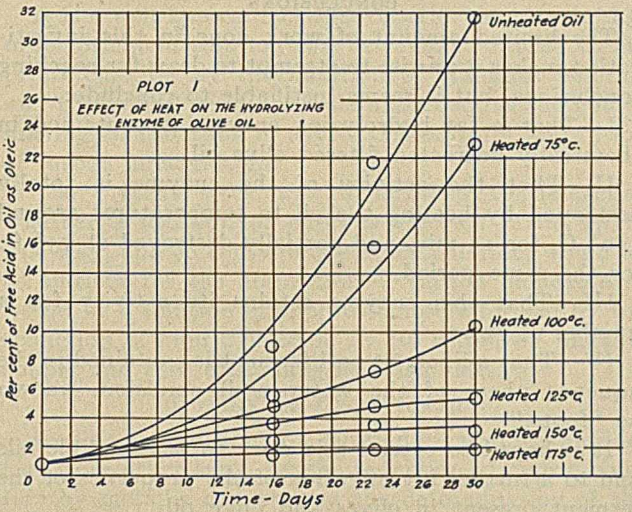
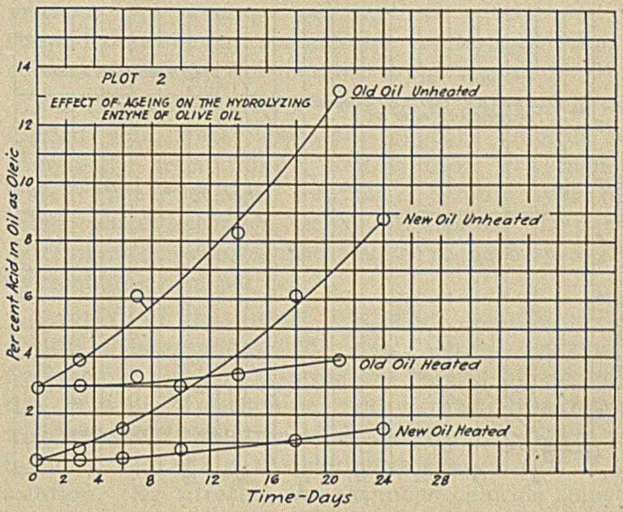
Received August 5, 1919

It has long been known that oil-bearing seed contains lipolytic enzymes which function in the germination of the seed, converting the oil into a form available as food for the young plant. The enzymes of these oil seeds, especially of castor seeds, have been extensively investigated. In fact, several commercial methods have been evolved by which oils are split into fatty acids and glycerin by means of the enzymes of castor seed and a few others of similar nature.





A fat hydrolyzing ferment, called "olease" by its discoverer, Tolomei,[1] has been isolated from olive pulp. It is claimed to be the active agent in the fermentation of the olive after crushing. Oils pressed from stored pulp or from olives that have been roughly handled often contain more than 50 per cent free acid, and for this reason olives must be pressed as soon after crushing as possible in order to obtain an oil of low acid value.

The better grades of edible olive oil come into the market without treatment other than settling and filtration. It therefore seemed possible that freshly filtered oil might contain a sufficient quantity of enzymes to produce a measurable amount of fatty acids if the oil was emulsified with water and kept at a favorable temperature. In a preliminary test such an emulsion was rapidly hydrolyzed, whereas the acidity of an emulsion of the same oil previously heated to 200° C. remained nearly constant. Further experiments were therefore made.

## EXPERIMENTAL

EXPERIMENT 1. EFFECT OF HEAT ON THE ENZYME.—In order to test the effect of heat on the catalytic body present in the oil, five 100 cc. portions of oil were measured into 200 cc. Erlenmeyer flasks and heated as rapidly as possible to temperatures ranging from 75° to 175° C. After remaining at the desired temperature for 15 min. the flask was cooled in a stream of cold water.

Emulsions of the heated oils were prepared in the following manner: 50 cc. portions of the oils were placed in 200 cc. Erlenmeyer flasks, 4 g. of gum tragacanth and 2 cc. of toluene were added to each flask, and the mixture shaken until free of lumps. 50 cc. of water were then added, and the flasks corked and shaken violently. By this treatment such a thick emulsion was produced that the flask could be inverted without the contents flowing out.

As a control test an emulsion was made in the same way with unheated oil. The acidity of these emulsions was determined at the beginning of the test period and at intervals during a period of 30 days, according to the customary method of determining the acid value of oils; that is, a sample of about 10 g. of the emulsion was weighed into a 300 cc. flask, 50 cc. of neutral, 95 per cent alcohol added, and the whole heated on the water bath for 30 min. The sample was then removed from the bath and titrated with $N/10$ sodium hydroxide in the usual way. In Table I the results are expressed as per cent of oleic acid in the oil phase of the emulsion (see also Plot 1).

TABLE I

| | | At Start | 16 Days | 23 Days | 30 Days |
|---|---|---|---|---|---|
| Unheated | .... | 0.7 | 8.9 | 21.6 | 31.6 |
| Heated | 75° C. | 0.7 | 5.5 | 15.8 | 22.8 |
| Heated | 100° C. | 0.7 | 4.8 | 7.2 | 10.3 |
| Heated | 125° C. | 0.7 | 3.6 | 4.8 | 5.3 |
| Heated | 150° C. | 0.7 | 2.3 | 3.5 | 3.1 |
| Heated | 175° C. | 0.7 | 1.4 | 1.7 | 1.7 |

EXPERIMENT 2. EFFECT OF AGE OF OIL ON ENZYMIC ACTIVITY—The oil used in the previous series of tests was about 8 mo. old. In the second experiment the enzymic activity of this oil was compared with that of oil which had been kept in a tightly corked bottle in a wooden case for a period of about nine years. Emulsions were accordingly prepared with the old oil, both heated and unheated, and the oil used in Expt. 1 heated and unheated.

TABLE II—INCREASE OF ACIDITY IN OIL WITH TIME (See Plot 2)

| | At Start | 3 Days | 6 Days | 7 Days | 10 Days | 14 Days | 18 Days | 21 Days | 24 Days |
|---|---|---|---|---|---|---|---|---|---|
| Old Oil Unheated | 2.9 | 3.9 | ... | 6.1 | ... | 8.3 | ... | 13.2 | ... |
| Old Oil Heated | 2.9 | 3.0 | ... | 3.3 | ... | 3.4 | ... | 3.9 | ... |
| New Oil Unheated | 0.4 | 0.8 | 1.5 | ... | 3.0 | ... | 6.1 | ... | 8.8 |
| New Oil Heated | 0.4 | 0.4 | 0.5 | ... | 0.8 | ... | 1.1 | ... | 1.5 |

Since the emulsions used in the first series of experiments were semi-solid and very difficult to handle, the formula was changed to give a less viscous mixture as follows: 100 cc. of the oil and 2 cc. of toluene were rubbed in a mortar with 3 g. of finely powdered Indian gum, a gum similar to tragacanth, until all lumps were disintegrated; 75 cc. of water were added all at once and the mixture stirred vigorously with an egg beater. A thick emulsion was formed almost instantly. This was diluted with 75 cc. of water, added a little at a time with continued stirring. By this method there was formed a freely flowing, finely divided emulsion which did not separate after a month in the incubator at 37° C.

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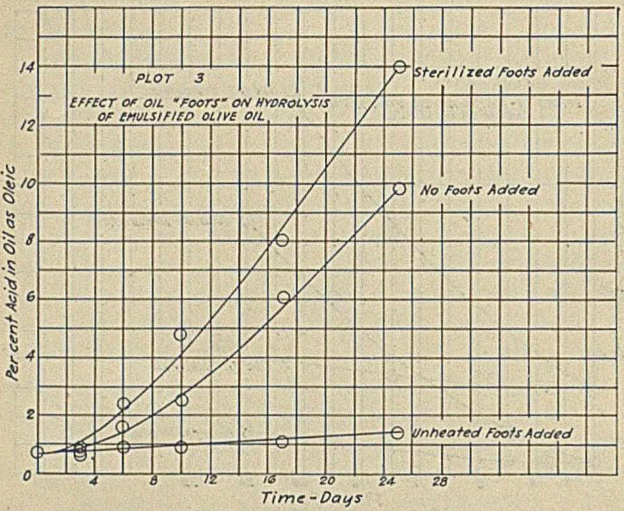
[1] *Atti. Acad. Lincei*, 1896.



EXPERIMENT 3. EFFECT OF OLIVE OIL "FOOTS" ON THE HYDROLYSIS OF OIL BY ENZYMES—It was thought probable that fat-splitting enzymes would be concentrated in the sludge settling in the bottom of the olive oil tanks, known to the trade as "foots." Accordingly some very "footy" oil was run through a Sharples centrifuge at 17,000 r. p. m. A thick, black slime was deposited in the interior of the separator bowl. This concentrated oil "foots" gave the following figures on analysis:

| | |
|---|---|
| Water | 27.40 per cent |
| Ash | 9.27 per cent |
| Oil | 26.79 per cent |
| Undetermined | 36.54 per cent |

50 g. of this concentrated "foots" were suspended in sufficient water to make 500 cc. This mixture was divided in two portions, one of which was heated in a steam sterilizer for 15 min. at 15 lbs. pressure. Emulsions were then made up by the same procedure as in Expt. 2, according to the following formulas:

3*a*

| | |
|---|---|
| Olive Oil | 100.0 cc. |
| Indian Gum | 3.0 g. |
| Toluene | 5.0 cc. |
| Water | 150.0 cc. |
| Unheated "foots" | 2.5 g. |

3*b*

| | |
|---|---|
| Olive Oil | 100.0 cc. |
| Indian Gum | 3.0 g. |
| Toluene | 5.0 cc. |
| Water | 150.0 cc. |
| Heated "foots" | 2.5 g. |

3*c*

Identical with *a* and *b* but without "foots."

It was found that in Emulsion 3*a* containing the unheated "foots" the hydrolysis of the oil was almost completely inhibited. In 3*b*, however, which contained the heated "foots" the hydrolysis ran parallel to that of the control emulsion. From this it seems apparent that the "foots" contained an anti-ferment, the effect of which is nullified by heat. The data on this series of experiments are as follows:

TABLE III—INCREASE OF ACIDITY IN OIL WITH TIME (See Plot 3)

| | At Start | 3 Days | 6 Days | 10 Days | 17 Days | 25 Days |
|---|---|---|---|---|---|---|
| Heated "foots" added | 0.7 | 0.9 | 2.4 | 4.8 | 8.0 | 13.9 |
| No "foots" added | 0.7 | 0.8 | 1.6 | 3.0 | 6.0 | 8.8 |
| Unheated "foots" added | 0.7 | 0.7 | 0.9 | 0.9 | 1.1 | 1.4 |

CONCLUSIONS

The limited amount of work done in this investigation makes it unwise to attempt to draw far-reaching conclusions, but it seems justifiable to conclude:

I—That a fat hydrolyzing enzyme is contained in chemically untreated filtered olive oil.

II—That the activity of the enzyme is totally destroyed by heating the oil to temperatures around 150° C. for 15 min. and partially destroyed at 75° C. for the same period.

III—That this enzyme retains its activity for a number of years.

IV—That a lipolytic anti-ferment is contained in the aqueous phase of the water-in-oil emulsion, known as "foots."

It is hoped to extend this work to other edible oils and to a further investigation of the properties of the ferment present in olives and olive oil.

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## A CONVENIENT METHOD FOR THE PREPARATION OF A HYDROCHLORIC ACID SOLUTION OF CUPROUS CHLORIDE FOR USE IN GAS ANALYSIS

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Cuprous chloride, dissolved either in ammonium hydroxide or in hydrochloric acid, is used extensively in gas analysis for the absorption of carbon monoxide. Unless kept from contact with the air, cuprous chloride, especially in solution, changes to the stable cupric chloride, which is not an absorbent for carbon monoxide. For this reason the methods of preparing solutions of cuprous chloride for gas analysis are more or less tedious, and care is necessary to prevent oxidation.

As an absorbent for carbon monoxide in gas analysis, Winkler[1] prepares a hydrochloric acid solution of cuprous chloride as follows:

> 17 g. of finely divided copper (preferably copper powder from copper oxide reduced by hydrogen) are mixed with 86 g. of copper oxide, and the mixture is added to 1086 g. of hydrochloric acid (sp. gr. 1.124). This is tightly stoppered to exclude air and allowed to stand several days. The brown solution becomes colorless, indicating that all the copper is in the form of cuprous chloride.

Sandmeyer[2] treats 25 parts of crystallized copper sulfate and 12 parts of sodium chloride with 50 cc. of water, and heats until the copper sulfate dissolves. Sodium sulfate separates out, but is not removed. To this solution 100 parts of hydrochloric acid and 13 parts of copper turnings are added and the mixture boiled until it becomes colorless.

Frischer[3] suggests the preparation of an ammoniacal solution of cuprous salt by adding ferrous sulfate to an ammoniacal solution of copper sulfate.

Thus it appears that the presence of such compounds as ammonium chloride, sodium sulfate and ferric sulfate do not affect the efficiency of solutions of cuprous salts for the absorption of carbon monoxide.

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[1] Dennis, "Gas Analysis," p. 232.

[2] *Ber.*, **17** (1884), 1633.

[3] *Chem.-Ztg.*, **32** (1908), 1005.

It is a well-known fact that cupric chloride in hydrochloric acid solution can be readily reduced to cuprous chloride by the addition of stannous chloride and this would seem a simple and effective method of making up a solution of cuprous chloride for absorption of carbon monoxide gas.

The present work was undertaken to determine whether a solution of cuprous chloride made up in this way, and so containing stannic chloride, would be as efficient for the absorption of carbon monoxide as would be a solution of cuprous chloride formed by the reduction of cupric chloride by its action on metallic copper and thus containing no other salts.

### OUTLINE OF INVESTIGATION

1—The preparation of a solution of cuprous chloride, free from other salts, by the reduction of cupric chloride by metallic copper, and the determination of the acidity and copper content of this solution.

2—The preparation of a solution of cuprous chloride, equivalent to the above in its acidity and copper content, by the reduction of cupric chloride by stannous chloride.

3—A comparison of these solutions as to their efficiency for the absorption of carbon monoxide under conditions similar to those of ordinary gas analysis.

### PREPARATION OF MATERIAL

**CARBON MONOXIDE**—The carbon monoxide used was prepared by the action of concentrated sulfuric acid on oxalic acid. The carbon dioxide and the carbon monoxide formed in this reaction were slowly passed through a train of three wash bottles of caustic potash and two wash bottles of alkaline pyrogallol to remove all carbon dioxide and oxygen. The purified carbon monoxide was then stored in a glass gasometer. Every 50 cc. of this sample were found to contain 40.2 cc. of carbon monoxide and 9.8 cc. of nitrogen.

**CUPROUS CHLORIDE SOLUTION FREE FROM OTHER SALTS**—Crystals of cupric chloride were dissolved in water, and enough concentrated hydrochloric acid added to hold in solution the cuprous salt which was to be formed. This solution was placed in a flask with strips of metallic copper, and heated under a reflux condenser until the reduction was well started. The solution, which will hereafter be referred to as Solution A was then placed in a well-stoppered flask and allowed to stand until colorless.

**STANNOUS CHLORIDE SOLUTION**—About 300 g. of metallic tin were placed in a 500-cc. flask and covered with concentrated hydrochloric acid. The mixture was heated to a slow boil, over a sand bath, for several days, and a small amount of fresh acid added from time to time until the solution was saturated with stannous chloride. The solution was then filtered and placed in a flask containing metallic tin to prevent the oxidation of the stannous chloride.

### CONCENTRATION OF THE SOLUTIONS

**COPPER IN SOLUTION A**—One cc. of the cuprous chloride solution was oxidized to cupric chloride by the addition of dilute nitric acid and then diluted with water to 30 to 40 cc. The amount of metallic copper present was then determined by the ordinary iodometric method. An average of duplicate determinations showed that the cuprous chloride solution, Solution A, contained 0.1272 g. of metallic copper per cc.

**ACIDITY OF SOLUTION A**—Ten cc. of Solution A were diluted with water until the cuprous chloride was completely precipitated. The solution was then titrated with a standard solution of sodium hydroxide, using phenolphthalein as an indicator. Duplicate determinations showed the acidity to be 0.2518 g. of hydrochloric acid per cc.

**ACIDITY OF STANNOUS CHLORIDE SOLUTION**—The acidity of the stannous chloride solution was determined by precipitating and filtering out the tin by the addition of sodium carbonate, and titrating the filtrate with a standard solution of silver nitrate. There was found to be 0.934 g. of chlorine in every 2.5 cc. of the solution. By titrating the stannous chloride solution with a standard copper solution, 2.5 cc. were found to contain 0.934 g. of chlorine combined as $SnCl_2$. Since this amount is the same as the total amount of chlorine found to be in 2.5 cc. of the stannous chloride solution when it was titrated with silver nitrate, there was no free acid in this particular solution.

By titration it was also found that 1 g. of cupric chloride was completely reduced to cuprous chloride by 0.7 cc. of stannous chloride solution.

**PREPARATION OF CUPROUS CHLORIDE SOLUTION BY REDUCTION WITH STANNOUS CHLORIDE**—Jones[1] found that cuprous chloride moistened with water to form a paste or suspended in water would absorb carbon monoxide to the same extent as if it were dissolved in acid, but found that the absorption was the more rapid the greater the concentration of the acid. Because of this fact the acidity as well as the amount of metallic copper was taken into account in the preparation of a cupric chloride solution which was to be reduced to cuprous chloride by the addition of stannous chloride. This new solution was made up as nearly as possible the equivalent of Solution A, both as to acidity and amount of copper present.

Calculating on the basis of 500 cc. of Solution A, the new solution of cuprous chloride was made up as follows, and diluted to 500 cc. with water:

| | |
|---|---|
| Cupric Chloride | 134.5 cc. |
| Stannous Chloride Solution | 94.15 cc. |
| Conc. Hydrochloric Acid (11.176 *N*) | 308.13 cc. |

This will hereafter be referred to as Solution B.

### PROCEDURE

In ordinary gas analysis it is customary to use two pipettes of cuprous chloride for the absorption of carbon monoxide in order that the second pipette may absorb all traces of gas not taken up by the first solution. In order to keep as nearly as possible to actual conditions of gas analysis this plan of using two pipettes for each solution was carried out.

200 cc. of Solution A were placed in each of two Hempel double pipettes, which were designated as Solution IA and Solution IIA. The same was done with Solution B, and designated as Solution IB and Solution IIB.

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[1] *Am. Chem. J.*, **22** (1899), 287.

TABLE I

SOLUTION A

Amount of CO already absorbed........................ 0.0 cc.
Volume of gas taken........................ 50.0 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 40.0 | 1 | 0.0 |
| 2 | 1.0 | 2 | 0.0 |
| 3 | 0.0 | 3 | 0.0 |

Amount of CO already absorbed........................ 368.7 cc.
Volume of gas taken........................ 50.2 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 39.8 | 1 | 0.0 |
| 2 | 0.4 | 2 | 0.0 |
| 3 | 0.2 | 3 | 0.0 |

Amount of CO already absorbed........................ 769.1 cc.
Volume of gas taken........................ 50.4 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 38.8 | 1 | 0.6 |
| 2 | 0.9 | 2 | 0.0 |
| 3 | 0.2 | 3 | 0.0 |

Amount of CO already absorbed........................ 1159.9 cc.
Volume of gas taken........................ 50.2 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 37.6 | 1 | 1.2 |
| 2 | 0.6 | 2 | 0.6 |
| 3 | 0.0 | 3 | 0.0 |

Amount of CO already absorbed........................ 1490.5 cc.
Volume of gas taken........................ 50.2 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 35.2 | 1 | 3.4 |
| 2 | 0.6 | 2 | 0.4 |
| 3 | 0.0 | 3 | 0.0 |

SOLUTION B

Amount of CO already absorbed........................ 0.0 cc.
Volume of gas taken........................ 50.2 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 39.6 | 1 | 0.0 |
| 2 | 0.6 | 2 | 0.0 |
| 3 | 0.6 | 3 | 0.0 |

Amount of CO already absorbed........................ 365.5 cc.
Volume of gas taken........................ 50.2 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 39.0 | 1 | 0.4 |
| 2 | 0.6 | 2 | 0.2 |
| 3 | 0.2 | 3 | 0.0 |

Amount of CO already absorbed........................ 764.5 cc.
Volume of gas taken........................ 50.0 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 38.6 | 1 | 1.0 |
| 2 | 0.6 | 2 | 0.0 |
| 3 | 0.1 | 3 | 0.0 |

Amount of CO already absorbed........................ 1156.0 cc.
Volume of gas taken........................ 50.2 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 37.6 | 1 | 1.6 |
| 2 | 0.8 | 2 | 0.2 |
| 3 | 0.0 | 3 | 0.0 |

Amount of CO already absorbed........................ 1499.7 cc.
Volume of gas taken........................ 50.2 cc.

| Pipette I | | Pipette II | |
|---|---|---|---|
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 37.6 | 1 | 2.2 |
| 2 | 0.0 | 2 | 0.4 |
| 3 | 0.0 | 3 | 0.0 |

A sample of 50 cc. of the carbon monoxide and nitrogen mixture was transferred from a burette to Pipette I containing the cuprous chloride solution, shaken for one minute and then run back into the burette and measured to note the amount of absorption. This was repeated for a second, third, and fourth minute. The unabsorbed residue of gas was then transferred to Pipette II and the amount absorbed by the fresher solution noted for each minute.

This procedure was repeated with successive samples of 50 cc. each until about 1500 cc. of carbon monoxide had been absorbed by the 200 cc. of cuprous chloride solution in Pipette I, and the solution showed signs of becoming so saturated with carbon monoxide that it no longer gave efficient absorption. The results are given in Table I in a somewhat condensed form, but in enough detail to show a complete comparison between Solutions A and B as to their absorbing power for carbon monoxide. The data given include the results of the absorption of every tenth sample. In no case did any further absorption take place after the third minute.

Table I shows clearly that the two solutions of cuprous chloride have the same capacity for the absorption of carbon monoxide, both as to speed and completeness of absorption.

Jones[1] found that the compound between cuprous chloride and carbon monoxide was so unstable that if a solution of cuprous chloride was saturated with carbon monoxide and then heated to 60° or 70° C., exactly the same amount of gas was given off as was originally absorbed, and that as soon as the cuprous chloride solution was cooled the gas could be reabsorbed.

The following experiments were made in order to throw some light on whether or not this fact can be used to advantage in gas analysis. That is to say, can a solution of cuprous chloride saturated with carbon monoxide be freed from this gas by heating, and then have an absorption efficiency equal to that which it had originally?

Solutions IA and IB, which had previously absorbed about 1500 cc. of carbon monoxide each, were transferred from their respective pipettes to separate flasks and heated to 60°–70° C. for several hours over water baths under reflux condensers in order to drive off the carbon monoxide gas absorbed, and were then returned to their pipettes. A new sample of gas had to be made, and this contained a greater percentage of carbon monoxide than the first mixture; namely, 50 cc. of gas contained 48.4 cc. CO and 1.6 cc. of nitrogen.

Solutions IA and IB were tested as before, by running 50 cc. of the prepared gas into each pipette and taking observations as to the amount of gas absorbed each minute for 4 min.

The data given in Table II include only the results of every fifth sample, beginning with the absorption of the first 50 cc. of gas in the renewed solutions.

A comparison of results in Tables I and II would at first seem to indicate that the solutions were more efficient after renewal. In Table I, after about 900 cc. of carbon monoxide had been absorbed, Pipette I of each solution was capable of taking up 39 cc. of a possible 40.2 cc. of carbon monoxide. In Table II the same solution was able to absorb the carbon monoxide almost completely after having already absorbed over 900 cc.

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[1] *Loc. cit.*

TABLE II

| SOLUTION A | | SOLUTION B | |
|---|---|---|---|
| Amount of CO already absorbed | 0.0 cc. | Amount of CO already absorbed | 0.0 cc. |
| Volume of gas taken | 50.0 cc. | Volume of gas taken | 50.0 cc. |
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 48.0 | 1 | 47.4 |
| 2 | 0.4 | 2 | 0.6 |
| 3 | 0.2 | 3 | 0.4 |
| Amount of CO already absorbed | 433.2 cc. | Amount of CO already absorbed | 433.6 cc. |
| Volume of gas taken | 50.0 cc. | Volume of gas taken | 50.0 cc. |
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 47.8 | 1 | 48.0 |
| 2 | 0.6 | 2 | 0.2 |
| 3 | 0.0 | 3 | 0.0 |
| Amount of CO already absorbed | 912.4 cc. | Amount of CO already absorbed | 912.4 cc. |
| Volume of gas taken | 50.0 cc. | Volume of gas taken | 50.0 cc. |
| Time Min. | Amt. CO Absorbed | Time Min. | Amt. CO Absorbed |
| 1 | 47.4 | 1 | 47.6 |
| 2 | 0.4 | 2 | 0.2 |
| 3 | 0.4 | 3 | 0.4 |

R. P. Anderson[1] states that the rapidity with which a solution absorbs a relatively pure gas is much greater than that with which it absorbs a gas from a mixture.

This fact undoubtedly explains why Solutions A and B seem to be more efficient after renewal. The gas which was run into the renewed solutions was more nearly pure carbon monoxide than the gas used with the fresh solutions, and hence the greater speed with which the second sample of gas was absorbed.

Since this second series of tests was otherwise run under practically the same conditions as in the first series, it is evident that solutions of cuprous chloride which have been saturated with carbon monoxide may be renewed by driving off the carbon monoxide by heating, and the solution made as efficient for the absorption of carbon monoxide as it was originally.

### CONCLUSIONS

I—The presence of stannic and stannous chlorides, even in relatively large amounts, in a hydrochloric acid solution of cuprous chloride, does not impair the efficiency of the solution for the absorption of carbon monoxide.

II—A practical and efficient method for the preparation of a solution of cuprous chloride for absorbing carbon monoxide consists in dissolving cupric chloride in concentrated hydrochloric acid and reducing to cuprous chloride by the addition of stannous chloride. If a slight excess of stannous chloride is added the solution may be transferred from one container to another and the pipette filled without oxidation of the cuprous chloride.

III—A hydrochloric acid solution of cuprous chloride, when saturated with carbon monoxide, may be renewed by heating to 60° and 70° C. to drive off the carbon monoxide. A solution treated in this manner will be as efficient for the absorption of carbon monoxide as it was originally, and if in renewing the solution in this way a small amount of the copper is oxidized, and the solution is not colorless, a few drops of a concentrated stannous chloride solution will again reduce it.

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[1] THIS JOURNAL, 7 (1915), 587.

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## THE DETERMINATION OF OXYGEN BY THE COPPER-AMMONIA-AMMONIUM CHLORIDE REAGENT

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Hempel[1] described a reagent for the determination of oxygen which consists of spirals of metallic copper covered with a solution which consists of a mixture of equal parts of saturated ammonium carbonate solution and ammonia of specific gravity 0.93. He states that such a solution has a vapor tension which may be neglected in most cases, and that it will absorb twenty-four times its volume of oxygen. Dennis[2] repeats Hempel's account of this reagent practically word for word. No investigation seems to have been made since Hempel's original statement.

It seemed to the writer that a different concentration of reagent might be desirable, and that other ammonium salts might be substituted for the carbonate. In determining the capacity of this reagent, the conception of Anderson[3] of the specific absorption of a gas reagent was followed. The reagent was used to determine oxygen in air, and attempts were made to determine the point at which this reagent no longer gave quantitative results on air after 5 minutes' shaking. All the analyses were made over water and the value of 20.9 per cent oxygen was adopted with an allowable error of ±0.1 per cent. The apparatus employed is illustrated in Fig. 1. A and B form a standard Hempel pipette for solid reagents. The additional bulb C and the leveling bulb D were filled with mercury which acted as a seal to prevent access of oxygen to the reagent. E is a Hempel burette modified[4] by attaching a three-way stopcock to the top instead of the ordinary two-way stopcock. The manipulation was as follows: The bulb A was filled with spirals of clean copper wire, and the whole apparatus was flushed out with nitrogen. A definite quantity of the solution to be investigated was introduced through Stopcock 1. This was forced over into A and up into the capillary just to Stopcock 2. By means of the funnel and Stopcock 3, the whole of the apparatus between Stopcocks 2 and 4 was filled with water. In the burette was measured a 100-cc. sample of air, and in passing it over into A the water in the capillary connections was forced out through the third way of Stopcock 2, thus preventing any dilution of the reagent. With the three-way stopcocks as shown, the volume of the capillary was entirely eliminated and, therefore, a capillary of rather large bore was used, making the manipulation more rapid. The sample of air was shaken for 5 min. with the reagent, and on returning it to the burette, the reagent was allowed to rise in the capillary only up to Stopcock 2. Water was then introduced through the third way of Stopcock 2 to finish flushing the gas through the capillary connection into the burette.

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[1] "Gasanalytische Methoden," 1900 Edition, p. 142.

[2] "Gas Analysis," **1913**, p. 166.

[3] THIS JOURNAL, 7 (1915), 575.

[4] White and Campbell, *J. Am. Chem. Soc.*, **27** (1905), 734.

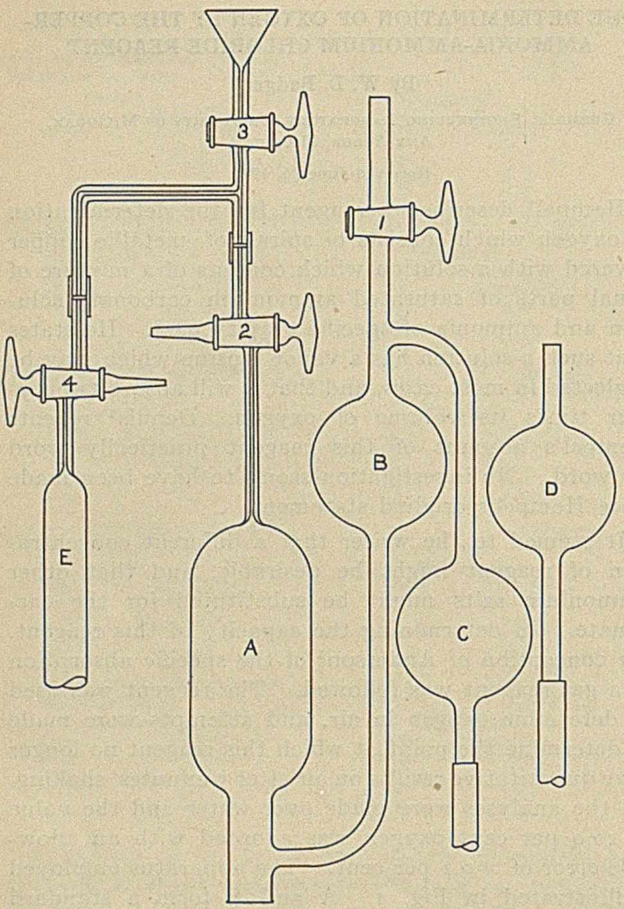

Fig. 1

Since the capacity of the reagent for oxygen proved to be so large that it would require many hundreds of samples of air, a large receiver filled with commercial oxygen was substituted at intervals for the burette E and 500 or 1000 cc. at a time introduced into A. The residual impurities were, of course, measured and allowed for in the calculations. Oxygen was thus introduced and, at frequent intervals, analyses of air made until the reagent either became so foul that the gas could no longer be handled quantitatively or until it failed to give 20.9 per cent in 5 min.

Table I—Hempel's Solution

Equal parts $NH_4OH$, sp. gr. 0.93, and saturated $(NH_4)_2CO_3$ soln., 220 cc.

| Oxygen Taken Cc. | Total Oxygen in Soln. Cc. | Oxygen in Air Per cent | Carbon Dioxide Cc. | Ammonia Cc. |
|---|---|---|---|---|
| 20.9 | 20.9 | 19.0 | 1.5 | . . . |
| 20.7 | 41.6 | 20.3 | 1.0 | 1.4 |
| 20.9 | 62.5 | 21.0 | 2.5 | . . . |
| 20.8 | 83.3 | . . . | 1.6 | . . . |
| 20.8 | 104.1 | 20.7 | 1.6 | . . . |
| 20.8 | 124.9 | 20.8 | 1.5 | . . . |
| 2069.0 | 2193.9 | . . . | . . . | . . . |
| 20.3 | 2214.2 | 17.4 | 2.2 | 0.2 |
| 20.7 | 2234.9 | 20.0 | 0.8 | 0.0 |
| 20.7 | 2255.6 | 20.5 | 0.3 | 0.0 |
| 20.7 | 2276.3 | 20.2 | 0.0 | 0.0 |
| 20.7 | 2297.0 | 20.7 | 0.6 | 0.5 |
| 20.5 | 2317.5 | 20.6 | 0.7 | 0.2 |
| 20.9 | 2338.4 | 20.6 | 0.6 | 0.0 |
| 20.5 | 2358.9 | 20.4 | 0.2 | 0.0 |
| 98.8 | 2457.9 | . . . | . . . | . . . |
| 20.3 | 2478.0 | 20.4 | 0.2 | 0.0 |
| 98.4 | 2576.4 | . . . | . . . | . . . |
| 20.9 | 2597.3 | 20.8 | 0.1 | 0.3 |
| 98.2 | 2695.5 | . . . | . . . | . . . |
| 20.7 | 2716.2 | 20.6 | 0.2 | 0.0 |
| 97.6 | 2813.8 | . . . | . . . | . . . |
| 99.2 | 2913.0 | . . . | . . . | . . . |
| 20.9 | 2933.9 | 20.7 | 0.2 | 0.7 |
| 20.7 | 2954.6 | 20.3 | 0.1 | 0.1 |
| 98.0 | 3052.6 | . . . | . . . | . . . |
| 20.3 | 3072.9 | 20.5 | 0.0 | 0.4 |
| 98.0 | 3170.9 | . . . | . . . | . . . |
| 20.9 | 3191.8 | 20.8 | 0.3 | 0.1 |
| 196.6 | 3388.4 | . . . | . . . | . . . |
| 20.5 | 3408.9 | 20.8 | 0.0 | 0.7 |
| 292.6 | 3701.5 | . . . | . . . | . . . |
| 20.6 | 3722.1 | 20.9 | 0.8 | 0.0 |
| 185.5 | 3907.6 | . . . | . . . | . . . |
| 20.7 | 3928.3 | 19.8 | 0.1 | 0.7 |
| 20.6 | 3848.9 | 19.9 | 0.8 | 0.0 |

The first reagent experimented with was the one described by Hempel, namely, a mixture of one part of a saturated solution of commercial ammonium carbonate with one part of ammonia, sp. gr. 0.93. This reagent seldom gave 20.9 per cent of oxygen in air. It was found necessary to treat the nitrogen returned to burette E after an analysis, first with a caustic solution to remove the carbon dioxide, and then with a dilute sulfuric acid solution to remove the ammonia. The amount of ammonia reported by this manipulation naturally varied since considerable ammonia was dissolved by the burette water, and consequently the amount reported depends upon the rapidity of manipulation. Table I gives the results with the Hempel solution. It is evident that this solution will not give satisfactory results for the determination of oxygen.

Various ammonium salts were investigated, but preliminary experiments showed that ammonium chloride would possess the largest capacity and give the most satisfactory results. The following solutions were investigated:

SOLUTION 1—Concentrated ammonia, sp. gr. 0.90, saturated with ammonium chloride (see Table II). It is evident that this reagent is exhausted at about 5500 cc. of oxygen, giving a specific absorption of about 22.5 volumes.

Table II—200 Cc. of Solution 1

| Oxygen Taken Cc. | Total Oxygen in Soln. Cc. | Oxygen in Air Per cent | Ammonia Cc. | Remarks |
|---|---|---|---|---|
| 20.9 | 20.9 | 20.9 | 7.8 | |
| 20.8 | 41.7 | 20.8 | 30.5 | |
| 10.5 | 52.2 | 21.0 | 3.4 | |
| 10.4 | 62.6 | 20.8 | 2.6 | |
| 10.4 | 73.0 | 20.8 | 8.4 | |
| 968.2 | 1041.2 | .. | .. | |
| 20.9 | 1062.1 | 21.0 | 8.7 | |
| 20.9 | 1083.0 | 20.9 | 18.3 | |
| 10.4 | 1093.4 | 20.8 | 2.0 | |
| 970.9 | 2064.3 | .. | .. | |
| 10.6 | 2074.9 | 20.8 | 7.8 | |
| 10.9 | 2085.8 | 20.9 | 4.6 | |
| 971.2 | 3057.0 | .. | .. | |
| 18.2 | 3075.2 | 20.9 | 5.6 | |
| 20.9 | 3096.1 | 20.9 | 2.4 | |
| 16.7 | 3112.8 | 20.9 | 5.6 | |
| 968.1 | 4080.9 | .. | .. | At about 3600 cc. of oxygen a precipitate of cuprous oxide began to form |
| 16.7 | 4097.6 | 20.9 | 7.3 | |
| 16.7 | 4114.3 | 20.9 | 3.4 | |
| 16.7 | 4131.0 | 21.0 | 3.6 | |
| 16.8 | 4147.8 | 20.9 | 4.0 | |
| 483.7 | 4631.5 | .. | .. | |
| 16.7 | 4648.2 | 20.9 | 0.7 | |
| 16.7 | 4664.9 | 20.9 | 0.4 | |
| 481.9 | 5146.8 | .. | .. | |
| 16.9 | 5163.7 | 20.9 | 2.5 | |
| 15.5 | 5180.2 | 20.9 | 4.0 | |
| 481.8 | 5662.0 | .. | .. | |
| 16.3 | 5678.3 | 20.5 | 1.6 | |
| 16.3 | 5678.3 | 20.5 | 1.6 | |
| 16.6 | 5694.9 | 20.7 | 3.2 | |
| 483.9 | 6178.8 | .. | .. | Solution absorbs oxygen more rapidly after standing over night |
| 16.7 | 6195.5 | 20.9 | 3.3 | |
| 16.5 | 6212.0 | 20.7 | 5.6 | |
| 16.6 | 6228.6 | 20.8 | 5.6 | |
| 480.8 | 6709.4 | .. | .. | |
| 16.5 | 6725.9 | 20.4 | 1.9 | |
| 16.7 | 6742.6 | 20.5 | 3.8 | |
| 17.0 | 6759.6 | 21.0 | 3.2 | 10 min. |
| 16.9 | 6776.5 | 20.9 | 4.8 | 10 min. |
| 483.4 | 7259.9 | .. | .. | |
| 16.1 | 7276.0 | 20.2 | 3.9 | |
| 16.7 | 7279.7 | 20.9 | 3.3 | 10 min. |

SOLUTION 2—Two parts concentrated ammonia, one part water, the mixture saturated with ammonium chloride (see Table III). The limit in this particular case is about 9500 cc. of oxygen, although this is not due to a failure to react but to the precipitate slowing down the reaction until it takes longer than the 5 min. arbitrarily set. This would give a specific absorption of 45 to 47 volumes.

TABLE III—200 CC. OF SOLUTION 2

| Oxygen Taken Cc. | Total Oxygen in Soln. Cc. | Oxygen in Air Per cent | Ammonia Cc. | REMARKS |
|---|---|---|---|---|
| 20.5 | 20.5 | 20.9 | 1.0 | |
| 20.7 | 41.2 | 20.8 | 1.4 | |
| 953.9 | 995.1 | .. | ... | |
| 20.9 | 1016.0 | 20.9 | 4.8 | |
| 970.2 | 1986.2 | .. | ... | |
| 19.6 | 2005.8 | 20.9 | 2.8 | |
| 969.3 | 2975.1 | .. | ... | |
| 19.6 | 2994.7 | 20.9 | 1.8 | |
| 978.0 | 3972.7 | .. | ... | 7 min. for absorption |
| 978.0 | 4950.7 | .. | ... | 6.5 min. |
| 978.0 | 5928.7 | .. | ... | 6 min. precipitate began to form |
| 975.2 | 6903.9 | .. | ... | 7 min. |
| 20.9 | 6924.8 | 20.9 | 0.5 | |
| 977.5 | 7902.3 | .. | ... | 12 min. |
| 978.0 | 8880.0 | .. | ... | 20 min. |
| 20.9 | 8901.2 | 20.9 | 0.2 | Copper heavily coated with precipitate |
| 977.0 | 9878.2 | .. | ... | 35 min. |
| 20.9 | 9898.4 | 20.2 | 0.2 | |
| 20.9 | 9919.3 | 20.9 | ... | 10 min. |

SOLUTION 3—One part concentrated ammonia, one part water, the mixture saturated with ammonium chloride (see Table IV). The limit of this reagent came at the point where the precipitate was so bulky as to clog the capillaries or entrap bubbles of oxygen in the pipette. Otherwise the reaction was still quantitative. The limit is somewhere between 11000 and 12000 cc. of oxygen, giving a specific absorption of 55 to 60 volumes.

TABLE IV—200 CC. OF SOLUTION 3

| Oxygen Taken Cc. | Total Oxygen in Soln. Cc. | Oxygen in Air Per cent | Ammonia Cc. | REMARKS |
|---|---|---|---|---|
| 965.6 | 965.6 | .. | ... | 18 min. |
| 21.0 | 986.6 | 21.0 | 3.8 | |
| 964.8 | 1951.4 | .. | ... | 12 min. |
| 20.9 | 1972.3 | 20.9 | 3.0 | |
| 965.2 | 2937.5 | .. | ... | 10 min. |
| 20.9 | 2958.4 | 20.9 | 1.9 | |
| 966.1 | 3924.5 | .. | ... | 10 min. |
| 20.9 | 3945.4 | 20.9 | 1.6 | |
| 977.5 | 4922.9 | .. | ... | 10 min. precipitate beginning to form on coils |
| 20.9 | 4943.8 | 20.9 | 1.6 | |
| 977.7 | 5921.5 | .. | ... | 6.5 min. |
| 20.9 | 5942.4 | 20.9 | 0.1 | |
| 977.3 | 5919.7 | .. | ... | 8.5 min. |
| 20.9 | 6940.6 | 20.9 | 0.1 | |
| 978.0 | 7918.6 | .. | ... | 8.5 min. |
| 21.0 | 7939.6 | 21.0 | None | |
| 977.0 | 8916.6 | .. | ... | 12 min. |
| 20.9 | 8937.5 | 20.9 | None | |
| 977.0 | 9914.5 | .. | ... | 15 min. |
| 20.9 | 9935.4 | 20.9 | None | |
| 978.0 | 10913.4 | .. | ... | 35 min. |
| 20.9 | 10934.3 | 20.9 | None | |
| 964.0 | 11898.3 | .. | ... | 45 min. |
| 20.9 | 11919.2 | 20.9 | None | Precipitate very heavy on coils and in solution. At this point capillary became clogged |

SOLUTION 4—One part of concentrated ammonia, two parts water, the mixture saturated with ammonium chloride (see Table V). Here the limit was somewhere above 6000 cc. of oxygen, giving a specific absorption of 30 volumes.

The figures in Tables II to V showing the amount of ammonia given off were determined by passing the gas residue left after the analysis of air into a sulfuric acid pipette and noting the decrease. These figures are fairly reliable because, by this time, so many analyses had been run that the manipulation was very uniform.

In spite of the fact that during the earlier part of its use considerable quantities of ammonia are liberated, it would seem that Solution 3 represents the most desirable composition. Some tests have been made which indicated that in these solutions, after considerable copper has been dissolved, the absorption of acetylene is as rapid and as complete as the absorption of oxygen; and much more rapid than any of the other reagents for acetylene noted in the literature. Systematic investigation of this point has not been made.

Van Brunt[1] says that in the use of this reagent, a considerable amount of oxygen is absorbed by the cuprous salts in solution. The present set of experiments and some four years' experience with this reagent in large classes in gas analysis have shown that this is not true. Even with reagents containing large amounts of cuprous salt in solution, if the copper in the absorption pipette falls below the surface of the liquid, absorption of oxygen almost completely stops.

TABLE V—200 CC. OF SOLUTION 4

| Oxygen Taken Cc. | Total Oxygen in Soln. Cc. | Oxygen in Air Per cent | Ammonia Cc. | REMARKS |
|---|---|---|---|---|
| 975.0 | 975.0 | .. | ... | 30 min. |
| 974.8 | 1949.8 | .. | ... | 12 min. |
| 20.9 | 1970.7 | 20.9 | None | |
| 974.9 | 2945.6 | .. | ... | 10 min. |
| 974.8 | 3920.4 | .. | ... | 8 min. precipitate began to form |
| 974.7 | 4895.1 | .. | ... | 10 min. precipitate very heavy; trouble with capillary |
| 20.9 | 4916.0 | 20.9 | None | |
| 975.0 | 5891.0 | .. | ... | 14 min. copper heavily coated and solution foaming badly |
| 20.9 | 5911.9 | 20.9 | None | |
| 974.5 | 6886.4 | .. | ... | 25 min. |
| 20.9 | 6906.6 | 20.9 | None | |
| 20.9 | 6927.5 | {20.5<br>{20.9 | None | 5 min. shaking<br>10 min. shaking |

In the analysis of commercial oxygen, where the residue of unabsorbed gas is very small, care must be taken that one or two copper wires project clear up into the entrance to the capillary; for if the gas residue is not in contact with metallic copper, the last traces of oxygen will not be absorbed. It would seem, then, that the mechanism of the reaction is that the copper is first oxidized, and the function of the solution is simply to dissolve this oxide, leaving fresh and active copper surfaces for further oxidation.

## CONCLUSION

I—The solution of ammonia and ammonium carbonate recommended by Hempel and copied by Dennis is not a satisfactory reagent for oxygen.

II—The most convenient solution is made by saturating with ammonium chloride a mixture of one part concentrated ammonia and one part water. This solution will absorb from fifty to sixty times its volume of oxygen, and then fails, not by refusing to absorb quantitatively, but by the formation of so heavy a precipitate that it becomes unmanageable. The reagent is still useful for a considerable time after the precipitate begins to form.

III—The advantages of this reagent are: that it is cleaner to use and has a longer life than pyrogallate;

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[1] *J. Am. Chem. Soc.*, **36** (1914), 144.

it is free from the danger and the influence of catalyzers which interfere with phosphorus; it is readily prepared from common reagents; and it is active at almost any temperature.

IV—Its disadvantages are that it cannot be used on gas mixtures which contain either carbon monoxide or acetylene; and when fresh, it leaves measurable amounts of ammonia in the gas. This last may be remedied by keeping the burette water slightly acid.

ACKNOWLEDGMENT

The writer wishes to express his appreciation of the work of Mr. Wyatt A. Miller, who made the analyses on Hempel's solution, and to Mr. E. O. Scott, who did all the rest of the analytical work.

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# EQUILIBRIA IN SOLUTIONS CONTAINING MIXTURES OF SALTS. II—THE SYSTEM WATER AND THE CHLORIDES AND SULFATES OF SODIUM AND MAGNESIUM AT 25°

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## INTRODUCTION

The equilibria which exist in aqueous solutions containing chlorides and sulfates of sodium and magnesium were discussed by Hildebrand[1] who prepared the phase-rule diagram representing the system at 25° based upon data from a number of sources, but owing to the incompleteness of these data two of the important points on his diagram were conjectural only. In attempting to ascertain by actual experiment the location of these points it became evident that some of the results used in the preparation of the diagram were incorrect, and since the diagram is of immediate importance in discussing methods for the recovery of magnesium salts from bittern and from the waters of certain lakes, it was thought desirable to redetermine all the data needed for the construction of the complete diagram. In carrying out the experimental work needed to obtain these data I have received much valuable assistance from Miss Carolyn Steel.

## EXPERIMENTAL METHODS USED

This system forms a reciprocal salt pair, which can be represented graphically by reference to two axes intersecting at right angles, provided the concentrations are expressed in double equivalents per unit weight of water, that is, by using one axis to represent the relative proportions of $MgSO_4$ and $Na_2Cl_2$, and the other of $Na_2SO_4$ and $MgCl_2$. The previous work on the subject indicates that the solid phases to be expected at this temperature are $MgSO_4.7H_2O$, $MgSO_4.6H_2O$, $MgSO_4.H_2O$, $Na_2SO_4.10H_2O$, $Na_2SO_4$, $MgCl_2.6H_2O$, NaCl and the double sulfate $MgSO_4.Na_2SO_4.4H_2O$ known as astracanite. The problem presented was to determine the limits of the fields representing the composition of all the solutions which can be in equilibrium with each of the eight solid phases. Since the system can be expressed in terms of three components, and since a liquid phase is always assumed to be present and the pressure is constant, it would be impossible to prepare solutions which are in equilibrium with more than three of these solids simultaneously, unless the transition temperature had been chosen fortuitously, in which case four solids might be present.

In ascertaining the limits of the eight fields the following procedure was adopted: First, the compositions of solutions saturated with respect to the four simple salts $MgSO_4.7H_2O$, $Na_2SO_4.10H_2O$, $MgCl_2.6H_2O$ and NaCl were determined, and the ends of the two axes already referred to were fixed. Second, the solubility of each of these four salts in solutions containing increasing concentrations of a second salt which yielded a common ion, and, therefore, contained three ions, was determined up to the point at which a second solid phase appeared; this fixed a number of points lying between the extremities of the two axes representing solutions in equilibrium with two solid phases. Third, starting with solutions saturated with respect to two solids, the composition of solutions saturated with respect to each pair of solids in the presence of increasing concentrations of that salt which yielded a fourth ion was ascertained up to the point at which a third solid was separated.

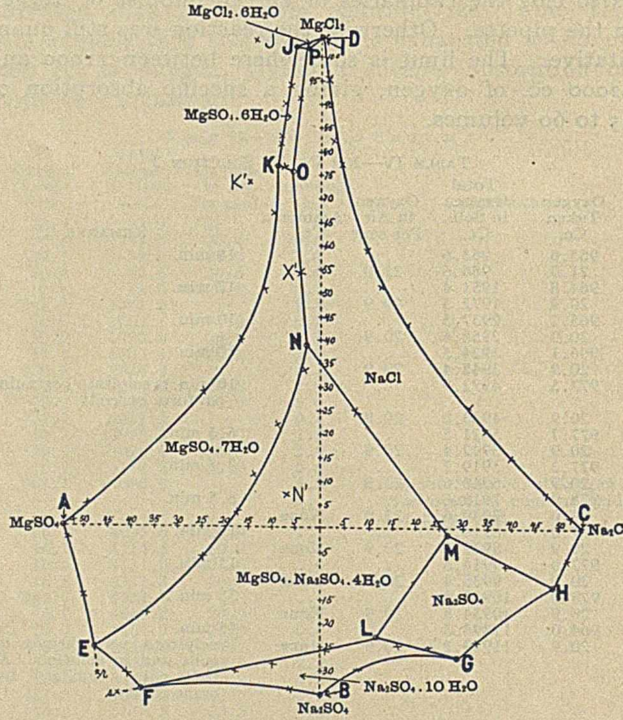

Fig. 1—The System $MgSO_4$–NaCl at 25°

This procedure made it possible to check each step in the process of establishing the critical points of the diagram, and gave more detailed information regarding the exact form of the different fields than is usually shown on similar diagrams. The details of procedure adopted in carrying out the solubility determinations differed in no essential respect from those used in similar

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[1] This Journal, 10 (1918), 96.

work on the sulfates and chlorides of sodium and potassium already reported.[1]

### REPRESENTATION OF THE RESULTS OBTAINED

All the data obtained, and the complete diagram which is based upon it, are represented in Fig. 1, in which the horizontal axis is used to represent the relative number of moles of $MgSO_4$ and $Na_2Cl_2$ and the vertical axis the relative number of moles of $MgCl_2$ and $Na_2SO_4$ per 1000 mols of water. The composition of each of the saturated solutions prepared and analyzed is represented by a cross, and when two or more solutions saturated with respect to the same solids were prepared the mean value of the results obtained is shown by a dot surrounded by a circle. It is obvious that all points on the diagram, except those on the peripheral lines, represent relative values only, and the actual composition of such solutions cannot be deduced from the diagram unless the total number of moles present is also known. For this reason the composition of all those solutions which represent critical points on the diagram is given in Tables I and II.

TABLE I—COMPOSITION IN MOLES PER 1000 MOLES OF WATER, OF SOLUTIONS SATURATED AT 25°

| | Saturated with | $MgSO_4$ | $Na_2SO_4$ | $Na_2Cl_2$ | $MgCl_2$ | Sum |
|---|---|---|---|---|---|---|
| A | $MgSO_4.7H_2O$ | 54.36 | ... | ... | .. | 54.36 |
| B | $Na_2SO_4.10H_2O$ | ... | 35.41 | ... | .. | 35.41 |
| C | NaCl | ... | ... | 54.90 | .. | 54.90 |
| D | $MgCl_2.6H_2O$ | ... | ... | ... | 103.90 | 103.90 |
| E | $MgSO_4.7H_2O$ and astracanite | 47.99 | 24.97 | ... | .. | 72.96 |
| F | $Na_2SO_4.10H_2O$ and astracanite | 37.96 | 34.36 | ... | .. | 72.32 |
| G | $Na_2SO_4.10H_2O$ and $Na_2SO_4$ | ... | 27.50 | 29.00 | ... | 56.50 |
| H | $Na_2SO_4$ and NaCl | ... | 12.44 | 49.56 | .. | 62.00 |
| I | NaCl and $MgCl_2.6H_2O$ | ... | ... | ... | 103.90 | 103.90 |
| J | $MgCl_2.6H_2O$ and $MgSO_4.6H_2O$ | 5.40 | ... | ... | 102.10 | 107.50 |
| K | $MgSO_4.6H_2O$ and $MgSO_4.7H_2O$ | 9.53 | ... | ... | 77.00 | 86.53 |
| L | $Na_2SO_4.10H_2O$, $NaSO_4$ and astracanite | 11.54 | 23.67 | 23.89 | .. | 59.10 |
| M | $Na_2SO_4$, NaCl and astracanite | 18.84 | 1.28 | 45.72 | .. | 65.84 |
| N | $MgSO_4.7H_2O$, NaCl and astracanite | 18.00 | ... | 15.08 | 38.71 | 71.79 |
| O | $MgSO_4.7H_2O$, $MgSO_4.6H_2O$ and NaCl | 9.78 | ... | 3.39 | 75.50 | 88.67 |
| P | $MgSO_4.6H_2O$, NaCl and $MgCl_2.6H_2O$ | 3.78 | ... | 0.28 | 101.85 | 105.91 |

TABLE II—COMPOSITION IN GRAMS PER 100 GRAMS OF WATER, OF SOLUTIONS SATURATED AT 25°

| | Saturated with | $MgSO_4$ | $Na_2SO_4$ | NaCl | $MgCl_2$ |
|---|---|---|---|---|---|
| A | $MgSO_4.7H_2O$ | 36.39 | ... | ... | ... |
| B | $Na_2SO_4.10H_2O$ | ... | 27.93 | ... | ... |
| C | NaCl | ... | ... | 35.63 | ... |
| D | $MgCl_2.6H_2O$ | ... | ... | ... | 54.97 |
| E | $MgSO_4.7H_2O$ and astracanite | 32.07 | 19.68 | ... | ... |
| F | $Na_2SO_4.10H_2O$ and astracanite | 25.36 | 27.09 | ... | ... |
| G | $Na_2SO_4.10H_2O$ and $Na_2SO_4$ | ... | 21.68 | 18.82 | ... |
| H | $Na_2SO_4$ and NaCl | ... | 9.81 | 32.16 | ... |
| I | NaCl and $MgCl_2.6H_2O$ | ... | ... | ... | 54.87 |
| J | $MgCl_2.6H_2O$ and $MgSO_4.6H_2O$ | 3.61 | ... | ... | 54.01 |
| K | $MgSO_4.6H_2O$ and $MgSO_4.7H_2O$ | 6.37 | ... | ... | 40.74 |
| L | $Na_2SO_4.10H_2O$, $Na_2SO_4$ and astracanite | 7.71 | 18.67 | 15.50 | ... |
| M | $Na_2SO_4$, NaCl and astracanite | 12.59 | 1.01 | 29.67 | ... |
| N | $MgSO_4.7H_2O$, $MgSO_4.6H_2O$ and astracanite | 12.03 | ... | 9.79 | 20.47 |
| O | $MgSO_4.7H_2O$, $MgSO_4.6H_2O$ and NaCl | 6.53 | ... | 2.20 | 39.94 |
| P | $MgSO_4.6H_2O$, NaCl, and $MgCl_2.6H_2O$ | 2.53 | ... | 0.18 | 53.88 |

In Table I the concentrations are expressed in terms of the number of moles of salts whose formulas are given, per 1000 moles of water; in Table II the composition of these solutions is expressed in grams of these salts per 100 g. of water.

### DISCUSSION OF RESULTS

#### (1) CRITICAL POINTS REPRESENTING THE COMPOSITION OF SOLUTIONS SATURATED WITH RESPECT TO A SINGLE SOLID

POINT A. SATURATION WITH RESPECT TO $MgSO_4.7H_2O$—The result obtained (54.36) is in fair agreement with that obtained by van Klooster[2] (54.7), but differs decidedly from the earlier result (58.0) of Lowenhertz,[1] which was used in the Hildebrand diagram.

POINT B. SATURATION WITH $Na_2SO_4.10H_2O$—This value, 35.4, was reported in the preceding paper of this series[2] and is in good agreement with the value 35.5 found by Seidell.[3]

POINT C. SATURATION WITH NaCl—This value, 54.9, is also taken from previous work of the writer and is in good agreement with the recent determinations.

POINT D. SATURATION WITH $MgCl_2.6H_2O$—This value, 103.9, represents the mean of three closely agreeing determinations. The value found by Lowenhertz[1] and used in the Hildebrand diagram was 108. A more recent value obtained by Biltz and Marcus[4] was 104.5.

#### (2) CRITICAL POINTS REPRESENTING THE COMPOSITION OF SOLUTIONS SATURATED WITH RESPECT TO TWO SOLIDS

POINTS E AND F—Some difficulty was experienced in determining the positions of these points owing to formation of solutions supersaturated with respect to astracanite, as is indicated by the fact that solutions corresponding to the point *r* on the curve AE and to the point *s* on the curve BF were prepared without difficulty; obviously astracanite can exist in equilibrium with solutions of the composition *r* and *s* as a *m*-stable form only. This salt invariably separated in the form of a dense crust composed of small crystals, which usually show only poorly defined planes. It was found possible to prepared small but well-formed crystals, one of which is represented in Fig. 2. This figure represents a sketch based upon such measurements as could be made by rotating the slide sustaining the crystal with respect to the cross hairs of a microscope. The values obtained for the composition of the Solutions E and F are comparable with those obtained by Roozeboom[5] at 24.5°, who found for E, 47.6 $MgSO_4$ and 26.85 $Na_2SO_4$ instead of 47.99 $MgSO_4$ and 24.97 $Na_2SO_4$; and for F, 36.25 $MgSO_4$ and 34.5 $Na_2SO_4$ instead of 37.96 $MgSO_4$ and 34.36 $Na_2SO_4$.

POINTS G AND H—The values of these points were determined and reported in the previous article of this series.[2] The corresponding values obtained by interpolation from the data reported by Seidell[6] are for G, 27.42 $Na_2Cl_2$ and 28.00 $Na_2SO_4$ instead of 29.0 $Na_2Cl_2$ and 27.5 $Na_2SO_4$; and for H, 49.30 $Na_2Cl_2$ and 11.41 $Na_2SO_4$ instead of 49.56 $Na_2Cl_2$ and 12.44 $Na_2SO_4$.

POINT I. SATURATION WITH $MgCl_2.6H_2O$ AND NaCl—It was not found possible to ascertain the correct position of this point or to show that there is a discontinuity in the curve connecting the points C and D. The solutions obtained by adding NaCl to solutions already saturated with $MgCl_2.6H_2O$ and stirring for a

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[1] THIS JOURNAL, **10** (1918), 344.

[2] *J. Phys. Chem.*, **21** (1917), 513.

[1] *Z. physik. Chem.*, **13** (1894), 478.

[2] *Loc. cit.*

[3] *Am. Chem. J.*, **27** (1902), 52.

[4] *Z. anorg. Chem.*, **71** (1911), 168.

[5] *Z. physik. Chem.*, **2** (1888), 518.

[6] *Am. Chem. J.*, **27** (1902), 56.

period of 5 days, showed on analysis only negligible amounts of sodium, and those obtained by adding increasing amounts of $MgCl_2.6H_2O$ to saturated solutions of NaCl also finally attained a composition corresponding essentially to that of solutions saturated with pure $MgCl_2.6H_2O$. This indicates that the point I approaches so nearly the position of the point D that it cannot be distinguished from the latter by the ordinary methods of analytical procedure. No evidence of the formation of solid solutions composed of $MgCl_2.6H_2O$ with small concentrations of NaCl could be obtained. It was also pointed out to the writer by Prof. G. N. Lewis that the line CD must approach the BD axis asymptotically since intersection with it would imply a negative value for the solubility of sodium chloride. This relation is of general application to similar cases but is of peculiar significance in dealing with a pair of salts which differ so greatly in solubility as those considered here and explain why difficulty was experienced in recognizing a discontinuity on the curve.

The work of van't Hoff and Meyerhoffer[1] assigns to the point under discussion a definite position corresponding to a solution represented by the composition 103 $MgCl_2$ and 2.50 $Na_2Cl_2$.

The points on the curve CI are of much interest in showing that the rate at which the solubility of NaCl is decreased by increasing concentrations of $MgCl_2$ is far from uniform. This and similar curves on this diagram also show how large an error is involved in the assumption commonly made in preparing such diagrams where the critical points are connected by straight lines.

POINTS J AND K—These points represent the composition of solutions saturated with respect to $MgCl_2.6H_2O$ and $MgSO_4.6H_2O$, and with respect to $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$, respectively. The heptahydrate of magnesium sulfate rapidly changed into the hexahydrate when stirred with solutions whose composition varied from J to K. The crystals thus obtained showed monoclinic symmetry, but owing to the number and variations in the relative development of the faces represented, the range of crystal habit exhibited by them was large. One example of a well-developed crystal is shown in Fig. 2. A value of approximately 86° for the angle α shown in this sketch is characteristic of this hydrate. When brought into contact with a drop of water on the stage of the microscope, these crystals rapidly changed into a mass of *o*-rhombic prisms with abrupt terminations which are easily identified as crystals of the heptahydrate.

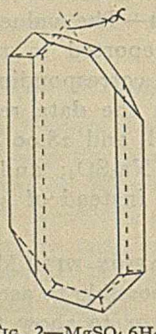

FIG. 2—$MgSO_4.6H_2O$

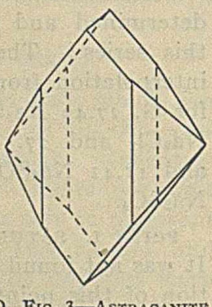

FIG. 3—ASTRACANITE

No definite evidence for the formation of any other hydrates along the line JK could be obtained, and the crystals showing the wide range of variation in habit already referred to were shown to be stable in the same solution even when the composition of this solution varied with respect to the concentrations of magnesium chloride present. Van't Hoff and Estreicher[1] were able to prepare hydrates of magnesium sulfate containing five and four molecules of water, and also to ascertain the composition of solutions saturated with respect to the hexa- and penta- and the penta- and tetrahydrates, which solutions correspond to points on the line JK. Subsequently van't Hoff and Estreicher[1] concluded that the penta- and tetrahydrates were *m*-stable at all temperatures, as a result of a study of the dissociation pressures of these hydrates, and it is not improbable that neither of the lower hydrates was actually present as solid phases in contact with the saturated solutions prepared and analyzed by them.

The values found for the points J and K differ greatly from those obtained by Lowenhertz[2] who reported for J, 104 $MgCl_2$ and 14 $MgSO_4$ instead of 102.1 $MgCl_2$ and 5.40 $MgSO_4$; and for K, 73 $MgCl_2$ and 15 $MgSO_4$ instead of 77 $MgCl_2$ and 9.53 $MgSO_4$. His values appear on the diagram at the points J′ and K′. The large discrepancy between the two sets of values can be attributed to the indirect method used by Lowenhertz for the determination of sulfate ion, namely, addition of a known amount of lead nitrate, separation of the lead sulfate, precipitation of lead in the filtrate as lead sulfide removal of the lead sulfide and determination of the nitric acid in the filtrate by titration with sodium hydroxide solution. This method clearly offers more and larger sources of error than the direct separation of sulfate ion as barium sulfate used by the writer.

### (3) CRITICAL POINTS REPRESENTING THE COMPOSITION OF SOLUTIONS SATURATED WITH RESPECT TO THREE SOLIDS

POINT L. SATURATION WITH RESPECT TO $Na_2SO_4$, $Na_2SO_4.10H_2O$ AND ASTRACANITE—This is one of the points for which no data were previously available. The values found are in fair agreement with the position assumed in the Hildebrand diagram.

POINT M. SATURATION WITH RESPECT TO NaCl, $Na_2SO_4$ AND ASTRACANITE—This point was fixed by the work of van't Hoff and Meyerhoffer[3] who found as the mean of four experiments 46 $Na_2Cl_2$, 16.5 $MgSO_4$ and 3 $Na_2SO_4$ instead of 45.72 $Na_2Cl_2$, 18.84 $MgSO_4$ and 1.28 $Na_2SO_4$, representing the mean of five closely agreeing results obtained by the writer.

POINT N. SATURATION WITH RESPECT TO ASTRACANITE, NaCl, AND $MgSO_4.7H_2O$—This point was also fixed by the work of van't Hoff and Meyerhoffer[4] who found as the mean of two experiments 26 $Na_2Cl_2$, 34 $MgSO_4$, 7 $MgCl_2$, corresponding to the point N′ on the diagram (Fig. 1) instead of 15.08 $Na_2Cl_2$, 18 $MgSO_4$, and 38.71 $MgCl_2$ found by the writer. The correctness of the latter values seems to be sufficiently con-

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[1] *Sitzb. Akad.*, Berlin, 1898, 591

[1] *Sitzb. Akad.*, Berlin, 1898, 488, 497.

[2] *Loc. cit.*

[3] *Sitzb. Akad.*, Berlin, 1898, 594.

[4] *Loc. cit.*

firmed by the positions found for a number of points on the lines EN, MN, and ON.

POINT O. SATURATION WITH RESPECT TO $MgSO_4.7H_2O$, $MgSO_4.6H_2O$, AND NaCl—The values obtained by van't Hoff and Meyerhoffer[1] for this point were 10.5 $Na_2Cl_2$, 53 $MgCl_2$, and 15 $MgSO_4$ which are represented by the point X′ on the line ON of the diagram.

POINT P. SATURATION WITH RESPECT TO $MgSO_4.6H_2O$, $MgCl_2.6H_2O$ AND NaCl—The values obtained by van't Hoff and Meyerhoffer,[1] namely, 1 $Na_2Cl_2$, 102 $MgCl_2$, and 5 $MgSO_4$, are in fair agreement with those of the writer, namely, 0.28 $Na_2Cl_2$, 101.85 $MgCl_2$, and 3.78 $MgSO_4$.

(4) ELIMINATION OF KIESERITE FROM THE SYSTEM

The work of van't Hoff seems to show that $MgSO_4.H_2O$, kieserite, should be formed in this system at 25° from solutions whose composition is represented by a very small field below and to the left of the point P, but not in solutions represented by the point J, that is, solutions saturated with $MgCl_2.6H_2O$ and $MgSO_4.6H_2O$ only. It does not seem probable that the vapor pressure of the solution of the composition P should be markedly less than that of the solution of the composition J, and it is therefore difficult to understand why the former should be able to change $MgSO_4.6H_2O$ into $MgSO_4.H_2O$ if the latter is unable to do so. Repeated attempts to prepare kieserite in such solutions, even when inoculated with small amounts of the pure hydrate, failed, and the writer is compelled to believe that it does not constitute a part of this system at a temperature of 25°.

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[1] *Loc. cit.*

# LABORATORY AND PLANT

## NEW TURBIDIMETER FOR SOLUTIONS OF GELATIN, CELLULOSE, AND VARNISHES

By S. E. Sheppard

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Received August 12, 1919

Turbidimeters as used in water analysis, based on the vanishing of a line or filament for a given depth of liquid, are well known, the turbidities being expressed generally on an arbitrary scale. For this method there is generally assumed a more or less unlimited amount of the liquid.

In many cases, however, especially in research and development work with nonaqueous systems only a limited amount of the material may be available, for example, in development of a new lacquer or varnish. For such work an instrument operating on a small constant thickness becomes desirable. While this could be attained photometrically, measuring either the relative transmitted light (transparency) or the relative side scattered light (turbidity),[1] yet in some respects the method of judging distinctness of some standard object seems the simplest for practical purposes. What is required now for the case of a limited thickness of fluid is an object the visibility of which can be varied in some continuous and easily measurable way. For this purpose advantage was taken of the well-known properties of crossed gratings, on lines similar to those employed by H. E. Ives[2] in his test object for visual acuity. The essential part of the apparatus consists of two superposed opaque line gratings arranged to rotate relatively to each other about an axis perpendicular to their plane. Viewed by transmitted light, at such a distance that the grating lines are below the limit of resolution, parallel dark bands are seen. The separation of these alters quite continuously as the gratings are rotated, so that we have a continuous change from extreme visibility to invisibility—when the bands can no longer be resolved. The average brightness of the field remains constant, and also the variation of brightness from the center of a bright band to that of the adjacent dark band is the same for all sizes of bands.

The following diagrams, taken from H. E. Ives' paper, illustrate the important relationship between the width of the irradiation bands and the angle of relative rotation of the gratings.

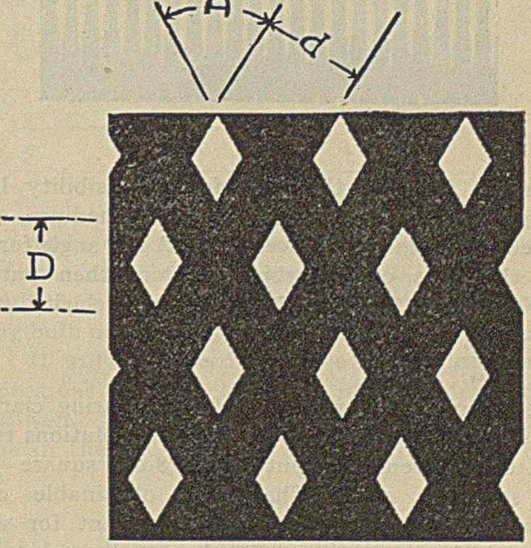

Fig. 1

In Fig. 1, *d* is the distance between centers of the grating lines, A the angle of relative rotation, and D the distance between those regions where continuous straight lines can be drawn across without meeting a clear space. These latter lines form the centers of the dark bands visible on viewing the crossed gratings.

The distance between them is given by the formula

$$D = \frac{d}{2 \sin A/2}.$$

In Fig. 2 is shown a photomicrograph of a pair of crossed gratings, turned through a small angle. At a sufficient distance—several yards—the component lines vanish, only the interference (or irradiation) bands showing. At the ultimate resolving distance

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[1] A convenient apparatus for this will be described in a later paper.

[2] *Elec. World*, **1910**, p. 939; *J. Opt. Soc. Am.*, **1917**, p. 100.

the variation of intensity over the width of the bands is lost and they appear as sharp, black lines. For details as to their use in forming visual acuity tests, reference should be made to Ives' paper. Their application to turbidimetry depends on an inversion of the same principles. If a scattering (turbid) medium be placed in front of the crossed gratings, the visibility limit $1/D = 2 \sin A/2$ will be lowered, according to the turbidity. For relatively small angles, secured by a proper choice of $d$, the expression $1/D = 2 \sin A/2$ reduces to $1/D = \sin A = A$; from this the visibility limit—for one and the same observer, *i. e.*, for the same visual acuity—can be measured by the angle through which the gratings must be turned to make the bands just disappear.

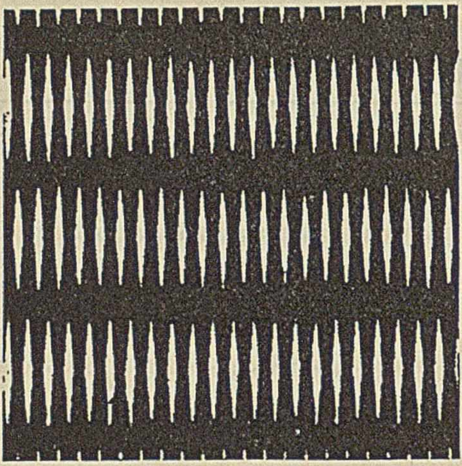

FIG. 2

If now, $A_{max.}$ be the angle for the visibility limit for a given thickness of some standard medium, *e. g.*, distilled water, lacquer solvent, and A the angle for the same thickness of a turbid solution, then putting $A_{max.}/A = 100/C$, gives C, the per cent clarity, from

$$C = \frac{100\ A}{A_{max.}}.$$

The instrument constructed for measuring clarities in this way is shown in Fig. 3. The solutions to be tested are conveniently put up in 8-oz. square jars, with screw-on caps. These are obtainable commercially and are much more convenient for work with varnishes, lacquers and other sticky substances than corked or stoppered bottles. Since, however, the sides are not perfectly plane parallel, distortions of the grating image will occur on placing in position in front of the gratings. To eliminate this refraction error, the test jars are placed in a cell with glass walls parallel to the gratings, and immersed in a liquid of refractive index equal to the glass, monochloronaphthalene proving very satisfactory and eliminating all distortion. The readings of A are made on a circle and vernier reflected in the concave mirror above, readings being possible to 2′ of arc. Error in zero can, if necessary, be eliminated by alternate reading on either side. Readings can be taken so rapidly that it is easy to secure a mean of 5 or 6 for each observation. As with all methods depending upon visibility of interference fringes, the possible precision is much higher than that practically obtainable, owing to the fatigue factor in making such readings. But this error, for a normal observer, does not appear to be at all prohibitive, as the following results indicate. They were made without special precautions, such as dark room, resting the eye, or head rest, and the gratings were not of first-class quality.

| SAMPLE | A | P. E. | C | P. E. |
|---|---|---|---|---|
| Solvent | 41°24′ | ±16′ | 100 | .... |
| Dope 1 | 2°30′ | ± 2′ | 6.0 | ±0.2 |
| Dope 2 | 3°38′ | ± 9′ | 8.7 | ±0.4 |
| Dope 3 | 10°15′ | ±17′ | 24.7 | ±0.5 |
| Dope 4 | 22° 0′ | ± 8′ | 53.1 | ±0.5 |
| Dope 5 | 30°28′ | ±21′ | 73.5 | ±0.95 |
| Dope 6 | 35°10′ | ±23′ | 84.9 | ±1.00 |

The probable error for A is for the mean of five readings, hence the P. E. for a single observation would be larger, amounting for the largest value to 10 per cent on the reading. The P. E. on the per cent clarity C is calculated from the value

$$\text{P. E.} = \pm \frac{\sqrt{\left(\frac{Aa}{A_{max.}}\right)^2 + b^2}}{A_{max.}} \times 100$$

where $A_{max.}$ = reading for solvent; A = reading for sample; $b$ = P. E. for setting of A; $a$ = P. E. for setting of $A_{max.}$.

The probable error of a single setting increases on the whole with the angle of setting, *i. e.*, with the clarity, but the per cent P. E. remains much the same. The readings are made as rapidly as with the polarimeter or refractometer.

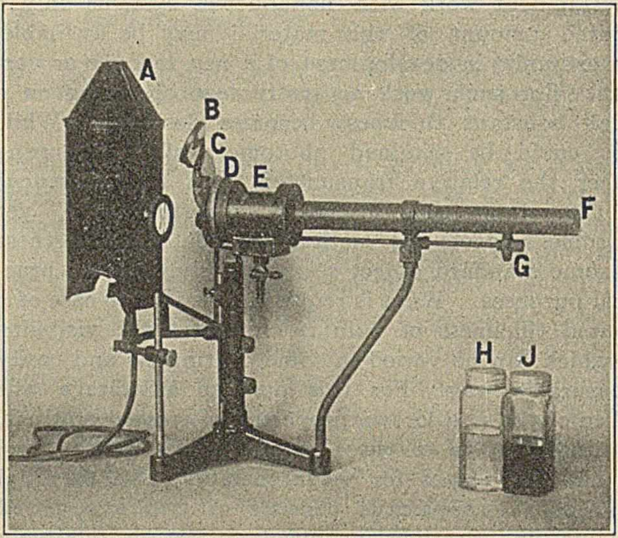

FIG. 3

A—Concentrated filament lamp and hood
B—Mirror for reading scale
C—Diffusing and reducing glasses
D—Grating mounts, with vernier and scale
E—Cell to hold sample
F—Eyepiece
H—Sample clear liquid
J—Sample lacquer

In the instrument constructed two photographic line gratings were used, having about 50 lines per in., and $A_{max.}$ was about 40° for normal visual acuity. The error using the simplified formula

$$C = A/A_{\text{max.}} \times 100 \text{ instead of } \frac{\sin A/2}{\sin A_{\text{max.}}/2} \times 100$$

is not, however, serious for the work required. Thus for $A = 5°$, $A_{\text{max.}} = 40°$, we have

| | Approximate | Accurate |
|---|---|---|
| C = | 12.5 per cent | 12.7 per cent |

There appear to be several advantages in replacing such expressions as "water-clear," by definite per cent clarity and definite colorimetric values, where color is a factor.

Figs. 1 and 2 are reproduced by kind permission of Mr. H. E. Ives and the American Optical Society from the *Journal of the Optical Society of America*. My thanks are also due to Mr. Tompkins for assistance in making observations and computations.

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## THE EFFECT OF CHLORIDES ON THE NITROMETER DETERMINATION OF NITRATES[1]

By M. T. Sanders

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The nitrometer furnishes a very rapid and accurate means of analyzing a substance which quantitatively liberates a gas when treated with liquid reagents, and is usually used to determine nitrogen in nitrates. The nitrate solution is washed into the decomposing bulb and some sulfuric acid drawn in after it. In the presence of the acid, the mercury reduces the nitrate, liberating nitric oxide. The gas is then run into the measuring tube, allowed to cool, and the volume read. Nitrometer measuring tubes are of two kinds, one for guncotton, which is graduated to read per cent nitrogen when a one-gram sample is used; the other, the so-called "universal tube," is so graduated that 0.01 mole of a gas, at 20° C. and 760 mm., will read 100.

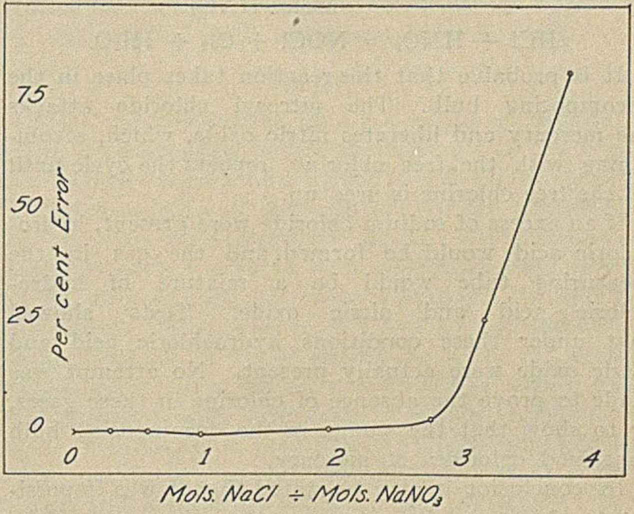
Crude sodium nitrate nearly always contains a few per cent sodium chloride. The purpose of this work was to determine the maximum quantity of sodium chloride which can be present in the sample and yet permit accurate analyses to be made on the nitrometer. As no reference to the effect of sodium chloride on the nitrometer determination of nitrates could be found in such literature as was available at the laboratory, it was thought best to determine the accuracy of the nitrometer method for samples of sodium nitrate containing varying quantities of sodium chloride.

The samples used in the nitrometer are small, 0.85 g. for sodium nitrate. To avoid the difficulty involved in mixing small quantities of the dry salts, nearly saturated solutions of sodium nitrate and sodium chloride were made up, and the samples prepared by mixing weighed portions of these solutions in a bottle.

The actual sample for analysis was weighed by means of a Lunge pipette. The procedure was as follows: The three-way stopcock and capillary tube of the decomposing bulb were filled with mercury. The sample was placed in the cup of the decomposing bulb and drawn into the bulb. The cup was then washed with 2 one cc. portions of water, followed by 25 cc. of 96 per cent sulfuric acid in three or four portions.

The decomposition was started by gentle shaking of the bulb. When the gas was no longer rapidly liberated, the decomposing bulb was put under a vacuum of 10 in. of mercury, the lower stopcock closed, and the bulb shaken violently for 4 min. The liberated gas was run into the measuring tube, allowed to cool for 15 min., and the reading taken.

A mirror was used in comparing the levels of mercury in the various tubes, thus avoiding any errors due to parallax. The samples used were of such size that the effect of slight errors in reading the volume of gas would be negligible.



The more chlorides in the sample, the more sludge was formed in the decomposing bulb, and the more difficult it was to clean the mercury in the decomposing bulb preparatory to the succeeding determination. It will be noticed in Table I that duplicate determinations on samples high in chlorides did not check well. This is probably due to the fact that the sludge in the decomposing bulb trapped some of the gas.

Table I

| $\frac{\text{Moles NaCl}}{\text{Moles NaNO}_3}$ | Per cent $NaNO_3$ by Analysis I | Per cent $NaNO_3$ by Analysis II | Mean of Results Per cent $NaNO_3$ | Per cent $NaNO_3$ Actually Present | Error | Per cent Error |
|---|---|---|---|---|---|---|
| 0.00 | 42.21 | 42.20 | 42.21 | 42.18 | +0.03 | +0.07 |
| 0.2918 | 31.87 | 31.90 | 31.89 | 31.86 | +0.03 | +0.09 |
| 0.5749 | 25.63 | 25.64 | 25.64 | 25.58 | +0.06 | +0.23 |
| 0.9776 | 20.22 | 22.13 | 22.18 | 20.24 | —0.06 | —0.30 |
| 1.950 | 13.57 | 13.31 | 13.44 | 13.34 | +0.10 | +0.75 |
| 2.728 | 11.00 | 10.63 | 10.82 | 10.48 | +0.34 | +0.324 |
| 3.129 | 11.82 | 11.99 | 11.90 | 9.44 | +2.46 | +26.1 |
| 3.782 | 14.96 | 14.68 | 14.82 | 8.12 | +6.70 | +62.5 |

From the compositions and weights of the solutions of sodium nitrate and sodium chloride used, the per cent of sodium nitrate actually present in the sample was calculated. The results of the nitrometer determinations were also calculated as sodium nitrate. From these figures the percentage error of each determination was calculated.

In Table I are tabulated the ratio of moles of sodium chloride to moles of sodium nitrate in the sample

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 5, 1919.

used, the actual per cent of sodium nitrate present, the per cent of sodium nitrate as determined on the nitrometer, and the percentage error of each determination. This table shows that if the percentage error in a determination is to be kept below the usual value of 0.1, the ratio of the moles of sodium chloride to moles of sodium nitrate present in the sample must be less than 1 : 3. This corresponds to about 17 per cent sodium chloride in a mixture of the dry salts.

When the ratio of the moles of sodium chloride to moles of sodium nitrate and the percentage error are plotted, it is seen that the curve makes a sharp break at the point where

$$\frac{\text{Moles NaCl}}{\text{Moles NaNO}_3} = 3.0.$$

This is also the ratio of $\frac{\text{Moles HCl}}{\text{Moles HNO}_3}$ in the equation

$$3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O.$$

It is probable that this reaction takes place in the decomposing bulb. The nitrosyl chloride attacks the mercury and liberates nitric oxide, which, recombining with the free chlorine, repeats the cycle until all the free chlorine is used up.

If an excess of sodium chloride were present, hydrochloric acid would be formed, and the gas in the measuring tube would be a mixture of hydrochloric acid and nitric oxide. Tests showed that under these conditions hydrochloric acid and nitric oxide were actually present. No attempt was made to prove the absence of chlorine in these gases, or to show that the sludge in the decomposing bulb contained chlorides of mercury.

In conclusion it may be stated that it was impossible to obtain results accurate to 0.1 per cent if the sample contained more than 15 to 17 per cent sodium chloride, on a dry basis.

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# A MODIFICATION OF THE THOMPSON METHOD FOR THE DETERMINATION OF ACETIC ACID IN WHITE LEAD

By L. McMaster and A. E. Goldstein

Chemical Laboratory, Washington University, St. Louis, Mo.

Received August 18, 1919

Of the several methods described in the literature for determining acetic acid in white lead, that of Thompson[1] is the most reliable, both for white leads which have not been ground in oil and for those from which the oil has been extracted.

In this method 18 g. of dry white lead are placed in a 500 cc. flask which is arranged for connection with a steam supply and also with a condenser. To the white lead are added 40 cc. of sirupy phosphoric acid, 18 g. of zinc dust, and about 50 cc. of water. The mixture is distilled down to a small bulk and steam passed in until the flask is half full of water, when the steam is shut off and the mixture again distilled to the same bulk. This operation is conducted twice. The distillate is then transferred to a special flask and one cc. of sirupy phosphoric acid added. This mixture is distilled until about 20 cc. remains in the flask, and steam is passed through the flask until it contains about 200 cc. of condensed water, when the steam is shut off and the liquid again distilled. These operations are repeated until 10 cc. of the distillate require but one drop of $N/10$ alkali to change the color of phenolphthalein. The bulk of the distillate is titrated with $N/10$ alkali, and the acetic acid calculated.

We have used this method to determine the acetic acid in a number of samples of white lead, but the method is long and tedious, and it is necessary to use a special, rather fragile flask. Thompson states that "if the dry white lead under examination has been obtained by the extraction as a residue from white lead paste, it is well that this extraction should be exceedingly thorough, as otherwise fatty acids may be held and distilled with the acetic acid. Even then they will not interfere with the final titration, as they may be filtered from the distillate before titration." In the analysis of a number of samples of extracted white lead by this method we were never able to get a clear filtrate free from fatty acids, even after long extraction; nor were we able to remove all of the fatty acids by filtration since a great part of them was present in colloidal suspension. The results, therefore, were always somewhat high.

We have found that the time of an analysis can be materially shortened, and the passing over of the fatty acids into the distillate obviated by performing one initial steam distillation followed by a second distillation under reduced pressure.

The reduced-pressure method is as follows: 18 g. of extracted white lead are placed in an ordinary 500 cc. flask, arranged for connection with a steam supply and also with a condenser, and 40 cc. of sirupy phosphoric acid (85 per cent) and 50 cc. of water are added. The flask is heated directly and the material distilled down to a small bulk. Steam is next passed into the flask and the distillation continued until about a 600 cc. distillate is obtained. After adding about 0.5 cc. of the phosphoric acid, the distillate is transferred to a heavy-walled flask. Into the neck of the flask is inserted a two-hole stopper. Through one hole is passed a very small bore capillary tube through which a minute stream of air is allowed to pass during the distillation. Through the other hole is passed a connecting bulb tube attached to a condenser. The whole apparatus is so arranged that the distillation may be conducted under a reduced pressure of about 150 mm., using an Erlenmeyer filtering flask as a receiver. When 10 cc. of the distillate require but one drop of $N/10$ alkali to produce a color change in phenolphthalein, the distillation is stopped, the distillate titrated with $N/10$ alkali and the acetic acid calculated. It is seldom necessary to distil over more than 500 cc. At no time should the liquid in the distilling flask be allowed to go much below 100 cc. because of the fact that phosphoric acid is often drawn over by the suction.

We have used the same quantities of materials as were used by Thompson so that the two methods could be compared. We found it unnecessary to use the zinc dust.

A series of determinations was carried out by the Thompson method and by the reduced-pressure method

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[1] J. Soc. Chem. Ind., 24 (1905), 487.

on a sample of white lead, made by the old Dutch process, which had been ground in oil. As much as possible of the linseed oil was first removed by shaking the white lead with portions of gasoline until the supernatant liquid was no longer yellow on standing with the white lead for several hours. The greater part of the gasoline was decanted and the remainder removed by filtration with suction. The white lead was then dried and extracted with ether for 72 hrs. by the Soxhlet method.

| | Per cent Acetic Acid | |
|---|---|---|
| Expt. | Thompson Method | Reduced-Pressure Method |
| 1 | 0.035 | 0.031 |
| 2 | 0.035 | 0.031 |
| 3 | 0.035 | 0.032 |
| 4 | 0.036 | 0.031 |
| 5 | 0.035 | 0.032 |
| 6 | 0.036 | 0.032 |
| 7 | 0.035 | 0.031 |
| 8 | 0.035 | 0.031 |

Although the results by the Thompson method check with each other, every distillate was cloudy from fatty acids in spite of the very thorough extraction; furthermore, we were not able to remove all of the fatty acids by filtration. By the other method, regardless of how cloudy the initial distillate may have been, the final distillate was always perfectly clear and the results obtained are accordingly slightly lower than those obtained by the Thompson method. If the sample had not been so thoroughly extracted, there would have been greater differences between the results obtained by the two methods, and in a commercial analysis of white lead such a long extraction is seldom made.

We have also used the reduced-pressure method for several determinations of acetic acid in white lead, ground in oil, without first extracting the oil, and find that we can obtain results that agree not only with each other but also with those obtained on the extracted sample. It is, of course, necessary to know the per cent of oil in the sample. Further experiments will be made on this part of the work.

It is thus seen that more accurate results can be obtained by this reduced-pressure method than by the Thompson method. The time necessary for a determination is also shortened and the use of a fragile special flask is unnecessary.

## A RAPID METHOD FOR THE DETERMINATION OF SULFUR IN PETROLEUM OILS

By A. W. Christie and C. S. Bisson

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Received August 13, 1919

In the examination of petroleum oils, two of the most important determinations are fuel value and sulfur content. The rinsings from the bomb after a determination of the fuel value not only serve as a means of finding the total acidity due to nitric and sulfuric acids, but also furnish a solution which can be used for the determination of sulfur. As shown by previous investigators,[1,2] the combustion of fuels in the calorimetric bomb under an oxygen pressure of 30 atmospheres insures complete oxidation of sulfur to sulfur trioxide. The resulting sulfuric acid is usually determined gravimetrically as barium sulfate.

For an accurate determination of sulfur, the barium sulfate must be allowed to stand several hours before filtration. This, together with the time necessary to filter, wash, dry, ignite, cool, and weigh the precipitate, makes the determination very long. Furthermore, in the analysis of oils containing very small amounts of sulfur the weight of barium sulfate obtained is so small as to make results inaccurate. A method which would be accurate for small amounts of sulfur and which could be completed in a short time would have distinct advantages over the barium sulfate determination. Such a method was proposed by Raiziss and Dubin.[1] The procedure consists in the separation of the sulfur as insoluble benzidine sulfate and the subsequent titration of the benzidine in acid solution with potassium permanganate.

### METHOD

After the combustion of a 0.5 to 0.6 g. sample of oil in a calorimetric bomb, the contents of the bomb are washed through filter paper into a 250 cc. beaker. The total acidity of this solution is then determined by titration with standard alkali. The solution is made to such a volume in a calibrated flask that a 25 cc. aliquot part will contain between 0.2 and 1.5 mg. sulfur. (The total acidity will give an indication of the amount of sulfur present.) A 25 cc. aliquot part is placed in a 300 cc. wide-mouthed conical flask and acidified with one drop of dilute hydrochloric acid. Ten cc. of a benzidine hydrochloride solution (8 g. per l.) are added, the solution shaken several times, and allowed to stand 15 min. or longer. It is then filtered on a small asbestos pad supported by a Witt filter plate in a Gooch filter tube. (The asbestos should have been previously treated with potassium permanganate.) The flask is washed 3 times with approximately 5 cc. cold water, allowing each portion to run through before the succeeding portion is poured on the filter. The asbestos pad and precipitate are then washed back into the original flask with distilled water. One cc. of 10 per cent sodium hydroxide is added and the solution allowed to heat on the steam bath a few minutes to dissolve the benzidine sulfate. Water is then added to bring the volume to about 100 cc. and 5 cc. concentrated sulfuric acid added. The flask is returned to the steam bath and when hot the solution is titrated with $N/20$ potassium permanganate until the yellow color which first forms has disappeared and the red color slowly fades. An excess of 10 cc. of permanganate is added and the flask replaced on the steam bath for exactly 10 min. Ten cc. of approximately $N/20$ oxalic acid are added and as soon as the solution clears the titration with $N/20$ potassium permanganate is continued to a permanent pink color. The total number of cubic centimeters of $N/20$ potassium permanganate used minus the volume of $N/20$ potassium permanganate equivalent to the oxalic acid used, multiplied by the factor

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[1] S. H. Regester, This Journal, **6** (1914), 812.

[2] A. C. Fieldner, Bureau of Mines, *Tech. Paper* **26**, 10.

[1] *J. Biol. Chem.*, [2] **18**, 297.

0.041 gives the number of milligrams sulfur in the aliquot part from which the percentage of sulfur can be calculated. The factor 0.041 has been established by the analyses of solutions of known sulfate content.

The above method has been used to determine the sulfur content of several fuel oils and the results of duplicate determinations on different weights of oil are tabulated in Table I, together with the percentage of sulfur obtained by the gravimetric barium sulfate method.

Table I—Percentages of Sulfur in Fuel Oils

| Sample No. | Barium Sulfate Method Per cent | Benzidine Sulfate Method Per cent |
|---|---|---|
| 1 | 0.71 | 0.73 |
| | 0.74 | 0.71 |
| 2 | 0.96 | 0.97 |
| | 0.96 | 0.97 |
| 3 | 0.97 | 0.92 |
| | 0.87 | 0.96 |
| 4 | 0.83 | 0.85 |
| | 0.77 | 0.85 |
| 5 | 1.70 | 1.71 |
| | 1.66 | 1.72 |

From a consideration of Table I it is evident that the volumetric method gives essentially the same result as the gravimetric method, and, on the whole, closer agreement between duplicates is obtained by the benzidine method. In each of the benzidine sulfate determinations, the aliquot parts used never exceeded one-fourth of the bomb rinsings. By using the entire rinsings, after concentration to 25 cc. or less, equally accurate results could be obtained on oils containing only 0.1 per cent sulfur. After the titration of the bomb rinsings, the time required to complete a sulfur determination by the volumetric method is about 45 min., as compared with several hours for the barium sulfate method.

### SUMMARY

I—A rapid volumetric method for the determination of sulfur in petroleum oils is described.

II—After combustion of the oil in a bomb, the sulfur is separated as insoluble benzidine sulfate and determined by titration with standard potassium permanganate.

III—Comparative analyses show that this method gives as accurate results as the barium sulfate method.

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## THE FORMALDEHYDE METHOD FOR DETERMINING AMMONIUM NITRATE[1]

By J. T. Grissom

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In the manufacture of ammonium nitrate by the double decomposition method it is necessary to keep a close analytical control of the percentage of ammonium nitrate in the reacting system. A study was made of the various proposed methods of determining ammonium salts with a view of selecting a rapid method which would give sufficiently accurate results for chemical control.

There are three more or less standard methods in general use for analyzing ammonium nitrate, *i. e.*, the Kjeldahl method, the nitrometer method, and the impurity method. The first two are very accurate, but take from $^3/_4$ to $1^1/_2$ hrs. for duplicate analyses, which is too long for most control work. The third method, while commonly used, is unsatisfactory, in that any errors of omission or commission are combined here.

A fourth method, making use of formaldehyde, is much more rapid but likely to give results from 0.5 to 1, or even more, per cent low. The method depends upon the ease with which formaldehyde reacts with ammonia or ammonium salts to form hexamethylenetetramine:

$$6CH_2O + 4NH_4NO_3 + 4NaOH = C_6H_{12}N_4 + 4NaNO_3 + 10H_2O$$

The method is very simple and in general is as follows: A neutral[1] 20 per cent solution of formaldehyde is added to the ammonium nitrate solution, warmed, and titrated with standard NaOH, using phenolphthalein as indicator, since the latter is not sensitive to hexamethylenetetramine. The amount of NaOH used gives the amount of ammonium nitrate present. There are certain objections to this method. In titrating at room temperature the reaction is slow, but by heating to 60° C. before titrating, the same end-point is obtained in a much shorter time. Upon heating to higher temperatures before titrating, however, low results are obtained. This is probably due to the conversion of hexamethylenetetramine back to ammonia at high temperatures.

The formaldehyde method was compared with the other three with a view of finding out why the results were low and of modifying it so as to obtain accurate and rapid results.

A sample of pure ammonium nitrate was prepared by repeated recrystallization until no tests were given for chlorides, sulfates, nonvolatile residue and insoluble residue. The results of check analyses are shown in the table.

Analysis of Purified Ammonium Nitrate—Per cent $NH_4NO_3$

| | | | | Formaldehyde Method | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Direct Titration NaOH | | | | Excess NaOH | |
| | Kjeldahl | Nitrometer | Impurity | 2*N* | *N* | *N*/3 | *N*/10 | *N*/3 | *N*/10 |
| | 99.84 | 99.85 | 99.845[1] | 99.15 | 99.20 | 99.59 | 98.79 | 100.10 | 99.01 |
| | 99.79 | 99.78 | ..... | 99.07 | 99.32 | 99.50 | 98.93 | 100.15 | 98.87 |
| | 99.82 | 99.88 | ..... | .... | 99.28 | 99.56 | 98.89 | 100.14 | .... |
| | ... | 99.88 | ..... | .... | .... | .... | .... | .... | .... |
| Av. | 99.82 | 99.85 | 99.845 | 99.11 | 99.27 | 99.55 | 98.87 | 100.13 | 98.94 |
| Diff.[2] | 0.0 | +0.30 | +0.025 | —0.71 | —0.55 | —0.27 | —0.95 | +0.31 | —0.88 |

[1] $NH_4NO_3$ determined by difference—Triplicate of very closely checking analyses gave moisture 0.14 per cent; acidity ($HNO_3$) 0.015 per cent; sulfates, chlorides, insoluble and nonvolatile, none.

[2] Kjeldahl taken as standard.

It will be noted that the above formaldehyde determinations were made in part by direct titration and in part by using an excess of standard sodium hydroxide solution and titrating back with standard acid.[2] Direct titration with *N*/3 NaOH gives the best results. In the presence of an excess of alkali, some of the formaldehyde is apparently converted into formic acid, *i. e.*, sodium formate. For example, 32.78 cc. normal NaOH were added to 25 cc. neutral 20 per cent formaldehyde solution. After warming to 60° C.,

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[1] Read before the Division of Industrial and Engineering Chemistry at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 5, 1919.

[1] Exactly neutralized with *N*/3 NaOH, using phenolphthalein as indicator.

[2] G. H. C. van Bers, *Chem. Weekblad*, **14** (1917), 968–75; *J. Chem. Soc.*, **112**, II, 578; *Chem. Abs.*, **12** (1918), 1447.

the solution was titrated with normal $H_2SO_4$ and required only 31.00 cc., showing that an acidity of 1.78 cc. $N/1$ $H_2SO_4$ had developed. The more dilute the alkali, the less marked is this reaction.

### CONCLUSIONS

The rapid formaldehyde method for ammonium nitrate invariably gives low results by direct titration. By using an excess of alkali and titrating back, less reliable results are obtained, presumably owing to the formation of formic acid.

Direct titration with a $N/3$ NaOH solution gives results which are consistently about 0.25 per cent low. It would seem, therefore, that this method may be used for accurate work if a suitable correction is made by adding a constant factor to the results. This factor is obtained by running a Kjeldahl on a representative sample and comparing the result with that obtained by the formaldehyde method, using $N/3$ NaOH.

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## THE PREPARATION OF HEMATOXYLIN

By Percy A. Houseman and Clement K. Swift

Laboratory of MacAndrews & Forbes Co., Camden, N. J.

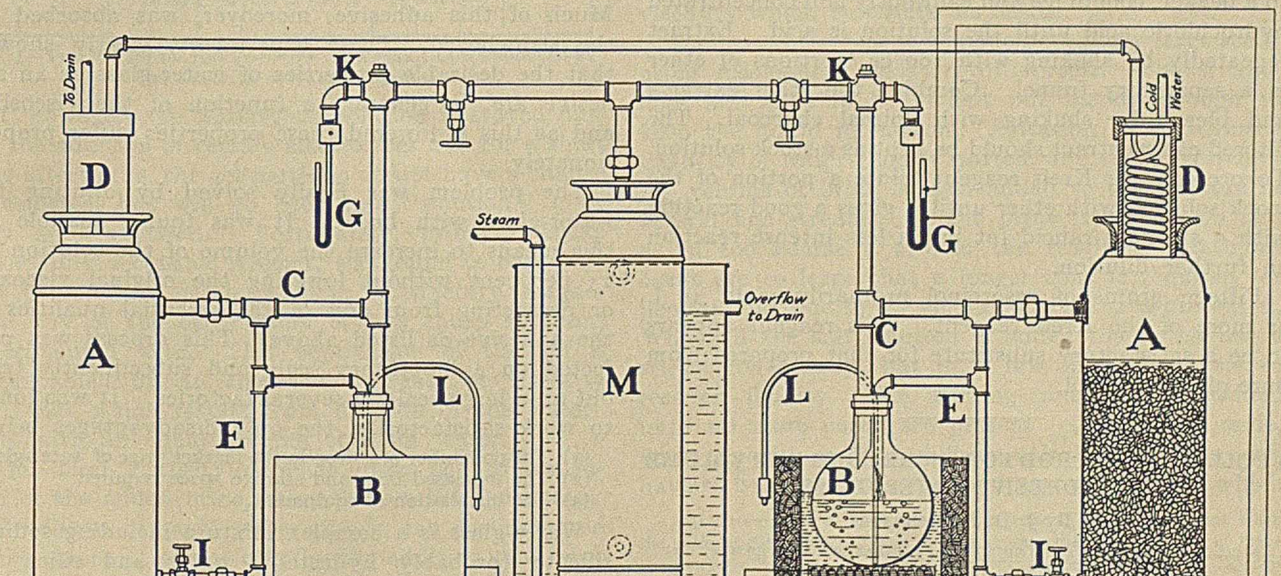
Received August 7, 1919

Hematoxylin has hitherto been made almost exclusively in Germany. During the war, a relatively large amount of hematoxylin was required for use in surgery as a bacterial stain, and in this emergency practically none was obtainable. A method was therefore sought to manufacture pure hematoxylin in commercial quantity for supply to the American government.

The apparatus developed for this purpose is shown in the cut.

The raw material used is a powdered extract of logwood which is prepared from a mild aqueous extract of unoxidized logwood chips. The powdered extract is made into small briquettes which are broken into pieces and the dust screened out. The pieces are then filled into the extractors A. B are flasks containing ether, surrounded by oil which is directly heated by electrical heaters made of Monel metal wire wound on slate. The ether vapor passing up the pipes C enters the top of the extractors A, is condensed by the copper coils D, and drops back on the logwood extract, dissolving hematoxylin from it, and enters the flasks B again through the constant level syphons E. G are mercury manometers from which an electrical connection is made to relay H, which cuts off the current from the heaters if pressure develops in the apparatus through failure to condense all the ether. The apparatus runs day and night. Every fourth day the valves I are closed and all of the ether distilled from the flasks into the extractors A. About 1500 to 2000 cc. of cold water are then introduced at K to each of the flasks. The water is heated by the oil baths and dissolves the crude hematoxylin in the flasks. The solution is blown out through the tubes L, and filtered hot. After standing for several hours pure hematoxylin crystallizes from this solution in colorless needles which are filtered at the pump, washed with ice water and dried on a porcelain tray. The extractors are changed every ten days, the exhausted extractor being transferred to the position M and the ether recovered from a hot water bath.

The apparatus described produces 100 g. of pure hematoxylin per day, the comparatively low capacity being caused by the slight solubility of the hematoxylin in ether which, however, seems to be the only practicable solvent. The loss of ether is almost nil.



The apparatus functions practically as a large-scale Soxhlet extractor with constant instead of intermittent syphon. For extractors it has been found very convenient to use 3-gal. copper fire extinguishers.

The apparatus described in this article has been found very useful for other continuous extractions with organic solvents when it is desired to treat several kilograms of material.

## METHOD OF PREPARING PHLOROGLUCINOL REAGENT FOR THE KREIS TEST

By Henry W. Dixon

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Received August 26, 1919

The Kreis[1] test has been found to be a useful chemical test for the detection and estimation of rancidity in fats when considered together with the taste, odor, and flavor. If a supply of phloroglucinol is not available, the Kreis reagent may be conveniently prepared by the following method, based on Barth and Schreder's synthesis of phloroglucinol from resorcinol.[2]

Dissolve 100 g. of sodium hydroxide in 40 cc. of water by heating slowly in an iron or nickel container. Cool to a temperature at which a few crystals of resorcinol dropped into the liquid do not become brown, and stir in 15 g. of resorcinol. Cover with a watch glass to exclude air and at the same time to permit observation, and heat for 2 or 3 hrs. in a sand bath until the melt is a dark chocolate-brown. (If the melt is heated too fast or too long, charring will take place with low yield of phloroglucinol. If the reaction is not carried to completion, unchanged resorcinol will interfere with the color of the Kreis test.) Cool, still excluding air. Dissolve the melt in about 500 cc. of water, heating gently if necessary. Transfer to a beaker, cool in ice and cautiously add concentrated hydrochloric acid until the solution is acid. Extract repeatedly by shaking with 100 cc. portions of ether in a separatory funnel. Combine the ether extracts and bleach by shaking with animal charcoal. The filtered ether extract should be kept as a stock solution. To prepare the Kreis reagent dilute a portion of the stock solution with ether until it gives a good reaction with a strongly rancid fat but a less intense reaction on further dilution.

Fifteen grams of resorcinol ordinarily yield 10 l. or more of the Kreis reagent. This reagent appears to be a satisfactory substitute for that prepared from pure phloroglucinol.

## A COLLOIDAL METHOD FOR INCREASING THE VOLUME OF ADHESIVE WATER-GLASS

By J. D. Malcolmson

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

Received May 28, 1919

Commercial silicate of soda, or water-glass, with a density of about 42° Bé., is used in very large quantities as an adhesive in the fiber container industry. In fact, this material is the only adhesive employed for gluing together the components of both double-faced corrugated board and laminated solid fiber board.

During a recent emergency created by freight embargoes and other war-time causes of delay, the stocks of water-glass in the box-makers' hands began to run low. This laboratory was at that time confronted with the problem of increasing the volume of the 42° Bé. adhesive without injuring its essential properties. These properties, which make water-glass of especial value to the box-board industry, may be classed as follows:

(1) Adhesive value. (A powerful adhesive is not required, but it must be equal to or greater than the "felted" strength of the paper fibers.)
(2) Proper viscosity. (This will be discussed below.)
(3) Low penetration. (This prevents loss of adhesive through absorption by the relatively porous corrugated strawboard. This property obviously depends upon the viscosity.)
(4) Fast setting and drying rate. (The boards are run through the pasting machines at a speed of upwards of 60 ft. per min.)
(5) Relative insolubility when dry.
(6) Relative flexibility when dry.
(7) Negligible effect of age.
(8) Relatively low cost. (This is necessary because container board is a product of relatively low cost.)

Water-glass at about 42° Bé. is a fairly viscous liquid. High viscosity is one of its desirable features for use in this industry, and is only limited by the fact that it must be fluid enough to be pumped to various parts of the factory and to flow over the troughs and rollers as fast as needed. High viscosity prevents loss by absorption and insures a satisfactory drying rate and adhesive power. Initial attempts to increase the volume of a given amount of the adhesive were made by diluting with water. This naturally lowered the viscosity to a very marked extent and the drying rate and adhesive power were correspondingly lowered to a prohibitive degree. Much of this adhesive, moreover, was absorbed by the strawboard. These experiments clearly showed that the desirable properties of water-glass as an adhesive are, in general, a function of the viscosity, and as this is lowered these properties suffer proportionately.

The problem was finally solved by diluting the water-glass with brine.[1] It was found possible by this means to increase the volume of the solution by 25 per cent without lowering the original viscosity or detracting from any of the essential qualities of the adhesive as listed above. This process was perfected on a laboratory scale and subsequently tried out on a large scale in several factories. It was found to work satisfactorily, the only disadvantages being:

(1) The possibility of a drop in the market price of water-glass.
(2) The increased floor and storage space required.
(3) The installation of equipment.

Water-glass is a complex mixture including sodium silicate (probably hydrated), water and silica (or silicic acid) in the colloidal state. The actual proportions of $Na_2O$ and $SiO_2$ to form the compound $Na_2O.xSiO_2$, and the proportion of $SiO_2$ in the colloidal form, are questions about which much uncertainty

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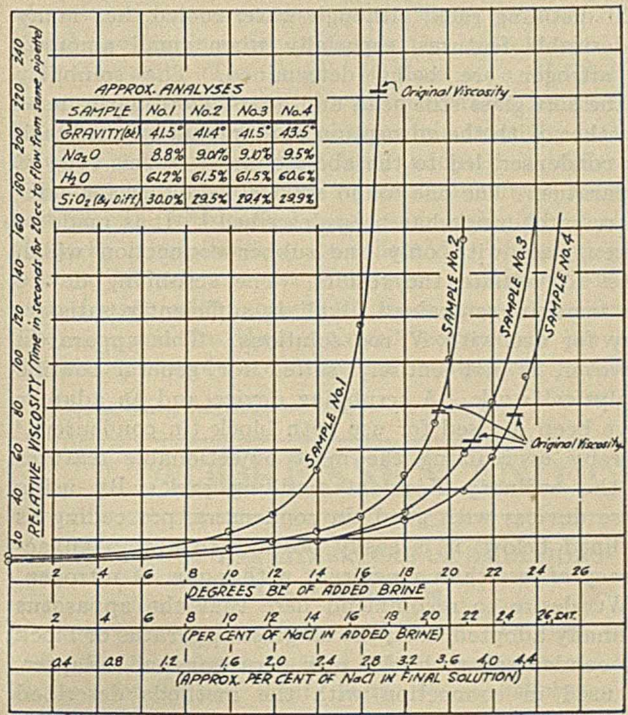
[1] Kerr, This Journal, **10** (1918), 471.

[2] *Ber.*, **12**, 503.

[1] The writer desires to acknowledge his indebtedness to Dr. E. W. Tillotson, Jr., assistant director of Mellon Institute, for his suggestions and assistance in the development of this method.

still exists. They no doubt vary in different lots of water-glass. Most investigators are of the opinion that the silica is in chemical combination to the extent of $Na_2O2SiO_2$ and that any excess $SiO_2$ over this amount is merely "dissolved." Analyses of water-glass are reported in terms of $Na_2O$, $SiO_2$ and $H_2O$. The adhesive grade usually contains from 3.0 to 3.5 parts of $SiO_2$ to one part of $Na_2O$.

When an electrolyte is added to water-glass the colloidal $SiO_2$ is coagulated. This forms what is sometimes termed a "weakly agglutinated gel" which, if undisturbed, soon coalesces to a dense mass. This, of course, is a well-known method of preparing the silicic acid gel, preparatory to dialysis.


APPROX. ANALYSES

| SAMPLE | No.1 | No.2 | No.3 | No.4 |
|---|---|---|---|---|
| GRAVITY (Bé) | 41.5° | 41.4° | 41.5° | 43.5° |
| $Na_2O$ | 8.8% | 9.0% | 9.0% | 9.5% |
| $H_2O$ | 61.2% | 61.5% | 61.5% | 60.6% |
| $SiO_2$ (by diff.) | 30.0% | 29.5% | 29.4% | 29.9% |

Fig. 1—The Effect on the Viscosity of Water-Glass Produced by the Addition of Various Brines

If, however, the water-glass solution is stirred during the addition of certain electrolytes and for a short time afterwards, the gel particles do not have a chance to coalesce, but will go back into "solution," *i. e.*, they are "peptized." Fortunately, brine, a cheap and readily accessible reagent, was found to coagulate and peptize the gel in a more satisfactory manner than any of the other more or less cheap solutions experimented with. This peptization of the gel is accompanied by an enormous increase in viscosity over that which results from dilution of the water-glass with an equal volume of plain water.

This final viscosity depends upon the concentration of the added brine, other factors being constant. The volume of most water-glasses can be increased to the extent of 25 per cent by the addition of a brine about two-thirds saturated, and with no loss in viscosity, adhesive power or drying rate. Small increases in the concentration of the brine beyond this point cause proportionately greater increases in the viscosity and the final solution soon loses all fluidity. This is shown graphically in Fig. 1. Twenty parts by volume of brine were added to eighty parts by volume of four different commercial brands of water-glass. All determinations were made at 20° C. All were increased in volume by the same amount with brines of varying concentration. The effect on each sample is distinctly different, yet the analyses of the original samples are so similar that a relation between analysis and the effect of brine is not clearly indicated.[1] This is due, perhaps, to variations in the relative proportion of silica in the colloidal state and would not be indicated by the nature of the analytical method. Owing to lack of time, the samples were not dialyzed, although dialysis would probably account for this action. It will be noticed, however, that the viscosity of all four samples was lowered to the same point by the addition of an equal amount of plain water, regardless of the original viscosity.

Water-glass thickens so rapidly when exposed to the air, and moves so slowly through ordinary viscosimeters, that only "comparative viscosities" were determined. These determinations were made by measuring with a stopwatch the time required for each solution to flow past marks at the top and bottom of the same 20 cc. pipette under constant conditions. This time, in seconds, was recorded as a measure of the "relative viscosity."

It was found in each case that an increase of 25 per cent in the volume of the water-glass was the maximum efficient amount. More brine than this makes the peptization process increasingly difficult, until a concentration is soon reached which entirely inhibits this action.

In practice the adhesive user can easily plot a viscosity curve by treating small lots of his particular supply of water-glass with a set of standard brines of different concentrations. He can then determine the proper brine concentration for reaching that final viscosity which best suits his needs.

The actual treatment is made on a fairly large scale, using mechanical agitators or stirrers. The stirring does not have to be violent but merely enough to keep the liquid in motion. Agitation of a measured quantity of water-glass is started, and the corresponding volume of brine is then added to the mixture in several fine streams. If the brine is added too fast or in too coarse a stream the resulting gelatinous curds are so large that a longer time is required for peptization, due to the smaller surface area presented. When all the salt solution is added the batch has a sticky consistency, but in a few minutes begins to recover fluidity. The stirring must be continued until no more curds are present. On a small scale, 20 to 30 min. suffice, while on a large scale this may have to be increased, depending upon the rate at which

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[1] In attempting to find some such relation it was noticed that when the ratio of $SiO_2$ to $Na_2O$ was plotted against the concentration of brine necessary to duplicate the original viscosity, the four samples fell approximately on a straight line (Fig. 2). More data would be necessary to establish the significance of this relation. It is no doubt true, however, that as the proportion of $Na_2O$ increases, stronger brines are necessary for reaching the original viscosity. Thus, a fifth sample having a ratio of 2 : 5 (10.65 per cent $Na_2O$) showed approximately the same final viscosity whether treated with plain water or saturated brine. Water-glasses of comparatively low alkalinity are, on the other hand, extremely viscous even in the original state.

the brine was added and upon the efficiency of the stirring operation.

The cost of this treatment is low, since the final increased adhesive only contains from 3 to 4 per cent, by weight, of NaCl. Any ordinary grade of salt seems to work satisfactorily.

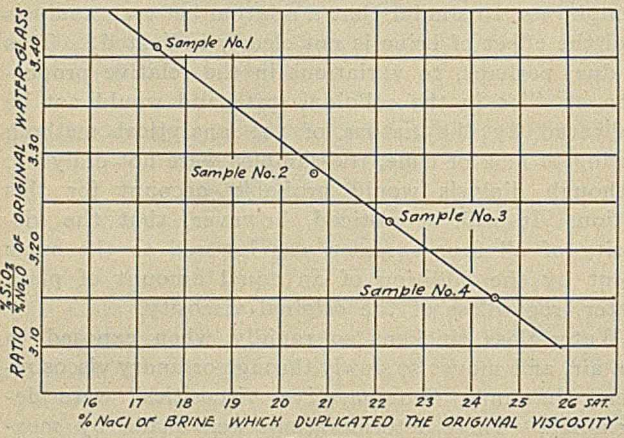

Fig. 2

The final viscosity can be varied to a large extent by small changes in the brine concentration. This is shown by the steepness of the curves in the neighborhood of the "original viscosities." This brine concentration, however, can be controlled very well in practice by the use of a standard hydrometer, since it is not at all difficult to read the latter to one-tenth of a degree, which corresponds to one-tenth of one per cent of NaCl.

The treated adhesive does not seem to be affected by age. Samples out of contact with the air have been kept and observed for over a year and show no appreciable change in adhesive power, and no loss of viscosity. After several months a flocculent sediment often settles out, but this apparently has no effect on the adhesive quality or the viscosity.[1]

Samples of corrugated container board made in both laboratory and factory, with the treated adhesive, also have remained unaffected by age for a period of more than one year.

### SUMMARY

I—The desirable properties of water-glass for use as an adhesive are, in general, a function of the viscosity.

II—A method is described of increasing, to the extent of 25 per cent, the volume of adhesive water-glass by the addition of brine, without impairing the viscosity and other desirable properties of the adhesive.

III—This method involves the practical application of certain phenomena of colloid chemistry, such as coagulation and peptization.

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[1] This same sediment is observed, to a lesser extent, when samples of ordinary water-glass are kept for some time in bottles, and is probably due to the action of the free alkali on the glass.

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## ON THE DISTILLATION OF AMMONIA

By B. S. Davisson

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Received August 8, 1919

The distillation of ammonia from an alkaline solution into standard acid and titrating or nesslerizing to determine the ammonia has long been in practice. Many procedures and forms of distilling apparatus have been suggested for transferring the ammonia into the standard acid, but all have one or more objectionable features.

A prolonged study of nitrogen methods made in connection with the biological studies of this laboratory[1] has involved the use of many different kinds of distilling apparatus. Both water- and air-cooled condensers have been used and, while many satisfactory determinations were made with air-cooled condensers, an apparatus suitable for the distillation of ammonia from an alkaline solution into standard acid should possess a water-cooled condenser. The ordinary Kjeldahl distilling rack, although water-cooled, has many undesirable features, especially when small amounts of nitrogen are being determined. The solubility of the soft glass still head and adapter ordinarily used together, with the adsorption of ammonia by the block tin condenser, led to the abandonment of this type of apparatus. The one found most satisfactory for careful research work has been described.[2] It is made of Pyrex glass with only one rubber connection which does not vitiate the results. The scrubbing device for removing entrained alkali is sufficiently satisfactory for use with *N*/100 solutions. This apparatus, however, is not entirely suited for general routine analytical work. A scrubbing device and an adapter have been devised for use with block tin condensers,[3] thereby overcoming the most objectionable features of the ordinary Kjeldahl distilling rack. By using these devices with good tin condensers, proceeding as outlined below, it is easily possible to obtain an accuracy of less than 1 per cent with 5 mg. of nitrogen.

We desire to recommend here that the apparatus as finally adopted, *i. e.*, the all-glass apparatus or block tin condensers with the new scrubber and adapter, be used in connection with the methods described from this laboratory. While the Mitscherlich distilling apparatus was found satisfactory in this laboratory for determining nitric nitrogen, it may not prove equally so in other laboratories. The procedures for using the distilling apparatus, as recommended, in connection with the determination of nitric nitrogen and total nitrogen are given below.

### PROCEDURE FOR DETERMINING NITRIC NITROGEN

The procedure[4] previously recommended is followed with the exception of the distilling apparatus, which is replaced by that described above. The cooled condenser is used for the first 20 min. of moderate boiling, after which it is drained and the boiling continued, more rapidly, for 20 min. longer. The receiver is then removed, cooled, and titrated.

### PROCEDURE FOR KJELDAHL NITROGEN DISTILLATION

The procedure followed in most laboratories consists in distilling through a water-cooled condenser until about 150° cc. of distillate have been collected.

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[1] This Journal, 7 (1915), 521; 8 (1916), 896; 10 (1918), 600; 11 (1919), 306; *Ann. Mo. Bot. Gardens*, 6 (1919), 1.

[2] *Ann. Mo. Bot. Gardens*, 6 (1919), 45.

[3] This Journal, 11 (1919), 465.

[4] *Loc. cit.*

The major portion of the ammonia passes over in the first few minutes but the prolonged distillation is necessary in order to remove the last traces of ammonia from the condenser. Benedict[1] found that the last traces of ammonia could be rapidly removed from the condenser by steaming for a short time, thereby lessening the time necessary for a distillation. He recommends draining the condenser after 15 min. of boiling and continuing the boiling until the receiving solution is slightly warmed.

Benedict's recommendation has been followed for two reasons, both to remove quickly the last traces of ammonia from the apparatus, and to keep the volume of solution in the receiver as small as possible, *i. e.*, about 110 cc., in order to reduce the hydrolysis of the indicator salt. The length of time of a distillation recommended by Benedict was found to be insufficient to remove the last traces of ammonia from the boiling solution. We have, therefore, adopted a different procedure. The solution is distilled slowly for the first 20 min. with cooled condenser, during which time about 80 cc. of distillate are collected. The condenser is then drained and the distillation continued for 15 min. longer with somewhat more rapid ebullition. The receivers are then removed, covered to prevent the absorption of carbon dioxide, cooled and titrated.

During the slow distillation with the cooled condenser the ratio of ammonia to steam passing over is much greater than with rapid boiling, yet the rate of distillation of ammonia is about the same. The steam passing over after the condenser is drained condenses in the receiving solution until the acid solution becomes hot, after which it passes out of the solution thoroughly scrubbed of any ammonia which it carried. That the ammonia is completely recovered by this method of distillation is shown by the data in Table I. The figures were obtained by digesting pure solutions of ammonium sulfate with 15 cc. of concentrated sulfuric acid, 0.5 g. copper sulfate, and 5 g. of potassium sulfate and distilling with 50 cc. of strong alkali (ammonia-free) into $N/50$ acid. The volume of solution in the receiving flask is kept small by this method of distillation and at the same time the solution in the distilling flask is not reduced in volume. The above procedure has been found entirely satisfactory for the amounts of nitrogen which are encountered in total nitrogen determinations.

TABLE I—THE RATE OF DISTILLATION OF AMMONIA
(Nitrogen Taken—5.045 Mg.)

| CONDENSERS COOLED First 10 Min. Mg. | Next 10 Min. Mg. | CONDENSERS DRAINED Next 15 Min. Mg. | TOTAL 35 Min. Mg. |
|---|---|---|---|
| 3.872 | 0.990 | 0.177 | 5.039 |
| 4.513 | 0.546 | 0.033 | 5.092 |
| 4.618 | 0.456 | 0.106 | 5.030 |

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[1] *J. Am. Chem. Soc.*, **22** (1900), 259.

# ADDRESSES AND CONTRIBUTED ARTICLES

## A REVIEW OF THE LITERATURE OF EMULSIONS[1]

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Emulsions have been the subject of lively comment in chemical literature for the past twenty years. No general theory for emulsification has been elucidated, although many have been proposed from time to time, only to be shown subsequently to apply to special cases. There has accumulated, however, a mass of arbitrary data which can be profitably applied.

An emulsion is a heterogeneous system consisting of one liquid dispersed as tiny droplets in another liquid. It has been definitely established that three phases are essential for the formation of a stable emulsion: (1) Liquid A, (2) Liquid B, and (3) an emulsifying agent. The two liquids must be immiscible, or nearly so, in one another. The common types of emulsion are those wherein water constitutes one of the liquid phases, and we recognize two main types: (1) A liquid (oil, for instance) dispersed in water, and (2) water dispersed in oil. The factor which controls the type of emulsion, *i. e.*, whether water or oil is the external phase, is the nature of the emulsifying agent.

In general, if the emulsifying agent is more easily wetted by water than by oil, then water will be the external phase and oil the dispersed phase, while if the emulsifier is more easily wetted by oil than by water, the reverse will be true. Or, as Bancroft[2] puts it: If the surface tension between Liquid A and the emulsifying agent is lower than the surface tension between Liquid B and the emulsifying agent, Liquid A will be the dispersing and Liquid B the dispersed phase. Since the emulsifying agent is almost always recognized as a colloidal substance, it is fairly safe to say that a hydrophile colloid as emulsifying agent will emulsify oil in water and a hydrophobe colloid will emulsify water in oil. This latter statement is subject to modification, however, which will be considered later.

There is a very simple and reliable method of determining the type of emulsion. Upon addition of an emulsion of oil-in-water (*i. e.*, oil dispersed phase and water external phase) to water, it will disperse. Similarly, a water-in-oil emulsion will mix with oil. In short, an emulsion will freely mix or dilute with more of its external phase, but not with more of its internal phase.

Robertson[1] suggested a method of staining with Soudan III (a fat-soluble dye). He stated that if Soudan III is sprinkled upon the surface of an oil-in-water emulsion the red color will be confined to the oil droplets and a mass of discontinuous red specks will result, whereas when sprinkled on the surface, a water-in-oil system will become uniformly red. This test has lately been severely criticized, and it has been shown that Robertson was led into misinterpretation of his olive oil-water-NaOH emulsions. He claimed to show critical concentrations leading to emulsions of water-in-oil. This has since been shown to be highly improbable.

### OIL-IN-WATER EMULSIONS

There are three main classes of this type of emulsion:

(1) The emulsifying agent is an electrical charge on the oil particles, probably due to selective adsorption of the $OH^-$ ion of water by the oil particles.

(2) The emulsifying agent is a water-soluble colloid.

(3) The emulsifying agent is an insoluble, or very slightly soluble colloid.

There are many cases also where a combination of two or even three of the above may function as emulsification agents.

(1) ELECTRICAL CHARGE AS EMULSIFYING AGENT—These emulsions are the simplest. They are identical with those observed

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[1] Read at the December 5, 1919, Meeting of the New York Section of the American Chemical Society, Chemists' Club, New York, N. Y.

[2] *J. Phys. Chem.*, **17**, (1913), 501.

[1] *Kolloid-Z.*, **7** (1910), 7.

in the condensate from steam engines. They may be prepared in any of three ways.[1]

(*a*) By shaking a small amount of mineral oil (2 cc.) with a larger volume of water (100 cc.) for 48 hrs.

(*b*) By boiling a drop of mineral oil with excess water under a reflux condenser for 30 hrs.

(*c*) When a small amount of mineral oil dissolved in alcohol is poured into water an emulsion results immediately.

Lewis found the size of the particles in these emulsions to be alike no matter how made, and of the order of 0.4 micron. They are negatively charged, the potential difference of the double layer (Helmholtz effect) being $-0.05$ volt. His measurement of the size of the charge on the droplets, by electrophoresis method, indicated $4.4 \times 10^{-7}$ electrostatic units. These emulsions owe their stability to the electrical charge and Brownian movement.

The origin of this electrical charge is obscure. Ellis[2] ascribed it to difference in dielectric constants, according to the rule of Coehn that a substance of high dielectric constant is positive to one of a lower dielectric constant when one is dispersed in the other. This, to be sure, does not explain. He prepared mineral oil emulsions by the shaking method and obtained a concentration of one part oil in 10,000 parts of water, the size of the particles being 1 to 2 microns in diameter, and the specific conductivity of the emulsion was $18 \times 10^{-6}$ mhos. He found the potential of the double layer to be $-0.05$ volt, as Lewis did; but his measurement of electrical charge showed $2.12 \times 10^{-6}$ electrostatic units for the 1-micron particles. He also noted that they were most stable in the presence of $N/1000$ sodium hydroxide. He ascribed the stability of this type entirely to the electrical charge and stated that surface tension had nothing whatever to do with it.

Hatschek[3] suggested that the stability of such mineral oil emulsions might be due to the fact that the specific gravities of the phases were close to each other, but Groschuff[4] contested this view.

Powis[5] prepared this type of emulsion by the shaking method and determined the double layer potential to be $-0.046$ volt, which checks fairly well with Lewis and Ellis. He studied the effect of addition of electrolytes to the emulsion and noted that anions have the power to increase this negative potential, while cations decrease it. Very small amounts of $KCl$ and $K_4Fe(CN)_6$ (up to 0.001 molar) increased it, while larger amounts decreased it. Salts with polyvalent cations always decreased it, due to the predominating positive charge of the cations over the anions. He noted later[6] that while an immediate sharp change in the contact potential occurred upon addition of salt, there always ensued a secondary slower change; in the case of a salt like $BaCl_2$ the change is continuous in the same sense, whereas in cases like $AlCl_3$, it reverts back a little, due to loss of $Al^{+++}$ on account of hydrolysis. Powis' studies on coagulation of these emulsions by means of electrolytes will be discussed later.

(2) WATER-SOLUBLE COLLOID AS EMULSIFYING AGENT—Good emulsifiers of this class are sodium and potassium soaps, egg albumin, gelatin, glue and other water-soluble proteins, gum arabic (acacia), gum tragacanth, Irish moss, milk, starch saponin and quillaia bark extract.

Previous to 1899, NaOH was classified as an excellent emulsifying agent for fatty oils in water, but Donnan's[7] investigation showed that its emulsifying powers were really due to the soap formed by interaction with the small amount of free fatty acid that is always present in fatty oils. He proved this by means of the drop number method, and stated that those fatty acid salts which greatly lower the surface tension are good emulsifiers, and that since they lower the surface tension they must concentrate in the surface layers about the droplets of oil, and since the soap layer is still more concentrated at the points of contact, where bubbles might happen to come together, capillary forces tend to separate them.

In a later work, Donnan and Potts[1] measured the drop numbers of aqueous solutions of the sodium salts of the fatty acids. They noted that all lowered surface tension, the lowering increasing with the higher molecular weights, but that it is strongly evident first with sodium caprylate. Emulsifying powers are not evident with this salt, but commence with sodium laurate. The emulsifying power increases with increase in concentration to $N/300$ soap solution, above which it decreases, due to the coagulating effect of $Na^+$ ions.

They objected to Pickering's theory (see later) and stated that stability of emulsions is due partly to the electrical charge and partly to presence of surface tension lowering substances which, according to the theories of Willard Gibbs, must concentrate in the surface layer.

A classic study of emulsions was published by Pickering[2] in 1907. He pursued his investigations in order to make a suitable germicidal spray for agricultural purposes. In all his experiments he emulsified a paraffin oil in water, by pumping it back and forth through a rose-nozzle garden syringe. He found potash soaps to be better than sodium soaps as emulsifiers and noted that a certain critical concentration of soap was required for each proportion of oil and water, *e. g.*, to emulsify 75 volumes of oil with 25 volumes of water, the latter must contain 0.7 to 1.8 per cent potash soap. For 40 volumes oil to 60 of water, 0.3 to 25 per cent soap can be used.

He noted that soaps vary greatly in emulsifying power, some brands being useless and, in fact, two batches of the same brand may vary greatly in emulsifying power. He noted also that while rise in temperature facilitated emulsification, it had no influence on the composition.

Pickering's 70 to 80 per cent oil emulsions were viscid like thick cream, even when benzine was used. Size of particles was about 0.1 micron. He succeeded in emulsifying 99 cc. of paraffin oil in 1 cc. of 1 per cent potash soap solution by successive additions of small portions. This famous emulsion was pure white and as stiff as a blanc-mange. It could be diluted with water but not with oil, hence was of the oil-dispersed-in-water type.

He noted that his strong emulsions were poor conductors of heat. It is possible to boil a beaker of such an emulsion at 160° to 170° C. for several minutes, while the center remains at less than 100° C. When kept in closed vessels they were permanent for months, but cracked soon after exposure to *dry* air. Strange to say, his emulsions generally separated, no matter what the starting composition, to form a permanent 65 to 82 volume per cent emulsion of oil in water.

Five emulsions of "Solar distillate" (a paraffin oil distilling between 240° and 350° C.) were prepared by Pickering, as follows:

| SAMPLE | Oil Vol.-Per cent | Soap Solution Per cent |
|---|---|---|
| 1 | 67 | 1 |
| 2 | 50 | 1 |
| 3 | 33 | 1 |
| 4 | 50 | 5 |
| 5 | 50 | 0.2 |

After standing 12 wks. they had all separated into emulsions containing from 72 to 82 per cent oil (as emulsion) in the upper layer and water below. Analysis showed a steadily decreasing oil content in the emulsions from the top downwards. In each case one-quarter of the column of emulsion from the top deviated but slightly from 84.5 per cent oil. The effect of de-

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[1] Lewis, *Kolloid-Z.*, **4** (1909), 211.

[2] *Z. physik. Chem.*, **78** (1912), 321.

[3] *Kolloid-Z.*, **9** (1911), 159.

[4] *Ibid.*, **9** (1911), 257.

[5] *Z. physik. Chem.*, **89** (1914), 91.

[6] *Ibid.*, **89** (1914), 179.

[7] *Ibid.*, **31** (1899), 42.

[1] *Kolloid-Z.*, **7** (1910), 208.

[2] *J. Chem. Soc.*, **91** (1907), 2001.

creasing the soap percentage is to increase the size of the globules finally to a point where permanence is no longer possible. Pickering reported some novel effects with solid emulsifying agents which will be discussed under that heading later. Of the water-soluble emulsifiers he stated that soap is the best and that dissolved starch, milk and flour are good, although the last named gives a flocculent rather than a creamy emulsion and milk forms solid clots. Glue is good. Egg albumin is good but gives rather frothy effects owing to inclosing air bubbles. Saponin and quillaia bark are good if proportion of oil is small.

In 1912 Newman[1] reported results of attempts to emulsify water and benzene, using oleates. He found that when benzene and water are emulsified by sodium oleate, water is always the external phase and that it is possible to make homogeneous emulsions up to 0.5 per cent benzene, and from 80 to 90 per cent benzene. Failure to make the intermediate emulsions, he ascribed to his method of shaking. He made a stiff jelly with 99 cc. benzene and 1 cc. water, using 0.05 g. sodium oleate. This emulsion was stable for more than 6 wks. With his shaking machine it was possible to get concentrated emulsions only by gradual addition of the liquid which is to be the internal phase.

Briggs[2] measured the amount of sodium oleate adsorbed by benzene emulsions in water and found that the amount of soap adsorbed increases with the degree of dispersion of the benzene particles. He constructed an ingenious laboratory type of homogenizer for the preparation of his emulsions.

In a subsequent paper[3] Briggs and Schmidt found that the drop number test cannot be used to judge the power of an emulsification agent for benzene in water. While 1 per cent solutions of both gum arabic and gelatin gave lower drop numbers than water when benzene was run into these solutions from a drop pipette, still the gum and gelatin will emulsify benzene in water, due, no doubt, to the elastic semi-solid films which they form around the benzene droplets. They are not as good as soaps, however. The optimum amount of soap to form a good emulsion was found to be 0.01 per cent of the total volume.

Fischer's[4] theory of emulsions is that a hydration compound is essential, *i. e.*, the oil globules must be covered with films of a hydrated colloid. He evidently is not familiar with the lubricating oil emulsions of Lewis, Ellis, Powis and Hatschek, nor with the solid emulsifying agents of Pickering.

Roon and Oesper[5] and later Crockett and Oesper[6] studied emulsions used in pharmaceutical practice. By the trituration-in-a-mortar method they learned that it is best to add the proper amount of water to the internal phase and the emulsifier and then triturate, and that it is best to form an emulsification nucleus in this manner, which can be modified afterwards. The proportions giving the best results are 4 parts of oil, 2 of gum arabic, and 3 of water. This nucleus is miscible in all proportions with water. Nuclei of one composition act as stabilizers for incomplete emulsions of other compositions and nuclei of one composition act as emulsifiers for other internal phases. They found Irish moss and gum tragacanth to be good emulsifiers, with the exception that tragacanth cannot be used with turpentine and forms unmanageable masses with fatty oils. They say "traces" of soap crack Irish moss emulsions, while they aid gum arabic emulsions. They are inclined to accept Fischer's hydration theory.

Davey,[7] in searching for a substitute for organic solvents in Japan varnish, found that he could emulsify linseed oil with water by addition of ammonium hydroxide and slowly stirring in a closed heated receptacle. He made the interesting discovery that such emulsions scum when exposed to air containing carbon dioxide at 17° C. or higher, but not when exposed at 16° C. or lower, or to air free from carbon dioxide at any temperature. The particles of dispersed phase were negatively charged. This emulsion proved to be a good paint.

(3) INSOLUBLE OR ONLY SLIGHTLY SOLUBLE COLLOID AS EMULSIFYING AGENT—Tfol[1] reported that Arabs in Northern Africa used an argillaceous earth as a substitute for soap in washing linen. He found that this earth readily emulsified oils in water.

Pickering[2] was probably the first to study the efficacy of certain solids as emulsification agents. He found that basic copper sulfate (made by adding 1 part of CaO to 7 parts $CuSO_4.5H_2O$) in solution in water is an excellent emulsifier. At least one part of $CuSO_4.5H_2O$ converted to the basic salt is needed to emulsify 120 parts of paraffin oil. Immediate and stable emulsification results by one stroke of the syringe and the product is very efficient as a germicidal spray in agriculture. These emulsions resembled his potash soap emulsions in all properties, except that the stable layer contained about 40 per cent oil. The ratio of CuO to emulsified oil was fairly constant, about 0.92 part of CuO to 100 parts of oil. His experiments with other solid substances yielded results as classified below.

*Substances which emulsify*—Basic ferrous sulfate, basic copper sulfate and basic nickel sulfate are the best. Ferrous and ferric hydroxides are good. Basic zinc and basic aluminum sulfates give good emulsions temporarily. The precipitate formed by adding sodium carbonate to copper sulfate is good. Calcium carbonate and arsenate are good when freshly precipitated but they soon become crystalline and de-emulsification follows. Lead arsenate and some unheated fine clays are good. Iron sulfide is good for small amounts of oil and zinc oxychloride is fair.

*Substances which produce quasi-emulsions*—Lime, silica, alumina and plaster of Paris, dried, and the following when freshly precipitated, act: Basic cadmium sulfate, magnesium hydroxide, copper hydroxide, basic zinc and aluminum sulfates, tin oxychloride, lead arsenate paste, copper sulfide, iron sulfide.

*Little or no emulsifying power*—Precipitated lead chloride, lead sulfate, barium sulfate, silica hydrosol, sulfur, flowers of sulfur, Paris green, alcoholic solution of rosin precipitated by water, ferrous ferricyanide, ferric ferrocyanide and purple of Cassius. In these cases the oil seems to wet the precipitates more than water does.

Later Pickering[3] stated that while high viscosity and low surface tension of a liquid facilitates the emulsification of an oil in it, yet it is possible to make an emulsion in a liquid which does not possess these properties. The most important condition is the presence of small particles insoluble in the dispersion medium which coat over the oil particles and prevent them from coalescing. In order that such particles have the power to form emulsions they must show only a slight tendency to unite with one another, must be readily wetted by water and must not be crystalline. He also made the novel discovery that potassium cupric tartrate will emulsify a mixture of alcohol and water. If this salt be added to an aqueous solution of alcohol, it will cause the water and alcohol to separate into two layers. Agitation results in emulsification.

Hofmann[4] used silver dichromate to emulsify chloroform in water.

In 1915, Briggs and Schmidt[5] found that colloidal ferric hydroxide (formed by hydrolysis of ferric acetate solution), was a fairly good emulsifier for benzene in water.

### WATER-IN-OIL EMULSIONS

Calcium and aluminum soaps are used in lubricating greases. Holde[6] published a discussion of these greases in 1908. They

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[1] *J. Phys. Chem.*, **18** (1912), 34.
[2] *Ibid.*, **19** (1915), 210.
[3] *Ibid.*, **19** (1915), 479.
[4] *Science*, **43** (1916), 468.
[5] THIS JOURNAL, **9** (1917), 156.
[6] *Ibid.*, **9** (1917), 966.
[7] *Physical Review*, **11** (1918), 138.

[1] *Pharm. J.*, [4] **6** (1898), 1228.
[2] *Loc. cit.*
[3] *Kolloid-Z.*, **7** (1910), 11.
[4] *Z. Biol.*, **63** (1914), 395.
[5] *Loc. cit.*
[6] *Kolloid-Z.*, **3** (1908), 270.

are solutions of lime soaps (15 to 23 per cent) in heavy mineral oil with 1 to 4 per cent water emulsified in them. Some American lubricating greases, especially for automobiles, consist of aluminum soaps dissolved in mineral oils with water emulsified in them by the aid of rosin.

Bancroft[1] states that lanolin is an emulsion of water (22 to 25 per cent) in wool wax and that it is possible to emulsify as much as 80 per cent water in wool wax. The writer believes that this may be due to the cholesterol which wool wax contains. These emulsions are stable for years.

Newman[2] found that while sodium oleate emulsifies benzene in water, magnesium oleate emulsifies water in benzene. He stated that it is never possible to emulsify water in an oil by means of sodium soaps, contrary to Robertson's findings. By using proper procedure he succeeded in emulsifying 96 per cent water in benzene. The stability is increased by the addition of a little sodium oleate. He stated that in mixed paints water is dispersed in the oil and that this is due to the presence of rosin as an emulsifying agent, and not to the pigments. In conclusion he presented his theory that whether one liquid is emulsified in another or not depends upon the emulsifying agent. A hydrophile colloid will tend to make water the external phase, while a hydrophobe colloid will tend to make water the internal phase and the colloid must be able to make a suitable coherent film around the globules to be an emulsifying agent.

Briggs and Schmidt[2] found that for the emulsification of water in benzene, magnesium oleate is fair (forms quasi-emulsions finer than aluminum palmitate). Magnesium resinate, copper resinate and lead oleate are unsatisfactory. Aluminum palmitate forms quasi-emulsions.

Clowes[3] has performed some striking experiments with soap emulsions of olive oil and water. By addition of calcium chloride to an emulsion of oil in water (with sodium oleate as emulsifying agent), when the calcium concentration exceeds the chemical equivalence to sodium, the emulsion passes through a critical point and changes to water dispersed in oil. He found that sodium, potassium and lithium soaps emulsify oil in water while magnesium, strontium, barium, iron and aluminum soaps emulsify water in oil. The first series of soaps are soluble in water and not in oil, while the second series are soluble in oil but not in water. The alkali soaps are wetted more by water than by oil and since it is thought that the surface tension is lower on the water side than on the oil side of the globules, the film will bend convex to the water and concave to the oil, enveloping the oil articles, because the area of the inner surface of a sphere is less than that of the outer surface. Similar reasoning holds for the dispersion of water in oil by the other soaps mentioned.

Clowes illustrates this phenomenon by the accompanying diagram.

In 1918 Schlaepfer[4] reported his experiments with carefully purified carbon black (gas black, soot) as emulsifying agent. This substance must be wetted more by oils than by water, because in all cases he obtained dispersions of water in the oil and never oil in water. As dispersion media he used kerosene, turpentine, benzene and toluene. With 60 cc. kerosene, 240 cc. water and 1.5 g. soot, he obtained an almost solid emulsion.

Moore[5] checked Schlaepfer's results. He was able to emulsify water and ammonium chloride solutions in kerosene with lamp black. Highly calcined lamp black and petroleum coke would not function as emulsifying agents. As the concentration of the ammonium chloride solutions was increased, the drops grew larger, due to high surface tensions of the solutions. He found that water wets raw lamp black more readily than extracted lamp black, while normal ammonium chloride solutions wet raw lamp black more readily than purified lamp black.

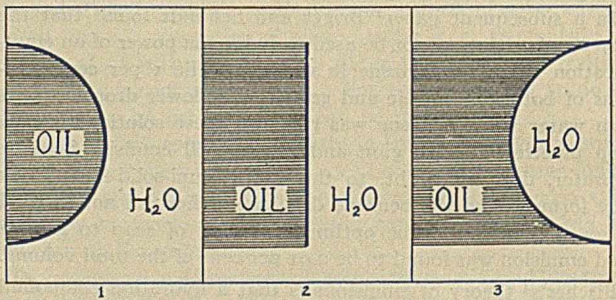
### BREAKING OF EMULSIONS

In general, de-emulsification can be accomplished by:

1—Addition of excess of dispersed phase.
2—Addition of a liquid in which the two liquid phases are soluble.
3—Destruction of the emulsifying agent.
4—Filtration.
5—Heating.
6—Freezing.
7—Electrolyzing.

The problem of breaking mineral oil emulsions in steam engine condensates has interested engineers for a long time.

Hatschek[1] offered a solution of the difficulty in a filtration method. He found that such emulsions when filtered through *amorphous* $MgCO_3$ or $CaCO_3$ (causticizing mud) came through free from oil. On a 4.5-sq. ft. filtering surface covered 0.125 in. thick with amorphous $CaCO_3$ he was able to filter 30 cu. ft. per hr. under 10 lbs. per sq. in. pressure. The adhering oil broke loose from the filtering surface and floated to surface. The permeability of the filter was but slightly diminished after 6 hours' filtration. He advises using the $CaCO_3$ in a filter press at not higher than 50 lbs. pressure because higher pressures squeeze the emulsified oil drops between the interstices in the filter bed.



| Emulsifying Agent or Film | Emulsion Formed |
|---|---|
| (1) Sodium oleate alone or sodium oleate in excess of calcium oleate equivalent | Oil in water |
| (2) Chemically equivalent proportions of sodium oleate and calcium oleate | Critical point |
| (3) Calcium oleate alone or calcium oleate in excess of sodium oleate equivalent | Water in oil |

This method worked also for emulsions of kerosene, petroleum oils, fatty oils, etc., where soap or saponin had been used as emulsifiers.

He also mentions that addition of alum and alkali, and also passing oily water between iron electrodes works well. Ferric hydroxide is formed at the anodes and combines with the oil particles and coagulates them. These methods do not appear to be practicable for commercial use.

For laboratory purposes, Hatschek recommends the ultrafilter, using Bechhold's 5 per cent collodion papers, as highly satisfactory.

In 1911 Hatschek[2] tried hydrochloric acid and sodium sulfate as coagulators. At, or near, the isoelectric point the particles did coalesce to form larger ones (about 3 microns diameter), but oil particles of even this size rise very slowly, about 2 cm. in 48 hrs.

Ellis[3] showed that these emulsions are most stable in presence of $N/1000$ NaOH; and least stable in presence of $AlCl_3$ (0.00022 g. molar); $CuCl_2$ (0.004 g. molar); NaCl (0.16 g. molar).

Powis[4] showed that greatest instability of these emulsions

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[1] *J. Phys. Chem.*, **17** (1913), 501.
[2] *Loc. cit.*
[3] *J. Phys. Chem.*, **20** (1916), 407.
[4] *J. Chem. Soc.*, **113** (1918), 522.
[5] *J. Am. Chem. Soc.*, **41** (1919), 940.

[1] *J. Soc. Chem. Ind.*, **29** (1910), 125.
[2] *Kolloid-Z.*, **9** (1911), 159.
[3] *Z. physik. Chem.*, **80** (1912), 597.
[4] *Ibid.*, **89** (1914), 186.

was attained when the contact potential reached ± 0.03 volt. This potential was found in the presence of

KCl, 51 millimolar
$BaCl_2$, 1.9 millimolar
$AlCl_3$, 0.02 millimolar
$ThCl_4$, 0.007 millimolar

A slight increase over these concentrations charges the particles with positive electricity and they become stable again.

In 1914 Ellis[1] showed that colloidal ferric hydroxide from 0.0017 to 0.0039 per cent final concentration coagulates this type of emulsion. Higher concentration results in reversal in charge of the dispersed phase and stability ensues.

Philip[2] advised that the emulsification tendencies of a lubricant be tested before using. He found that very slight contamination of a good nonemulsifying mineral oil by Mexican, Trinidad or Persian crude oils greatly increased the tendency to emulsify. He described a test for the purpose.

Harris[3] proposes to break emulsions of water and petroleum oil by passing a heavy electrical current. The electrodes must be close together.

Dijxhoorn[4] removes emulsified lubricating oil from condenser water by passing 110-volt current through the water as it passes through the feed water pipe.

Rogers[5] breaks emulsions of mineral oil and water by adding sodium salt of a sulfonated mineral oil (0.25 to 4 lbs. per barrel of mixture) and heating.

McKibben[6] passes emulsion of petroleum and water (heated sufficiently to produce vaporization) through an intensified electrical field. The vapors are condensed and cooled and the water drops out.

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[1] *Z. physik. Chem.*, **89** (1914), 145.
[2] *J. Soc. Chem. Ind.*, **34** (1915), 697
[3] U. S. Patent 1,281,952 (1919).
[4] *Le Papier*, **22** (1919), 53.
[5] U. S. Patent 1,299,385 (1919).
[6] U. S. Patents 1,299,589 and 1,299,590 (1919).

McNear and Bowles[1] have patented an apparatus for electrical treatment of emulsions.

Attempts have been made to precipitate emulsified water in linseed oil, etc., by high tension electrical discharge, but so far as can be learned the method has not been perfected. The sparks tend to jump over the surface rather than through the mixture.

Pilat and Piotrowski[2] favor heat treatment under pressure for breaking of crude petroleum emulsions consisting of oil, salt water and earthy matter. In closed kettles holding 40,000 kg., the crudes were heated by steam to 120° to 130° C. at 3 to 3.5 atmospheres pressure. A practically quantitative separation took place in 5 hrs. at 3 atmospheres pressure. The separation was accomplished more quickly at higher pressures.

Koetschau[3] claims that by heating Roumanian and Galician petroleums to 120° to 130° C., the emulsions broke within a few hours. He recommends heating acidified distillates with steam at 3 to 4 atmospheres pressure.

Newman[4] found that emulsions of oil-in-water with soap as emulsifying agent are irreversibly broken by freezing.

One could continue indefinitely discussing special means of breaking emulsions, but from a knowledge of the nature of a given emulsion and application of the principles laid down at the head of this chapter, one ought to be able to deal with each special case.

Since foams are closely related to emulsions it is of interest to note here that Fiske[5] has found isoamyl valerate to be an excellent inhibitor of foaming. He describes methods of preparations of this ester.

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[1] U. S. Patent 1,297,378 (1919).
[2] *Petroleum*, **13** (1918), 1045.
[3] *Z. angew. Chem.*, **32** (1919), 45.
[4] *J. physik. Chem.*, **18** (1914), 34
[5] *J. Biol. Chem.*, **35** (1918), 411.

# FOREIGN INDUSTRIAL NEWS

By A. McMillan, 24 Westend Park St., Glasgow, Scotland

## FUEL DEPOSITS IN ESTLAND

According to an article in *Engineering*, Estland seems to be better off than most of her neighbors as regards fuel. Large deposits of shale extend from the coast to Wegenberg over an area 80 versts long by 10 versts wide, containing an amount estimated at 1,500,000 tons. The shale contains so large a percentage of oil that it burns if a light is applied. It is being used for the production of gas and electricity in Reval and also for factories and private houses. Preparations are also being made for its application in the driving of locomotives. In the powdered state it is used for firing boilers and is said to give satisfaction. While its calorific value is from 50 to 60 per cent that of coal, its cost is only one-fourth that of coal. The deposits are being worked by the Estnian state and are also attracting attention in England.

## SULFURIC ACID MANUFACTURE

A short account of the effective "Grillo" plant erected in England by the government for the manufacture of sulfuric acid by the contact process is given in the *Journal of the Society of Chemical Industry* for October 15. The catalyst employed is platinum, deposited on granules of calcined magnesium sulfate in the proportion of 0.3 per cent. The purified gases from the sulfur burners heated to about 350° C. are passed through two converters in parallel, each containing 10,000 lbs. of the platinized mass distributed on four trays. For absorbing the trioxide produced, towers packed with quartz are used and practically perfect absorption can be obtained. The purification of the gases, which is important in preventing deterioration of the catalyst, is effected by passing the cooled vapors through coke columns and sulfuric acid drying towers; arsenic is thus eliminated and less than 0.02 per cent of other impurities (water and inert dust) retained. Details of efficiency and production-costs are given.

## GROWTH OF FRENCH CHEMICAL INDUSTRY

According to *Schweiz. Chem. Zeit.*, September 10, 1919, the French chemical industry has developed greatly during the war. The annual output of sulfuric acid was doubled, increasing from 1,000,000 to 2,000,000 tons. The output of nitric acid per month is three times greater than the total annual output of pre-war days. The yearly output of cyanamide has increased from 8,000 tons in 1913 to 100,000 tons at the present time. Prospects are favorable for the absorption of the surplus war products for agricultural purposes, and viniculture should benefit in particular. Copper sulfate is indispensable in the vine industry and of the yearly output of 50,000 tons, 40,000 tons are absorbed by viniculture. The necessary copper, which is mined in Spain, is, however, controlled by English interests.

## JAPANESE CELLULOID INDUSTRY

According to the Japanese press, the following developments are taking place in the celluloid industry: Several Japanese business men have been asked to join in promoting a concern for the amalgamation of the 130 small celluloid factories in Tokyo, the new concern to be capitalized at $1,000,000. Another proposal by a prominent Japanese factory owner is for the formation of a concern with a capital of about $6,000,000, which is to amalgamate the present factory owned by him and the Sakai and the Abosh factories, the capital to be increased to $7,500,000 when and as necessary. The scheme will be extended to cover all the factories in the country. Another version of the proceeding is that eight large firms are to amalgamate shortly. The joint concern is to be called the Dai, Nippon Seruroido Kubushika Kaisha, and its capital is to be $6,250,000.

## ARSENIC COMPOUNDS

At a recent meeting of the Chemical Society, London, Prof. F. L. Pyman described a number of arsenic compounds which had been prepared with the hope that they might be used for direct intravenous injection in simple aqueous solution and so replace the elaborate technique required in the administration of salvarsan. These compounds are arseno-benzenes of a new type obtained by the reduction of benzodiazolearsinic acids, which are produced by the action of acetic or formic acid on diaminophenylarsinic acid and its homologs. The new arsenobenzenes form dihydrochlorides which are soluble in water, but, although weaker in acid properties than salvarsan, they still prove too acid for direct intravenous injection. These experiments, says *Nature*, 104, 342, are, however, of considerable value, as they form a starting point for further work on the replacement of amino groups by heterocyclic nuclei in arsenobenzenes.

## INDUSTRIAL SYNTHETIC AMMONIA

According to an article in *Compt. Rend.*, 168 (1919), 1001, the chief object for the fixation of nitrogen in peace times is the manufacture of fertilizers. Ammonia itself cannot be assimilated by the soil, while the nitrate is expensive and the sulfate requires the use of sulfuric acid. According to G. Ville, ammonium chloride is at least equal to the sulfate as a fertilizer and is less heavy than the sulfate. In the Solvay process the ammonia is recovered by the use of lime, but the lime and calcium chloride are wasted. By a new process both the sodium bicarbonate and the ammonium chloride can be precipitated, thus the chlorine and lime are no longer lost and a good transportable fertilizer gained from synthetic ammonia in addition to three tons of sodium carbonate per ton of fixed nitrogen.

## FREEING FATS AND OILS FROM METALLIC IMPURITIES

According to a German patent, the contaminated fats are treated with aqueous solutions of the lower organic acids or their salts which are capable of forming complex salts with the metallic impurities, the fats, etc., being oxidized or reduced by the reaction. For example, contaminated maize oil is dissolved in benzine or hydrocarbons and treated with a 5 per cent oxalic acid solution, and the mixture warmed to 90° C. and well mixed by stirring. At the end of 4 hrs. the emulsion is left in the warm until the oil and acid liquors have separated, the latter being then drawn off. The oil, which formerly was dark in color and malodorous and contained 0.1 per cent ash is now light brown, of agreeable odor and taste, and free from ash. Lactic, tartaric, citric, glycolic acid, or glycocoll, or their salts, may be used.

## NICKEL-IRON ACCUMULATORS

Arrangements have been made with Batteries (Ltd.), Redditch, to manufacture in England the nickel-iron-alkaline electric accumulator for which Dr. V. Jungner, a Swede, took out his first patent in 1899, and which began to be manufactured on a large scale by a Swedish company about eight years ago. The active material of the positive electrode is nickel hydroxide, mixed with other ingredients, to increase the conductivity. The composition is formed into briquettes which are fed between two inactive perforated nickeled steel strips. The strips are cut up into suitable sizes, folded together and fitted into a steel frame, the complete electrode being then put through a rolling process to ensure perfect contact between the active material and the steel strips. At the same time grooves are formed on the plate to keep the Para rubber insulators in position. The negative electrodes are constructed in the same way, the active material being iron oxide specially prepared and mixed with other materials to prevent self-discharge of the cell. The assembled positive and negative plates are immersed in a solution consisting chiefly of potassium hydroxide, contained in a steel cell with brazed joints. The batteries are made in two types, one for a normal slow discharge in 8 hrs., and the other for rapid discharge in 4 hrs. The average working voltage is 1.2 volts; it drops slightly during the first 15 min. of discharge and then remains practically constant until the cell is discharged.

## MANIHOT SEED AND OIL

The manihot, a well-known rubber plant found in Brazil, has not hitherto been considered as a very valuable source of vegetable oil. The Germans in their desperate search for oil from any quarter have turned their attention to this plant. They planted large areas of manihot in German East Africa for the production of rubber and they now propose to consider seriously the possibility of obtaining oil from the plant. Analyses of three varieties of manihot gave the following percentages of shell and oil:

| | *M. glaziovii* Per cent | *M. dichotoma* Per cent | *M. pianhyensis* Per cent |
|---|---|---|---|
| Shell; Kernel.......... | 73.25; 26.75 | 68.25; 31.75 | 74.25; 25.75 |
| Oil in kernel.......... | 41.34 | 46.14 | 48.95 |
| Oil in whole seed...... | 11.06 | 14.65 | 12.60 |

Technical manihot oil was prepared from a mixture of 67 per cent *dichotoma*, 30 per cent *pianhyensis*, and 3 per cent *glaziovii* unshelled manihot seeds, the yield by extraction being 13 per cent. On the basis of figures given above, the theoretical yield should amount to 14.15 per cent, and an analysis of the residue showed an oil content of 1.3 per cent. The fatty acids are hard and of brown color. This technical or unrefined oil is used for the manufacture of varnish and soap. The residual cake is said to be a valuable cattle food.

## MENTHOL AND PEPPERMINT MARKET IN JAPAN

According to a report from Tokyo, the menthol and peppermint market has become very dull and prices are still strikingly high. The amount exported is also decidedly lower. Last season more than 500,000 lbs. of menthol and peppermint were exported, the largest buyer being England, the second the United States, and the third Russia. The average price per pound was $2.30 for menthol crystals and 70 cents for peppermint oil. Before the war the exports amounted to 300,000 to 350,000 lbs. Germany was the largest buyer, England the second, and the United States came far down in the list. The pre-war prices were about $2 per lb. for menthol crystals and $1 for peppermint oil. The present prices of $5 and $1.50 per lb. are too high to tempt foreign customers.

# PERKIN MEDAL AWARD

Before an audience which overtaxed the capacity of Rumford Hall of the Chemists' Club, New York City, the Perkin Medal for 1920 was awarded to Dr. Charles Frederick Chandler at the meeting of the American Section of the Society of Chemical Industry on Friday evening, January 16, 1920.

It was a thoroughly sympathetic audience in that many of those present counted themselves among the former students of the recipient, and all felt the inspiration of the presence of the man who, with his eighty-three years upon him, daily continues to contribute his full share of work with a light heart and a cheery word to all. The tables were turned—he who had so often as senior American president of the Society presented the medal in years past, was now honored by its bestowal, and the outburst of applause following the presentation testified to the cordial approval of the action of the Committee of Award in thus recognizing the long life of useful service which Dr Chandler has devoted to the upbuilding of our chemical industries.

In his introductory remarks, Mr. Charles E. Sholes chairman of the Section, emphasized the fact that the medal was given this year, not for some one conspicuous piece of work, but for noteworthy achievements in almost every line of chemical endeavor.—[Editor]

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## PERSONALITIES

### By M. C. Whitaker

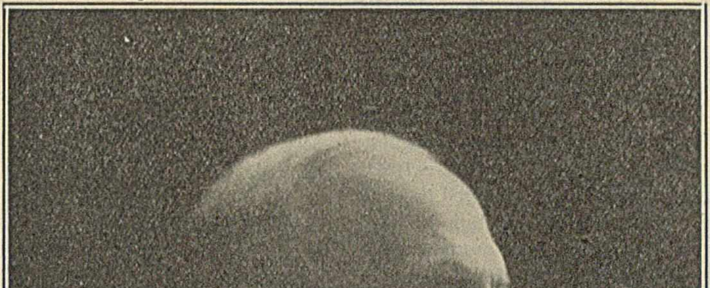
New York, N. Y.

To attempt to tell you something new about the personal side of Dr. Chandler's career is a difficult undertaking, when speaking to people who have been his friends and associates for years. It seems, on second thought, however, in view of my twenty-one years of intimate acquaintance with him that I might be able to recall a few instances to illustrate prominent characteristics and record the impressions which these observations have left upon my mind.

There is no man in the chemical profession who owes more to Dr. Chandler than I do, but it would be useless for me to attempt to express my gratitude in such English as I might command, and it would be out of place at this, his Perkin Medal meeting.

About thirty years ago as a student in a small western university, I became interested in the subject of industrial chemistry, and its correlated branches. I soon found that the national authority on this subject was C. F. Chandler, of Columbia. He probably does not realize that the reputation he enjoys extends far beyond the zone of his activities in New York, and reaches to every student in every school where applied chemistry is taught. Every mine and smelter which supports an assayer acknowledges its debt of gratitude to Chandler for the creation of one of the cleverest devices of that art, namely, the assay ton system of weights. It has saved millions of investments by eliminating bad arithmetic.

I little dreamed in those days that I might some time have an opportunity to know this leader of the profession which I sought to break into. In my wildest flights of imagination I did not picture myself as a student, an assistant, a confidant and an intimate friend of this great man.



Charles Frederick Chandler, Perkin Medalist, 1920

You may appreciate my surprise, therefore, when, a few years later, Chandler appointed me "unsight and unseen" an instructor in the Department of Chemistry at Columbia. The reason for this selection has never been understood by me, and it has never been explained by Chandler, because it is one of those unexplainable accidents. In any event, it was arranged that I should come to Columbia and assume the duties of an assistant in the great department of which he was chief. It was further agreed that he would require the University to force upon me a salary of \$83.33 per month. Salary was an extremely important consideration to me, because it was to be the first money I had ever received as a chemist, and, besides, in the absence of any other form of endowment, it was necessary to my sustenance. I was a little embarrassed by the fact that the University did not fully appreciate my position in the matter of sustenance and arbitrarily decided that the sum mentioned in the agreement should be paid, not in monthly instalments, but quarterly. However, I managed to establish the necessary credits with my landlady, and to pull through until the first quarterly check arrived.

In the meantime I was extremely busy with the work at the University. Between assisting at lectures, conducting quizzes, supervising laboratory work, correcting examination books, and interviewing students, I found time to become better and better acquainted with Chandler. By cutting out a few meals and some sleep, I was able to assist him in handling much of his burdensome detail work. During the year he suggested that I might use my vacations, holidays and such spare time as I might have by serving as his private assistant. The opportunity seemed to me the most wonderful I had ever had. Nothing was said about salary, and I thought of nothing but doing his work and getting the benefit of his experience and advice. After a few months, Chandler reminded me that I had not been paid for my work as private assistant, and handed me a check which was so big it embarrassed me, and which I could not help but feel was a great deal more than I was worth. The privilege of knowing and working with Chandler and being associated with his problems was worth more than money to me, and was all I had expected to receive.

During those early years I had an opportunity from time to time to see something of the human side of my distinguished chief. Tact is one of his greatest attributes.

It used to be, and probably still is, a source of great amusement to the students in the upper laboratories of Columbia, to drop paper bags filled with water on the heads of pedestrians. Now and then, when marksmanship is good, they hit a Fifth Avenue bus.

On one occasion, the victims were two handsomely gowned, unusually dignified, middle-aged ladies of evident social position. They swung into the Havemeyer Building, almost immediately after the accident, fairly sputtering with indignation and rage, and were met at the door by the ever-ready Chandler. They were somewhat disarmed by his genial smile, glistening eye and ready wit, and accepted his invitation to his office to discuss ways and means of properly punishing wayward students. Tea was served with liberal proportions of a flavoring extract made in New England, but named after what is destined to be a famous West Indian Island. Negotiations leading to the punishment of the students soon began to take a more hopeful trend, and in the course of half an hour the two ladies left the building, much improved in spirits, with their anger and rage replaced by smiling countenances and very audible laughter.

Chandler's earnings from his profession probably far exceed those of any other chemist in America. His generosity to others, however, keeps pace with his earnings. No one knows, not even Chandler himself, of the great financial assistance which he has given to many students. A few years ago an old Columbia graduate, unknown to most of us, died in the far west, and provided in his will that the money loaned him by Chandler from time to time should constitute the first claim upon his estate. It was with a great deal of difficulty, and without much assistance from Chandler, that we were able to determine how much money was involved. It turned out to be several thousand dollars in loans scattered over many years.

There are doubtless many cases of this kind, because during the forty-six years that Chandler was Dean of the School of Mines, he was the friend, confidant and father confessor of every one of that great army of students whose troubles are innumerable. It is out of the question for a man of Chandler's tender heart to refuse needed aid to a student. In proportion to his wealth, he gives away more than any American millionaire. His money is not spent on automobiles, yachts, fine wines, or lobster palaces, but is spent on others.

A few months ago I was invited to attend the private exhibition of the household effects of a late citizen of New York, chiefly known for his diamonds. As I stood in the center of a special room, gazing at the wonderful collection of necklaces, bracelets, handbags, slippers, garters, and stockings, I was suddenly struck with an idea. I thought of the Chandler Museum at Columbia, and recalled the innumerable times when Chandler would rush up to the University and disgorge from his pockets the most mysterious collection of teacups to illustrate some particular kind of porcelain, saucers typifying a style of decoration, vases of Wedgwood, decanters showing particular design of cutting or etching, wine glasses with special features, napkin rings, and even spoons. I wondered if there was anything in common between Chandler and "Diamond Jim," and then my thoughts turned to what a place must have looked like after a *joint raid* by these two collectors.

I have touched briefly upon Chandler's intuition, his ability to inspire others, his good-fellowship, his tact, his good-will towards others, and his hobbies. It seems to me that all of these qualities go to make up a great case for the human side of Chandler's character. I believe that we should write in large letters, and place high in the list of his distinguished achievements, and in words which I must leave to others to coin, something to express the human side of Chandler.

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## PRESENTATION ADDRESS

By Marston Taylor Bogert

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

The accomplishments of sixty years of tireless, skillfully directed activity cannot be reviewed in the brief time at my disposal this evening in more than a hasty, imperfect, and superficial way, and I know that my colleagues fully appreciate the magnitude of the task assigned me and the impossibility of telling Dr. Chandler in any one evening all that we would like to say in eulogy of his many notable contributions to civilization and in expression of our affection for him personally:

A day for toil,
An hour for sport,
But for a friend, life's all too short.

### ANCESTRY, BOYHOOD, AND TRAINING

The first Chandlers to arrive in this country were William Chandler and Annis, his wife, who came to Roxbury, Mass., from England in 1637; but it was in Lancaster, Mass., in the house of his grandfather, Nathaniel Chandler, who graduated from Harvard in 1792, that Charles Frederick was born, December 6, 1836.

His father, Charles Chandler, was a merchant in New Bedford, Mass., where the family home was located at the corner of Third and Bush Streets, and there Charles passed his early life, in company with his sisters, Catherine and Mary, and his brother, William H., later Professor of Chemistry at Lehigh University.

His maternal grandfather was John Whitney, an old Boston merchant, and his grandmother was a daughter of John Slack. On the paternal side, the Chandler ancestors were prominent in Massachusetts life, three successive John Chandlers having been Judges of Probate in Worcester County and Colonels in the Provincial Army. The Revolution broke out during the life of the last of these three, who begged to be permitted to remain neutral, as he certainly could not bear arms against his fellow-countrymen nor could he bring himself to fight against the flag under which he and his forebears had fought. But feeling ran so high that he and eight other royalists were expelled from the country and their property confiscated. This John Chandler settled in London where he lived until 1800, and where he was generally known as "the honest refugee," because he never uttered any complaint nor made any demand for reimbursement for the financial losses suffered. At his own urgent request, his wife and children had remained in America, and one of these children was the Nathaniel Chandler referred to above.

As a boy, Chandler learned much of botany and natural history in Sunday afternoon rambles with his father. At the age of 14, he attended occasional Lyceum lectures by the elder Agassiz on corals, fishes, and other zoölogical topics. The eminence of the lecturer, and the absorbingly interesting manner in which he presented his subject charmed and enthralled the budding scientist in the audience, and captivated his imagination with the splendid possibilities of such a career.

After graduating from the New Bedford High School, he continued his studies privately with a friend of the family for nearly a year, and then set out in the autumn of 1853 to secure a chemical education at Harvard, followed by study at Göttingen and Berlin from 1854 to 1856, when he received the degrees of A.M. and Ph.D. from the University of Göttingen.

### AS EDUCATOR

UNION COLLEGE—In January 1857, Dr. Chandler was appointed assistant to Professor Joy at Union College, Schenectady, N. Y., and in the spring of that year they the opened chemical laboratory there, enrolling six students in the first class. In April of the same year, Professor Joy was called to Columbia College, and Dr. Chandler succeeded him at Union, lecturing to 150 seniors, most of them older than their teacher.

SCHOOL OF MINES—Upon learning that Professor Chandler was conducting commercial assays of ores for gold and silver, and also lecturing on the subject, Dr. Egleston concluded in 1864 that Chandler was the man needed to join General Vinton and himself in the project of establishing a School of Mines in New York City as part of Columbia College. A formal invitation arrived not long afterward, and Dr. Chandler signified his acceptance. To the credit of his deep sense of patriotic duty be it recorded that he delayed his departure from Schenectady until after Election Day, 1864, in order that he might not lose his vote for Abraham Lincoln.

Some vacant rooms in the basement of the old college building on Madison Avenue and 49th Street were fitted up for the laboratories and accommodation there provided for twelve students. The new school opened its doors November 15, 1864, and twenty-four students presented themselves for admission on that date. Chandler has often told in his own inimitable way how he used to open the laboratory at seven A.M., start the fire to warm it up, sweep and clean the room, and do all in his power to make the place as attractive as possible and the lot of the students a pleasant one. It was inevitable that there was passed on to these students at the same time some of his own overflowing energy and enthusiasm.

The school was a phenomenal success practically from the beginning. During the entire winter, carpenters and plumbers were kept busy installing new desks for new students and the number of students for the first year finally rose to forty-seven. During the following vacation accommodations were arranged for seventy-two students. Eighty-nine registered for the second year. Prof. J. S. Newberry was called to the chair of geology, relieving Chandler of this subject, and a complete faculty of professors and junior officers was established. A new building was erected especially for this new school, the plans of which were drawn up by Dr. Chandler himself. It was designed to accommodate one hundred and fifty students and was soon overflowing.

Although at first appointed Professor of Geology, Analytical and Applied Chemistry, and Assayer, Dr. Chandler soon was made Dean of the school and became its leading figure, all-pervading genius and chief driving force. For thirty-three years he served as Dean, and of the many able and devoted men who have built their lives into this splendid institution, none has contributed so much as he. In 1897, when the University moved to its new site upon Morningside Heights, Professor Chandler resigned his post as Dean, but continued in charge of the department of chemistry as the "Mitchell Professor of Chemistry" until his retirement from active service, July 1, 1911. In the early days he lectured upon all branches of chemistry, both theoretical and applied, but as the staff grew in numbers he transferred to his younger associates most of this so that during the later years of his professorate his lectures were mainly upon general and industrial chemistry.

It was largely through Dr. Chandler's personal solicitation and influence that the Havemeyer family generously provided the funds for the erection of a splendid chemical building at the new site. Before drawing up the plans for this building, Dr. Chandler made a special trip to Europe for the purpose of examining the construction of the leading chemical laboratories there, with the result that Havemeyer Hall, when finally completed, embodied the best that was then known in regard to laboratory construction, and was universally regarded as the finest chemical laboratory in the United States.

The Chemical Museum of Columbia University is his own creation, begun and expanded through his indefatigable labors and personal generosity and, in recognition of this fact, the trustees have very appropriately named it the Chandler Chemical Museum. For many years it was unique, and is believed to be still the most complete of its kind in the world.

Under date of January 3, 1910, Professor Chandler addressed the following communication to the president of Columbia University:

> MY DEAR DR. BUTLER:
>
> After mature deliberation I have decided that it is much better to withdraw from active service while one is in the full enjoyment of health and strength, rather than to wait until the infirmities of age make it evident to all that one has outlived his usefulness.
>
> This is my forty-sixth year of service at Columbia, and my fifty-fourth year of college teaching, and I feel that I have had my fair share of this most agreeable life.
>
> I wish to take this opportunity to express my gratitude to you and the other members of the Board of Trustees and their predecessors for the confidence with which they charged me from the outset with the various duties of instructor, dean, bursar, and registrar, and the generous support which I have always received from them.
>
> I would respectfully request that I may be relieved from the active duties of my professorship at the end of the present academic year.
>
> Very respectfully yours,
> CHARLES F. CHANDLER

The minute adopted by the trustees in accepting this resignation, after reciting briefly his career, concludes with the following:

> Professor Chandler will carry with him into his retirement the affectionate regard and esteem of two generations of students, as well as of a host of colleagues on the teaching staff of the University. The Trustees record their grateful appreciation of this long and generous career of devoted service.

He was granted a year's leave of absence on full pay, and appointed Emeritus Professor of Chemistry to take effect upon the date of his retirement, July 1, 1911.

The Columbia Alumni established a Chandler Lectureship and Chandler Medal at Columbia, and gave a huge banquet in his honor. On that occasion, President Butler spoke with deep feeling of Dr. Chandler's approaching retirement and paid a glowing tribute to the man and his work, as follows:

> In the University, as in the nation, we mark most of all, and we cherish beyond all else, the coming and passing of personalities. No substitute has been found in specialized scholarship or in technical skill or in acquired art for those precious qualities of mind and heart that make a man a great teacher to generations of students. * * * It is by the coming and the passing of the services of these personalities that we mark the real history of Columbia, and we shall be poor indeed, no matter how magnificent our site, how splendid and how numerous our buildings, how large our endowments and how great our enrollment, we shall be poor and wretched indeed when personalities—great human personalities—are no longer found in Columbia's life * * * The world is full of chemists, but there are not very many Chandlers. * * * I know that we cannot get on without personality, and I mark with sadness and sorrow the retirement from active service of a personality which has been familiar to me for thirty-two years and which has always been full of charm, abounding in loyalty, generous in doing for Columbia and the public, and anxious to find new ways in which to serve. I call that a great academic and a great human service and am glad to have had this personality on the proud rolls of Columbia.

President Butler's Annual Report of November 7, 1910, contains the following additional reference to Dr. Chandler:

> To his teaching power as well as to his effective and conscientious service as administrator, the Department of Chemistry and the School of Mines, to which it primarily belonged, owed almost everything for many years. Professor Chandler has long been a point of contact between the University and the public, between science and industry and the public health. His career is unique of its kind, and we shall not soon look upon his like again.

In commenting upon the same subject, the *Columbia Jester*, a student publication, in its issue of January 20, 1910, has this to say as indicative of the students' attitude:

> Year after year he has taken the entering classes by the hand and has led them through a course of Chemistry, Ethics and Humor, so cleverly combined that it has made men of them. It is a striking tribute to his popularity that the class never fails to stamp their applause when he enters the room. It is a striking tribute to his splendid, practical ideas of health and to his wholesome, hearty, jovial nature that he is still only a boy, and with a mind and body sound enough to do all that a boy can do. * * * We, who have had the last chance to see him and hear him in the midst of the labors which were truly play to him, should be both proud and happy that this opportunity has not been missed. Truly do we fear for the future Freshmen who will not have him as a guiding spirit. And though we lament that so intimate and cherished a connection is finally to be severed, we rejoice that our last picture of him is one of a man hale and hearty, in the full possession of all his faculties and talents, working up to the last moment at his life's profession, and yielding finally to younger hands so that he may spend his remaining years as overseer of the work he carried to so high a development.

N. Y. COLLEGE OF PHARMACY—Professor Chandler's educational activities were by no means limited to the Columbia School of Mines. Another New York institution which owes largely to him its present proud position is the N. Y. College of Pharmacy.

During its early years, it had led a rather precarious existence, and in 1866, Prof. Peter W. Bedford, of its faculty, sought Dr. Chandler's assistance in the development of its work. It is typical of the man that, in determining upon his answer, the only question he asked himself was whether or not it was to the interest of the community that he undertake it. It did not occur to him to inquire, "What is there in it for me?" He said to himself, to quote his own words, "We must have apothecaries; we can't live without them, and they must be educated, for our lives are in their hands." He therefore accepted the invitation and lectured three evenings a week throughout the winter, year after year, until some of these lectures could be transferred to new members of the staff. At first he received $400, and provided apparatus and lecture material himself. The faculty then was composed of Professors Mayer, Bedford, and Chandler.

By 1878 the College had outgrown its one room in New York University, so it purchased and remodeled the old Morton Memorial Church at 209–211 East 23rd Street. In these more commodious quarters the College grew so rapidly that in 1892 it purchased the plot at 115–119 West 68th Street and erected thereon the fine modern fire-proof structure which still stands as an enduring monument to the untiring zealous efforts of Dr. Chandler and his associates, trustees and faculty, and to the loyal support of the druggists of this city. For many years Dr. Chandler served not only as a member of the faculty, but also as vice president and finally as president, which latter position he was occupying when he received a letter from President Butler, in 1905, inviting the College of Pharmacy to become affiliated with Columbia University. This invitation was accepted by the College, and it has since been the School of Pharmacy of Columbia University. Thus was justified the faith of those who in the days of small things labored so faithfully and self-sacrificingly.

That work of this kind is not without rewards which far transcend any financial remuneration is strikingly illustrated by the remarks of Dr. Chandler at a banquet tendered him by the officers, trustees, faculty, and alumni of the College upon his retirement from active duty in 1910:

> Wherever I see the green and red lights of the apothecary in New York, there I know I have a friend. I never go into a drug store but that some one comes up and tells me he was of the class of such and such a date, or is possibly a student still. Sometimes they are boys but newly matriculated at college. Sometimes they are old gray-haired men whose stooping shoulders and faltering footsteps make them seem older than I myself; always they are friends. This has been my highest reward, this has been my most cherished compensation. The feeling that I may have helped in the upbuilding of the institution, have aided in the formation of the characters of the rising generation of pharmacists, and that this help has brought me the friendship of my students, is a source of pride and will remain a source of pleasure so long as I live.

COLLEGE OF PHYSICIANS AND SURGEONS—Another New York educational institution in whose development Dr. Chandler was enlisted not many years after his arrival in New York, and where he served with his customary distinction and success, was the New York College of Physicians and Surgeons, which later became the School of Medicine of Columbia University.

In 1872 he was appointed Adjunct Professor of Chemistry and Medical Jurisprudence under Professor St. John, and on the death of the latter in 1876 succeeded to his chair, lecturing on physics and chemistry every afternoon from five to six o'clock. This chair he held for over twenty years, retiring in 1897.

His work there, as was the case always, was progressive and constructive, and this great school owes no small part of its present international reputation and prestige to what Dr. Chandler built into it.

### AS AUTHOR AND EDITOR

As an author, Professor Chandler has a long list of publications to his credit, embodying the results of research and invention, official reports, public addresses, sanitary regulations, analyses of waters, minerals, milk, etc., a survey of which shows at once the wide range of his interests and the versatility of his genius.

As an editor, he supplied for several years an American Supplement to the monthly edition of the *Chemical News* (of England) and, in July 1870, in association with his brother, Prof. William H. Chandler, of Lehigh University, founded the *American Chemist*, and continued its publication until April 1877, when it was given up to make way for the *Journal of the American Chemical Society*. Another editorial task, and one which proved most laborious, was that of Chemical Editor for Johnson's Encyclopaedia.

### AS INDUSTRIAL CHEMIST

Chandler was one of America's first great industrial chemists, and aided and enriched almost every chemical industry which this country supported during the two decades following 1866.

His services have always been in demand by those great corporations whose manufacturing processes are based upon chemistry, for he has not only a thorough knowledge of that science, but also an alert mind stored with original and valuable ideas. He has been generally acknowledged to be the highest authority in this country in the field of industrial chemistry. While other able and eminent chemists have their single specialties, Chandler has been called a specialist in all branches, and is especially expert in sugar refining, petroleum refining, the manufacture of illuminating gas, photo-mechanical processes, and calico printing. He has served as chemist for the New York Gas Company, and for the New York Steam Sugar Refining Company, as consultant for the Standard Oil Company, and for various other great business interests.

He has no rival to the title of dean of the industrial chemists of the United States. Even now, at the ripe age of 83, he is laboring daily in the offices of the Chemical Foundation, Inc., helping to prepare our country for the coming German chemical competition.

One of his first and far-reaching contributions to the progress of chemical industry was the invention of the system of assay weights, as outlined in his article entitled "A New System of Assay Weights," which appeared in the American Supplement of the *Chemical News* of August 1869. Although this system has been for years the one used by all assayers and metallurgists, it is safe to say that but few of them are aware of the fact that it was Chandler who introduced it, with the aid of Becker & Son, who manufactured the weights according to his specifications.

His observations and belief in the possibilities of the Castner Process for the production of caustic soda by electrolyzing sodium chloride in a "tipping cell" with a flowing mercury cathode were communicated to the Matheson interests and they later, acting upon his advice, purchased the American patent rights and established in this country a great electrochemical industry at Niagara Falls, N. Y.

It may be of interest also to note in passing a fact which is probably unfamiliar to many of this audience, namely, that it was due to Chandler's advice and urging that the firm of Eimer and Amend started their laboratory supply business in 1874. The founders of this firm were German apothecaries who were dissatisfied with the standard of purity of the American pharmaceutical products of that day and therefore began the importation of alkaloids, etc. Chandler urged them to extend this branch of their business and to include also the importation and manufacture of chemical apparatus. How great an assistance it has been to the cause of American chemistry to have had at hand the stores of fine chemicals and apparatus provided by this firm, it is difficult to overestimate.

So much of his time was occupied in great patent suits that but little was left for investigation. I well recall his advice, when I asked him to give me some guiding principles in serving as chemical expert in such litigation. His answer was brief and to the point: "Know your lesson; tell the truth; don't be afraid to say, 'I don't know.' "

The most famous suit in which he participated was that brought in the interest of the widow and assignees of the Rev. Hannibal Goodwin, an Episcopalian minister of Newark, N. J., and an amateur photographer, who was the first successful inventor of a flexible nitrocellulose film for the kodak camera and for moving picture negatives and positives. Goodwin's opponents kept him in the Patent Office ten years before he could get his patent, when he died. Thirteen years of most strenuous litigation were required to win against the infringer. Rather than have a court investigator examine the books to determine the proper award, the defendant settled with the plaintiffs by the payment of $5,000,000, which is believed to be the largest amount ever secured in a patent suit.

Other noteworthy suits were the first synthetic coal-tar color cases, of which there were five concerned with artificial alizarin, and others later which had to do with the Roussin patents, owned by Poirier & Co., of Paris, for the azo dyes obtained by diazotizing sulfanilic or naphthionic acid and coupling with suitable amines, amides, or phenols; but to review even briefly the many notable suits in which he has been engaged would take an entire evening, as they include subjects in almost every branch of chemical industry.

### AS BUILDER OF AMERICAN CHEMICAL ORGANIZATIONS

As a builder of American chemical organizations, Dr. Chandler has played a notable rôle.

He was president of the Convention of Chemists which gathered at the grave of Dr. Joseph Priestley, Northumberland, Pa., July 31 and August 1, 1874, to celebrate the centennial of chemistry, and where the first seeds were sown of what was later to become the largest and most powerful national organization of chemists the world has ever known, and of which Chandler has been twice president and many times a director—The AMERICAN CHEMICAL SOCIETY.

The founding of this SOCIETY is described in the issue of the *American Chemist* of May 1876. After the centennial meeting in 1874, the project of establishing a chemical society was often discussed by many of the New York chemists, and it was finally decided to call a meeting for the purpose. As was to be expected, Chandler at once became the recognized leader in the movement and, under date of January 22, 1876, a self-constituted committee, of which he was the guiding genius, sent out a circular letter to all chemists in New York and vicinity inviting coöperation in the formation of a local chemical society. Emboldened by the number of favorable replies received to this communication, the same committee, on March 22, 1876, distributed a second circular letter suggesting the desirability of organizing a national instead of a local chemical society, and submitting a tentative draft of a constitution and by-laws for an AMERICAN CHEMICAL SOCIETY. So many approved the proposal that a call for an organization meeting was issued on March 27, 1876, and on April 6, 1876, this meeting was held in the rooms of the New York College of Pharmacy, with 35 chemists in attendance, and with Dr. Chandler as presiding officer, and the AMERICAN CHEMICAL SOCIETY was born.

Chandler is thus the father of the AMERICAN CHEMICAL SOCIETY. It is also just to refer to him as the father of the Chemists' Club, for, although he was not the originator of the movement which led finally to its establishment, he had always spoken in favor of such an affiliation of our New York chemists, and he was the unanimous choice for the Club's first president. Without his wise and experienced guidance, his unquenchable optimism, and his financial assistance, the Club would have had a hard struggle for existence. He has been its chief reliance through good and bad weather.

### AS PUBLIC SERVANT

BOARD OF HEALTH—Unquestionably Dr. Chandler's greatest services in the utilization of science for the benefit of mankind have been in safeguarding the public health and saving human lives through improved sanitary measures.

In 1866 he was invited by the Metropolitan Board of Health to make some scientific studies of various sanitary questions affecting the health of the community. Although there was to be no pay for the service, Dr. Chandler undertook it unhesitatingly, and the commissioners were so well satisfied and so convinced of the importance of the work that at the end of the year they created the position of Chemist of the Board of Health for him, a position which he held until 1873, when he was appointed president of the Board by Mayor Havemeyer, and in 1877 reappointed by Mayor Ely, his second term expiring May 1, 1883.

Among the many important matters included within the wide sweep of his investigations were the gas nuisance, dangerous kerosene, the city water and milk supplies, adulterated liquors, poisonous cosmetics, offensive trades, the removal of the stalls around Washington, Fulton and Center markets, the abatement of the sludge acid nuisance, the regulation of slaughter houses, cattle driving, the construction of tenement houses, the introduction of a proper system of plumbing and house drainage, the establishment of the summer corps of visiting physicians, the permanent system of gratuitous vaccination, and the proper care of contagious diseases in special hospitals.

In 1866, out of every one hundred deaths in the city, 53 were of children under 5 years of age. The efforts at sanitary improvement so actively conducted under Dr. Chandler's leadership, together with the increased intelligence secured by the efforts of the sanitary authorities, the sanitary organizations, and the press, succeeded in reducing this ratio year by year until at the conclusion of Dr. Chandler's services, the 53 deaths per 100 had been brought down to 46.

This meant on the basis of the city's population at that time an annual saving of the lives of 5,000 children, without considering the reduction in the death rate of persons over 5 years of age. If the latter were also included, it is fair to estimate that at least 8,000 lives were saved to the city every year as a result of these sanitary reforms. As for each death there are 28 cases of severe sickness, the total amount of good accomplished becomes enormous.

Largely due to Dr. Chandler's activity, a State Board of Health was established of which he was made a member and chairman of its Sanitary Committee. He was always active in endeavoring to secure suitable legislation prohibiting the adulteration of foods and drugs throughout the state, and, when such laws were finally placed upon the statute books, their enforcement, as well as the regulation governing the sale of kerosene, was entrusted to him. Public analysts were appointed, samples of food, drugs and oils collected, and the necessary machinery set in motion to secure compliance with these laws throughout the state. For three years he served as chairman of this Sanitary Committee.

Upon completion of his second term as president of the Board of Health, May 1, 1883, Dr. Chandler was nominated by the Mayor for a third six-year term, but the Board of Aldermen refused to confirm the nomination, and he held over for about a year. The reason for this action by the Aldermen in failing to continue in office one who had done so much for their city is a striking illustration of the eternal fight between politics and probity, and in this particular case, to the disgrace of our city be it said, politics won.

His city and state made use of his scientific training and administrative abilities in many other ways also. For several years he was president of the State Charities Aid Association and took an active part in securing state care of the indigent insane. He served also as one of the scientific directors of the New York Botanical Garden, and chemist of the Croton Aqueduct Commission. As president of the Street Cleaning Improvement Society, he performed an effective part in bringing about the reorganization of the Street Cleaning Department.

Not only the city and state, but the nation as well, called upon Dr. Chandler for public service. Secretary of the Navy William C. Whitney selected Chandler as a member of a commission to investigate the preservation of timber, and soon thereafter the president of the National Academy of Sciences, at the request of the Secretary of the Treasury, placed him on commissions to investigate the manufacture of glucose, the denaturing of alcohol, and the waterproofing of fractional currency and bank notes.

When Chester A. Arthur was President of the United States, he named Chandler a special commissioner to study the subject of American hog products and report thereon, and in 1884 appointed him a United States delegate to the Health Exposition and the International Medical Congress at Copenhagen.

Three successive Presidents, Cleveland, McKinley, and Roosevelt, appointed him a member of the Visiting Committee of the National Observatory at Washington.

At the request of the Postmaster General, he investigated the postage stamps and refuted the stories of the newspapers that they contained poisonous constituents which made it dangerous to touch them with the tongue.

Twice, in 1880 and again in 1903, he was called upon by the Secretary of the Interior to examine the original Declaration of Independence, not from the standpoint of its justice or morality, but to advise how the faded signatures might be made more legible. Some years previously a publisher had been allowed to take a wet paper press copy of these signatures, which removed most of the ink from the parchment. All that could be suggested was to go over the signatures with India ink, but this seemed too hazardous and nothing was done.

### OTHER HONORS RECEIVED

In addition to the honors already recorded, the University of Göttingen, upon the fiftieth anniversary of his Ph.D. degree, officially renewed this degree and sent him a parchment to that effect.

He received the M.D. from the University of New York in 1873, and the LL.D. from Union College the same year. In 1900, Oxford University conferred upon him its D.Sc. This was indeed a signal distinction, as the only previous recipient of this honorary degree from Oxford had been the Prince of Wales. Chandler was thus the first scientist upon whom it was conferred. In 1911, Columbia also awarded its LL.D.

He is a member of the National Academy of Sciences, of practically all the leading chemical societies both here and in Europe, and of many other scientific, learned, and philanthropic organizations.

On April 30, 1910, a huge banquet was given in his honor by the chemists of America and a bronze bust of life size was presented to Columbia University. It is an excellent likeness, and now is housed in Havemeyer Hall where all may see it and where it shows to all students what the great builder of their Chemistry Department looks like.

When the Society of Chemical Industry decided to recognize its large and influential American Section, and to draw closer the bonds uniting the two nations, it made inquiry as to whether there was any one American chemist who, by the common consent of his colleagues and in virtue of his achievements, might properly be regarded as first among our industrial chemists. There was no question that Chandler was, and had been for many years, the leading figure in this field, and he therefore received the unprecedented compliment of election to the presidency of this great international society, being its first American president, and thus joined the group of distinguished men who had held that high office previously.

### CONCLUSION

In the foregoing narrative, albeit in a rather rambling and disconnected fashion, I have endeavored to give you some clearer view of what Dr. Chandler's busy life has meant to the cause of chemical education, as an industrial chemist and patent expert, as a builder of American chemical organizations, as editor, author, and investigator, and as beneficent public servant. The story is well known to the older generation of chemists, but is not so familiar to the younger ones, and it is a life history with which they all should be conversant. The picture is a very imperfect one and falls far short of doing the subject justice, as none knows better than your speaker, whose privilege it has been to work by his side for the past thirty years.

We can add but little in the way of honor to one who has been so showered already with honors of all kinds, and who is first in the hearts of so many American chemists, and yet it gives us pleasure to say to him, through the award of this medal that, in our opinion, the list of its recipients would not be complete nor would it be truly representative of our greatest accomplishments in the field of applied chemistry unless the name of Charles Frederick Chandler were also inscribed thereon.

Were Sir William Perkin himself alive, I am sure that nothing would have given him more pleasure than to have seen the Perkin Medal presented to his dear friend Chandler, for when Sir William and his family last visited our shores, the Chandler home was their home.

Perkin's contribution to applied chemistry was the founding of a great industry, which has had a most marvelous development and by which civilization has been brilliantly advanced. Chandler's greatest contributions have been in the most important chemical industry of all—the making not merely of chemists, but of men, and in applying his chemical knowledge in the service of mankind to protect the health of the community and to save human life.

Thousands of lives and an immense amount of suffering are saved annually as the direct benefit of the sanitary reforms which he initiated. Other thousands of lives have been so profoundly impressed by his noble example and inspiring altruism that the world is a better and a happier place to live in. The bounds of such an influence are far-reaching indeed and its duration outruns the lives of many generations.

No student ever attended his courses without being immediately struck with the fact that here was a man of lofty ideals and noble aims who was honestly and unwearyingly trying to be of service to his day and generation, and whose actuating impulse might not improbably have been expressed somewhat as follows:

> If men can say—if they but can—
> "He did his best; he played the man,
> His way was straight; his soul was clean;
> His failings not unkind, nor mean;
> He loved his fellow men and tried
> To help them"—I'll be satisfied.

I am sure that I speak not alone for myself, but also for this entire gathering and for all who know him, when I say that in our judgment he has consistently lived up to that standard throughout his long and useful life, and that he has achieved a wonderful measure of success in the sense of that word as defined by Dr. William H. Nichols, who regards it "not as the acquisition of property but the making the most of one's self."

The medal is awarded this year to Dr. Chandler because, in the opinion of the jury of award, in addition to his many valuable contributions to other branches of applied chemistry, he has made such notable advances in the great fields mentioned that he has placed the entire world in his debt and brought added prestige and dignity to the profession of which he is such a conspicuous ornament.

And now, my dear teacher, guide and friend, I cannot tell you how happy I am to be the agent selected to present this beautiful medal to you—I who have received so many favors at your hands, and who would not exchange for any amount of chemical knowledge the inspiration and encouragement derived from your example of a life worth while, and a character, like this medal, of pure gold.

May it be to you a token not only of our high appreciation of your brilliant scientific achievements, but also of our deep and abiding affection! May it bring to you and those dear to you immeasurable happiness, and may you long be spared to continue your useful work and to be the friend and guide of those setting out on life's journey!

> For, after all, life is a highway,
> And its milestones are the years,
> And now and then there's a tollgate
> Where we buy our way with tears.
>
> It's a hard road and a rough road,
> And it stretches steep and far,
> But it leads at last to a haven of rest
> Where peace and happiness are.

## ADDRESS OF ACCEPTANCE

By Charles F. Chandler

New York, N. Y.

Mr. Chairman, Ladies, and Brother Chemists: I never was more surprised than when I was notified that the Medal Committee representing the different societies interested in the Perkin Medal had awarded it to me.

I had never really considered myself eligible, as I supposed the Medal was intended particularly for discoverers and inventors of important processes in industrial chemistry. Nevertheless, I accept it with gratitude as an expression of appreciation and affection on the part of my brother chemists.

The selection of Milton C. Whitaker and Marston T. Bogert to speak for me this evening is most gratifying. There are no two men in the chemical profession for whose attainments I have a greater respect or for whose personal qualities I have a greater affection.

After having had the pleasure of presenting this most valued token of appreciation to eleven distinguished chemists, it seems odd to stand to-night in the position of the receiver instead of the giver. It is, however, eminently appropriate that Dr. Bogert should take my place on this occasion as it falls to the lot of the available senior ex-president of the Society of Chemical Industry residing in the United States to make the presentation.

I happen to be the first to receive this honor from the Society, there never before having been a foreign president. The experiment must have been satisfactory as it was soon followed by the election of Dr. William H. Nichols, then Prof. Ira Remsen, and finally by Dr. Bogert. Drs. Nichols and Remsen are not available to-night and so the duty falls upon Dr. Bogert as the representative of the Society of Chemical Industry.

I think that there was another reason for selecting Dr. Bogert to make the presentation address. He has had experience at the banquet of the chemists, April 30, 1910, when he conspicuously demonstrated his ability to say the kindest and most flattering things about his "old professor."

Dr. Bogert has given you such a comprehensive account of my life and experiences, it is hardly necessary for me to go very deeply into the subject. I will therefore select only a few incidents which may possibly interest you.

When I was about 14 years of age and attending the New Bedford High School, the incident occurred which settled my career for life. There was a young instructor who had a class in chemistry which I attended. He made the subject so interesting that I decided that I must be a chemist. I had a little work shop which I promptly converted into a chemical laboratory, had the tinsmith make me a gas holder and amused my three or four intimate playmates by making oxygen, hydrogen, olefiant gas, and various other experiments. The impression which this teacher made upon me has lasted ever since. Two or three years ago I had occasion to give a lecture in New Bedford and I opened it by recalling my school days and I enlarged upon the influence which this young teacher had exerted upon my life. I was subsequently informed that he died while still very young. It was in 1851–52 that I attended his courses. A few days afterwards I received the most touching letter from his aged widow who is still living and had been told what I had said of her husband. Her letter brought tears into my eyes. "Nothing had given her so much consolation and happiness since his death."

In 1853 I entered the chemical laboratory of the Lawrence Scientific School and spent a year under the instruction of Prof. Eben N. Hosford, a most charming man. Here I pursued a well-arranged course of instruction in qualitative and quantitative analysis.

Here another incident occurred which had a profound influence on my subsequent life. Two strangers visited the laboratory one day and we half-dozen young chemists were introduced to them. One was Prof. Josiah D. Whitney, the eminent mining engineer and geologist who five or six years afterward became a very intimate friend of mine; the other was Dr. Charles A. Joy, who had just been appointed professor of chemistry to take charge of the new laboratory at Union College, Schenectady. Professor Joy told us that he had just returned after a course of 4 years' study in Germany in the laboratories of Friedrich Wöhler and Heinrich Rose. I subsequently wrote him for further information on the subject of studying in Germany and received a full and enthusiastic account of the advantages not only of studying in Germany but of studying with these particularly distinguished chemists. It resulted in my spending my next year in the University of Göttingen. I was fortunate in being placed at once by Professor Wöhler in the laboratory for advanced students which was under his personal direction. I took several courses of lectures and practical instruction, not only in chemistry but in physics, botany, and mineralogy. We had a large colony of Americans in Göttingen during the year, most of whom were studying chemistry and some of whom have subsequently held most important positions in the United States. As I was the youngest of them all it was a great privilege for me to enjoy the companionship which was quite intimate in that small town with such men; one of them, Professor Goodwin, was a Harvard professor of Greek; another, Professor Harkness, who was there with his wife, was professor of Greek in Brown University. At the end of the year Professor Wöhler who had been a father to me and had invited me frequently to his house, induced Prof. Heinrich Rose to take me into his private laboratory as an assistant where I spent a year working in the same room with him. He, too, was a father to me, and invited me frequently to his house. His brother, Gustave, with whom I studied mineralogy, was equally friendly. I attended several courses of lectures in general chemistry by Heinrich Rose, industrial chemistry and physics by Professor Magnus, and physics by Professor Dove. At the houses of the two Roses, I used to meet some of the most distinguished scientists in Berlin, particularly Poggendorf, and Ehrenberg, the father of microscopy. I also had the pleasure while in Berlin of spending a couple of hours with Baron Von Humbolt in the Royal Palace in Potsdam. Both Wöhler and Rose gave me the most interesting material to work upon in their laboratories, either for the purpose of preparing a constituent in some quantity or for making accurate analyses of the minerals. For example, I worked upon the following materials: Selenium, tellurium, lithia, thoria, yttria, molybdic acid, tungstic acid, cerite, columbite, tantalite, sarmaskite, and yttrotantalite, and other more common materials.

At the end of my second year in Germany I was asked to put the work that I had performed in the laboratories of Wöhler and Rose into the form of a dissertation, which I did. It was accepted and printed in Göttingen at the University Press in 1856 and I received without examination, in consequence, my degrees of A.M. and Ph.D., or as they call it in Germany, Dr. Phil.

On my return to America late in the summer of 1856, I found an invitation awaiting me from Professor Joy to come to Union College and accept the position of assistant in the laboratory. This invitation I promptly accepted and on the 9th of January, 1857, I began my professional life. I felt under such obligations to Professor Joy for having directed me to Europe that I did everything I could in the laboratory for his convenience and comfort. In four months he was called to Columbia College and left at once to take the position. Fortunately for me, the venerable president of Union College, the Reverend Eliphalet Nott, had so much confidence in my abilities that he offered, if I could lecture to the senior class, to put me in charge of the chemical department and give me the title of Professor when I was old enough to merit it. I remained at Union College until the fall of 1864; was married and given a house which had formerly been occupied by President Nott; and established courses of lectures in the different branches of chemistry, including agricultural chemistry, and in mineralogy and geology. Then by a happy accident I was invited by Professor Egleston to join him and General Francis Vinton in establishing the School of Mines at Columbia College, which has proved such a great success. The most fortunate circumstance in connection with this embryo School of Mines was the fact that we had no salaries. My friends ridiculed and lamented what they considered my rashness in accepting what seemed such an unpromising appointment. But it turned out a great success. The School not only grew rapidly into a large enterprise but it gave a most powerful impetus to the growth and development of Columbia College, which, although it had been in existence for more than 100 years, had only 155 students, almost exclusively residents of New York City. This School of Mines, which quickly became a school of every variety of engineering and chemistry drew students from all over the United States, and spread the name and reputation of Columbia College everywhere, while the graduates, particularly the mining engineers, carried the name of Columbia to Australia, New Zealand, South Africa, South America and Mexico.

Starting at Columbia with no salary at all, with only the expectation of receiving one-third of the fees that might be paid by any student who might attend, we were naturally permitted to take any outside work that was congenial, which did not interfere with our duties in the School of Mines. I was soon enabled to take advantage of this privilege by giving afternoon lectures from five to six at the College of Physicians and Surgeons, and evening lectures at the College of Pharmacy, and also to accept invitations for professional work of different kinds.

One of the most promising invitations I received came to me from the Metropolitan Board of Excise. The members of this Board not being chemists were imbued with the idea that there was an enormous amount of adulterated alcoholic beverages sold in New York and as they had a very high license and a million of dollars to their credit in the bank, they started out to put a stop to this adulteration and I was invited to act as their expert to analyze the samples and to appear in the courts as their representative. When they inquired of me how much I would demand for making these analyses and appearing in court, I told them it would depend upon the number they were likely to have. They told me that there were 8000 liquor dealers and that it would certainly average three samples each, so I agreed to a fee of $20 for each case, no matter how troublesome it might be. This they considered reasonable, and when I figured it up I saw a prospective $480,000. They promptly sent me 40 samples upon which I exhausted every possible chemical test. These samples came from Mulberry Bend and other localities where the poorest liquors are probably dispensed. They consisted of brandies, whiskies, rums, and gins. Some were of very good quality, some were not so good, but not a single one contained any objectionable constituent; not one was adulterated. I must confess that I was not much surprised because I had had some previous experience in making such analyses, especially for the Vermont State Liquor Agency, and I knew that the newspaper stories of adulterated and poisonous liquors were without foundation. I received a check for $800 according to contract and never another sample for analysis, and I charged $479,200 to profit and loss.

### KEROSENE INDUSTRY

In the year ending October 31, 1869, there were 98 fires caused by kerosene accidents in New York City, and 31 in Brooklyn. There were 52 persons burned to death in New York City from the same cause, mostly women and children. It was generally supposed that these accidents were due to the fact that kerosene consisted of hydrocarbons, similar to those of "camphene" and "burning fluid," which were known to be inherently dangerous and could not be made safe. Camphene was refined spirits of turpentine, and "burning fluid" a mixture of this with alcohol; both extensively used, being very much cheaper than sperm oil, which retailed at $2.00 per gallon. When this matter was called to my attention, I said at once, "Kerosene can be made safe," and took up the investigation of the subject at once.

Manufacturers of kerosene and chemists had decided that all that was necessary to make the oil safe was to separate the lighter oils, gasoline, benzine, and naphtha, and I believed that they did so. A standard of quality had been adopted by them. The kerosene oil must not evolve a combustible vapor below 100° F., and must not take fire below a temperature of 110° F. On purchasing 78 samples in shops in the city, I found that one sample was pure naphtha, while every one of the other

78 was adulterated with naphtha. Not one of them came up to the standard of the manufacturers. I had a sample of real kerosene for comparison which I obtained from the works of a friend of mine, Dawner, of Boston, which had a flash point of 109° F. and a burning point of 128°.

Just as I finished my experiments there was a terrible accident in New York in which a mother and child were burned to death. I sat up all night and wrote my report, January 11, 1869. It was manifolded at the Board of Health and given to all the papers, in which it was printed in full, and later published all over the country. The Board of Health of New Orleans had it printed as a hand bill, and left a copy at every door. It was quoted in Berlin and in Rome.

On January 21, a supplementary report was made showing the temperatures reached in 23 house lamps, of glass and of brass, of different sizes, after periods from 1 hr. to 7 hrs. After 1 hr. the highest was in a brass lamp 100° F., the lowest in a glass lamp 77° F. After 7 hrs. the highest was in the same brass lamp 91° F., the lowest in a glass lamp 78° F.

The investigations were continued and later in the year a third report was made containing the following additional results, with a new collection of samples from retail shops in New York City:

| | Samples |
|---|---|
| 1—Safe oils complying with requirements | 21 |
| 2—Dangerous oils, flash point below 100° | 280 |
| 3—Still more dangerous, flash point below 100°, burning point below 110° | 306 |
| 4—Pure naphtha | 29 |
| TOTAL NUMBER OF SAMPLES | 636 |

A fourth investigation was made and reported, March 18, 1891, of a much more elaborate character which covered 110 printed pages. This was published and Mr. Charles Pratt asked permission to print 10,000 copies, placing an advertisement on the cover of his famous extra-safe oil, known as "Pratt's Astral Oil," which flashed at 125° F. and burned at 138° F. Permission was cheerfully granted.

The Board adopted a sanitary ordinance limiting the sale of oil having a flash point below 100° or a burning point below 110°, and appointed inspectors and equipped a testing laboratory, and before long kerosene accidents became very rare, and when they did occur generally resulted from kindling the fire with kerosene or some other kind of criminal carelessness. Not long after this I was engaged, in company with Professor Silliman, to act as an expert witness in a suit brought against infringers by Downer and Company, of Boston. This company had worked on oils obtained from the destructive distillation of coal, and also on petroleum. By employing a special process they produced, among other products, two specially "high test" oils:

1—"Downer's Standard Kerosene," flash point 115°; burning point 128°.
2—"Downer's Mineral Sperm," flash point 262°; burning point 300°.

I will quote here two paragraphs from a lecture on "Combustion," which I gave before the American Institute, January 5, 1872, immediately after the great fire in Brooklyn which was so disastrous to life.

> Naphtha is not explosive; vapor of naphtha is not explosive; it is a mixture of naphtha vapor and air, in certain definite proportions, which is explosive. If, in experimenting, we do not hit the proper proportions, we fail to produce an explosion. Any oil that will emit an inflammable vapor at any temperature below 100° F. is liable to form explosive mixtures of vapor and air, and is dangerous. I know of no process by which the lighter products of petroleum, gasoline, naphtha and benzine, can be made nonexplosive or safe, nor do I believe that there is any such process. If any oil takes fire at ordinary temperatures, or below 110° F., it is proof positive that it is dangerous, and no argument or experiment can prove anything to the contrary.
>
> This coat on its iron frame is a good representation for our purposes of a victim to kerosene. I will drench him with good kerosene; you see now that though I hold a candle to him he is in no danger. I will now throw a little of Smith's "Safety Oil" upon him; you see the moment the candle is brought near him he bursts into flames. I will save the poor wretch from a painful death by bringing the Babcock Fire Extinguisher to bear upon him. I have put him out; but were he human his days would be numbered, as a painful death would be sure to follow such frightful burns as those he has suffered from Mr. Smith's safety oil. It is said, and I believe with truth, that the burning of a square foot of the human body is sure to cause death.
>
> Before leaving this portion of the subject, I want to show you how safe it is possible to make petroleum oil. I have here a pail containing three gallons of Downer's "Mineral Sperm Oil." Into it I will plunge this mass of cotton waste till it becomes saturated with the oil; now as I raise it you see it is dripping with the oil. On holding the candle to the oily mass you see I have considerable difficulty in setting it on fire, but by heating it in one spot I shall finally heat a portion to a temperature above 300° F.—its burning point—when it will take fire. Now you see I have succeeded in starting combustion, and the burning oil quickly heats the rest of the mass till we have now a flame ten or fifteen feet high. You need not feel alarmed, for I have the flames entirely under my control. I will now plunge the burning mass into the pail of oil; you see it is at once extinguished. The "Mineral Sperm" is actually a fire extinguisher.
>
> But this oil will stand a much more severe test. Here we have a large pan of oil on a water bath. These two large alcohol lamps have raised the water to boiling; you see the steam escaping from this vent; the oil is at 212° F., 112° above the standard flashing point and at 102° above the standard burning point of safe oil. Yet you now see that this mass of cotton waste which was saturated with the oil, and was but a moment ago wrapped in flames, is now quietly extinguished. The "Mineral Sperm" is a fire extinguisher even when heated to 212° F. Am I wrong in saying it is practically as safe as whale oil?

The Standard Oil Company, then recently organized, manifested a great interest in my work on kerosene, and employed me as an expert in law suits, brought against them by persons who erroneously believed them using their patents, generally worthless, without their consent.

**OHIO OIL**.—Some years later, when what was known as "Ohio Oil" was obtained in Ohio, Indiana, and Illinois, in considerable quantities, the company received word from their German associates that the German government had been informed by their rivals that while the Standard Oil Company was supplying the American market with the superfine Pennsylvania oil, it was sending to Germany the poor, offensive Ohio oil. In consequence, the Imperial government was about to permanently forbid the importation of this Ohio oil into Germany. A high officer of the Standard Oil Company came to me and begged me to go at once to Germany and convince the German government that the Ohio oil which his company exported was first purified by the process invented by Herman Frasch. This was one of the inventions for which your committee, a few years ago, awarded to Frasch the Perkin Medal.

President Low granted me leave of absence, and I immediately visited the great works erected at Whiting, Indiana, for the special treatment of Ohio oil by the Frasch process. The impurities which had rendered the oil and all its products so offensive were certain compounds of sulfur, of which element the oil contained about one per cent. Frasch's process consisted in first dividing the crude oil by distillation into three fractions:

1—Lighter constituents—gasoline, naphtha and benzine.
2—Medium oil for lamps.
3—Heavy oil for lubricating, and paraffin.

These three fractions were then entirely freed from the sulfur compounds by distillation in huge stills, while mixed with large quantities of oxide of copper, with constant stirring. The effect was magical. Not a trace of the offensive odor was retained by either of the products.

I met at the Whiting works the chemist in charge, Dr. William M. Burton, a Heidelberg graduate. He showed me everything and answered every question. When I told him that I was going to Berlin to explain the situation, a longing look overspread his face, and he remarked that he had not been in Germany since he graduated. I caught the look and asked him if he would like to go with me. He replied that he would give anything to go. I found no difficulty in persuading the company to give him leave of absence, and so I had a most agreeable and useful companion.

Before I sailed I also visited the works at Olean, N. Y., at Philadelphia, and at Brooklyn. So there was nothing in the treatment of petroleum that was not imparted to me. We went off together. It seemed wise, before we called upon the representatives of the government, to visit and satisfy the men who would be most likely to be consulted by them. So after visiting the representatives of the Standard Oil Company, in either Bremen or Hamburg, I have forgotten which, we went to Carlsruhe and explained the whole matter to Dr. Engler, the German expert on petroleum, giving him samples of the Ohio kerosene, and explaining how he could prove the absence of sulfur, if the entire freedom from offensive smell did not satisfy him.

Then we went to Zurich and explained the matter to Dr. Lunge, the distinguished industrial chemist. On arriving in Berlin, we adopted the same tactics with the Imperial Health Department, with the same success. With all these parties I had enjoyed an acquaintance for some years, so we were cordially received and our statements readily accepted. An hour spent with Count Posidowski, the Imperial Minister of the Interior, settled the business.

A few years later I was sent to Germany to attempt to prevent the threatened establishment of an extra high standard for all imported oils to be considerably above 100° flash and 110° burning. This time I did not have the company of Dr. Burton. As before, I first went to Carlsruhe to argue the matter with Dr. Engler, but to my discomfort I found that he was in the Austrian Tyrol, near the glaciers. There was nothing to be done but to follow him, so I crossed Lake Constance and took the train for Vienna, leaving it the next morning at Bludence. Here I hired a man to drive me to my destination, which was a day's journey. At noon we stopped at a cross-road village for lunch and to change horses. After eating my simple lunch of "Butter brod" and "Schweizerkäse," and drinking my "Beyrich," I started out to see if there was anything interesting in the village. Strolling into the country store I inquired of the proprietor in German "if he sold petroleum." He replied, "Yes, indeed." I inquired what kind and he said, "Amerikanisches." "Is it not much more expensive than that from the neighboring wells in Roumania and Galicia?" "It is indeed," he replied, "but it is so much purer; it will burn in any lamp without smoking, while the other oils will burn only in a special lamp." He assured me that the peasants willingly paid the extra price. This interview gave me my trump card. Engler saw the point at once, and so did the Imperial Board of Health at Berlin, and so did Count Posidowski. I made it clear to them that if they raised materially the standard of oil to be permitted to enter Germany, the only result would be that the Standard Oil Company would get 50 gallons of such oil out of 100 crude, while they were getting 60 at that time. It would have no real advantage, while the German people would be obliged to pay as much for the 50 gallons as they were paying for the 60 gallons. He saw the point and that was the end of it.

Some years later a bill was introduced in Parliament to accomplish the same result in order to help the Scotch manufacturers who made a comparatively small amount of kerosene from the Bog Head mineral. I was in Paris at the time and, in response to a telegram from the Standard Company, I went before a Parliamentary Committee and made the same argument. A member from the Bog Head district, who was working for the bill, had before him a copy of my last report of 1871, and identified me as the author, and then asked me if I had not intimated therein that "the higher the flash point, the safer the oil." I replied that I had, but at that time we had not had as much experience as at present. Time had shown that "100° flash" was sufficient to insure safety, and that that grade of oil was generally used in the United States and exported all over the world, and that lamp accidents were very rare.

Further I reminded him of an English nobleman who lost his life by the explosion of an extra-high test oil, because the oil evolved just enough vapor to make an explosive mixture with the air in the lamp, while the 100° flash evolved enough vapor to render the air in the lamp nonexplosive.

Several distinguished English chemists, Sir Henry Roscoe, Sir Boverton Redwood, and others gave similar testimony and the bill never passed the committee.

In 1867 Dr. Elisha Harris, of the Metropolitan Health Department of New York, came to see me and told me that the Commissioners were not chemists and did not realize how much chemistry had to do with the public health and did not care to devote any portion of their income to this subject. He asked me if I would be willing to do some work for the Department without charge. I promptly accepted his invitation and interested myself at once in a great variety of subjects, most of which I shall have to omit discussing.

### WATER INVESTIGATIONS

CROTON WATER—There are two or three matters, however, which interested me very much, one of these was water. I began analyzing the Croton and Ridgewood waters every week during the three or four summer months, and I continued for several years, either myself, or, when I became president of the Health Department through Professor Waller, to keep informed with regard to the water supply of these two cities. I found that these waters were then and have been ever since among the purest waters supplied to any cities in the world. I do not believe that a case of sickness was ever caused by either one of them. General Green, who was at one time the engineer of the Croton aqueduct, was so interested in my work that he had me appointed consulting chemist for the department, and took me all over the Croton watershed that I might become familiar with the sources of the water. It is a source of constant regret to me that ill-informed persons, even physicians, are so ignorant on this subject that they advise families not to use the Croton water for drinking purposes unless it has been filtered or boiled, or both, and the result is that millions of dollars are spent in New York every year for bottled waters; not only in families who can ill afford the expense, but in down-town business offices. During the 56 years that I have lived in New York, I have used the Croton water in my family without filtering or boiling, and never has anything occurred to lead me to suppose that it was not perfectly satisfactory and wholesome.

BOILER WATERS—Another phase of the water question occupied my attention for a year when at the request of the New York Central Railroad Company I studied the subject of boiler corrosion in locomotives, boiler incrustations and feed water. I began this work at Union College and completed it in the School of Mines, publishing my results. I analyzed numerous specimens of incrustations, finding that some of them consisted of carbonate of lime; others of a mixture of carbonates of lime and magnesia; others of sulfate of lime. I also investigated the different brands of boiler medicines, most of which were frauds, and the one which seemed to be an excellent one was sold to the railroad for five times what it cost to make it, and the engineers couldn't bring their trains in on time unless this particular medicine was supplied by a particular firm. In the end, I analyzed all the feed waters employed on the road between Albany, Buffalo, and Niagara Falls, classified them as to quality, indicating those that were too bad ever to be used and causing the water stations to be abandoned, and directing the best choice to be made among the others.

HUDSON RIVER WATER—In 1871 I was called upon by the Water Commissioner of Albany to investigate the waters of the

Hudson River, to ascertain whether it would be safe to take the water above Albany and below Troy to supply the city as they had found it almost impossible to procure an adequate source of supply within reasonable distance and at such a cost as the city could afford to pay. I took up this investigation with great doubts of the fitness of this water for the city supply. I made the most careful investigations and analyses and was surprised to find that there was no reason why this water could not be used in the city of Albany. I sent in my report in 1872, stating my conclusions, with a special discussion of the destruction of the sewage contamination of large rivers caused by dissolved oxygen. I had obtained a great deal of information on this subject from the annual reports of the British Water Commissioners. The report was published and indignation meetings were held in Albany and no end of abuse was poured upon my head. The Water Commissioners were very sensible men, however; they said, "there is no sense in abusing Chandler, disprove his facts, meet his arguments, or keep quiet." My facts could not be disproved and my arguments could not be met, and consequently the Water Commissioners put up the pumping station, supplied the water to Albany, and in a short time the Health Officer of Albany informed me that the water was entirely wholesome and satisfactory.

In 1885 it became necessary to increase considerably the pumping facilities above Albany, and the Water Commissioners wrote me, calling attention to the fact that, since I made my first investigation and report in 1872, bacteria had become fashionable and were now supposed to be terrible creatures capable of producing all kinds of diseases, and whether I cared to revise the opinion which I gave them 13 years before. It happened that I was quite familiar with what had been published with regard to bacteria, having quite a library on the subject, and having had occasion to make myself specially familiar with them in order to prepare an article on fermentation for Johnson's Encyclopaedia about 1874, so I wrote the second report on the waters of the Hudson River, which was published in Albany in 1885, containing a discussion of possible bacterial contamination of water; it was not to be feared.

Fourteen years ago while in Europe I was cabled to look up the ozone treatment of city waters. Accordingly, I visited Berlin, Paderborn, and Paris, where experiments had been carried on. At Paderborn the process was in full operation, although the water supply was entirely above suspicion. The water descended slowly through a wide cylinder, while the ozonized air bubbled up through it. The effect was marvelous. The ozone seemed to destroy the organic matter, which, though minute, was sufficient to conceal the true color of the water, for when the treated water poured into a large snow-white vat it was very distinctly blue.

SARATOGA WATERS—In the early years of my residence at Union College I became interested in the Saratoga waters. I found a great diversity of opinion as to the nature of these waters, some local physicians telling their patients that there was such a great difference in the waters that it was not safe for them to drink them except after the physician had carefully diagnosed their cases, had directed them as to which waters they should imbibe, what quantities of each, and at what times of day. The owners of the Star Spring employed me to make a careful analysis of their water and soon it became the fashion to have the waters analyzed by me. As the waters contain a great variety of constituents, including small quantities of iodine. bromine, baryta, lithia, etc., I had to charge a good, round figure, which those who could afford it cheerfully paid; and as I was extremely anxious to analyze all the waters, for those who could not afford to pay my fee, I made the analyses gratuitously. Including springs and artesian wells, I analyzed about a dozen different springs in Saratoga and three at Balston. Instead of the waters differing from each other, I found that they all contained the same constituents, counting out one or two sulfur waters in out-of-the-way places which I never took the trouble to analyze. The total amount of solids varied from a minimum of 302 grains in one U. S. gallon to 1,184 grains, the latter being the amount in the Balston artesian lithia well, which was bored over 600 ft. deep. There is an interesting story about the Highrock Spring at Saratoga. It is the oldest known spring there and it consists of a volcano-shaped rock about 4 ft. above the level of the surrounding ground with a hole or crater in the center supposed at that time to be of almost unknown depth. This hole had a diameter at the top or mouth of 8 or 10 in. and the water rose to within about a foot of the top. Saratoga was first visited by a white man when Sir William Johnson went there in 1767. He was told by the Indians that according to their traditions the water formerly rose and overflowed regularly and continuously, but not within their recollection. This must evidently have been the case, for the Highrock is composed of tufa, carbonate of lime, and contains the impressions of leaves and the shells of snails here and there. It had evidently been formed gradually by a deposition of carbonate of lime from the water, which is a common occurrence with this class of waters. After a time, during my association with Saratoga, this spring changed hands and the enterprising purchaser decided to make the water resume its old habit of overflowing the rock. In order to do this he had oblique holes drilled on different sides around the edges of the rock toward the center. He then introduced wedges and succeeded in detaching the rock from its base. He then put chains underneath and hoisted it off one side. Then they enlarged the hole up through which the water came and went down expecting to find some leak which had prevented the water from rising any higher, and which they intended to close. They found beneath the high rock a layer of tufa 7 ft. thick, including some muck, below that they found 2 ft. of tufa clean, below that one foot of muck and below that again 3 ft. of tufa. Just below the rock itself they found 4 well-preserved logs put crosswise at right angles to make a curb for the spring which must have been placed there before the Highrock was formed, and, finally, at a depth of 17 ft. they found a considerable quantity of half-burned embers and charcoal, showing that visitors had made fires before that 17 ft. of material had been deposited.

An enterprising citizen of Saratoga was very anxious to ascertain when those fires had been made and remembering that the botanist ascertained the age of a tree by making a cross section of the stem and counting the lines or rings from the center to the circumference ascertained the number of years it had been growing, he took a piece of the Highrock, smoothed it against a grindstone, and found it showed 81 lines to the inch, so he said it must have taken 3,840 years to form. He continued his calculations for the remaining 13 ft. The following table shows his figuring:

THE HIGHROCK

| | | Years |
|---|---|---|
| The Highrock | 4 ft.—81 lines to inch | 3,840 |
| Muck and Tufa | 7 ft. | 400 |
| Tufa | 2 ft.—25 lines to inch | 600 |
| Muck | 1 ft. | 130 |
| Tufa | 3 ft. | 900 |
| | TOTAL | 5,870 |

According to his education the world had existed only

4,004 yrs. before the Christian Era
1,870 yrs. after the Christian Era

5,874 yrs. in all
5,870 yrs. since the fire was made

4 yrs. after the Creation

Consequently, there was no one living on the face of the earth excepting Adam, and he was 4 yrs. old. I hope you will pardon my frivolity in presenting this ridiculous proposition to you, but it went the rounds in Saratoga.

There is one other interesting matter connected with the Saratoga Springs. Some years ago a sanitarium near the Hawthorn Spring set up a pump and drew large quantities of water from a tube of some depth, with the result that the Hawthorn well was very seriously affected.

A law suit resulted in which my testimony and that of others was taken in favor of Hawthorn, with the result that the sanitarium was enjoined. At or about the same time, a company began to bore numerous wells some little distance from the Springs, introduce steam pumps, commercialize the carbonic acid gas, and permit the water to run to waste. In a short time the springs began to show the disastrous effects. The waters no longer spouted from the spouting springs, the others no longer came to the surface, and pumping had to be resorted to. In addition to this the diminished pressure of water in the springs permitted fresh water to permeate into them and dilute them.

Again I was called as an expert, and testified to the ruinous effects of this pumping. The company produced experts who declared that it was absolutely impossible for this pumping to have any effect whatever on the springs, and that the falling off of the springs must be due to natural causes. The judge, however, was a second Solomon. He directed the defendants to stop pumping for 48 hrs. to decide the question, and ordered the sheriff to see that the order was obeyed. Within 24 hrs. the whole town gathered around the Hawthorn Spring to see the water again rising, brilliant in the sun with gas bubbles, and overflowing the large glass cylinder placed over the spring. In the end the State bought all the springs and wells and established a State Reservation.

LEAD IN DRINKING WATER—The question of lead in drinking water came to my attention at an early day. Physicians reported cases of lead poisoning. I will mention as a single example an elderly gentleman's case which was diagnosed as lead poisoning. No probable source of the lead could be suggested till the doctor interviewed the cook, and learned that her first duty in the morning was to place the old gentleman's "wheaten grits" cereal in a bowl, draw water upon it, and after a while boil it. This fact suggested lead in the water. My attention was called to the subject and I found that water which had stood all night in the pipe of my own house contained a little lead, which might, as lead is a cumulative poison, ultimately produce serious results, if such water were often used. Looking further into the matter, I found that owing to the low pressure in the water pipes a great many houses were provided with pumps and tanks to supply the upper stories. Examination of the tanks developed the fact that they were usually lined with lead, and the water thus became contaminated.

Examinations were also made of Croton water, which had been in contact with lead for different lengths of time, under commonly occurring circumstances, of which the following are the results:

> 1—A gallon of Croton water from a lead-lined cistern, in which it had stood several weeks, was found to contain 0.06 grain of metallic lead.
>
> 2—A gallon of water which had remained 6 hrs. in the lead pipes of my residence yielded 0.11 grain metallic lead, a considerable portion of which was visible to the eye, in the form of minute white spangles of the hydrated oxycarbonate $(PbO_3.H_2O + PbO.CO_2)$.
>
> 3—Water drawn from one of the hydrants of the School of Mines laboratory, in the middle of the day, when the water was in constant motion, yielded traces of lead. This water reached the school through about 100 to 150 ft. of lead pipe.

The following paragraphs are quoted from a lecture delivered before the American Institute in the Academy of Music January 20, 1871:

> These results indicate the source of many hitherto unaccountable cases of lead poisoning, and are of a character to alarm the residents of New York, and lead them to adopt precautionary measures for protection against this insidious cause of disease.
>
> A celebrated case occurred in the royal family of France, at Claremont, where one-third of the persons who drank of the water were affected. This water contained only one-tenth of a grain of lead in a gallon. As little as 1-100 grain of lead to the gallon has been known to produce palsy in persons who habitually drank it. It is a great pity that the peculiar advantage of lead as a material for the manufacture of water pipes is more than counterbalanced by the danger of lead poisoning.

This subject attracted a great deal of attention at that time. The Board of Health put an end to the use of lead-lined tanks and the public was warned against drinking water that had stood long in the pipes. About this time tin-lined lead pipe was invented. It was made by casting lead around a hollow cylinder of tin, and then drawing the mass down to a pipe of the desired size. I found that the heat of the melted lead was liable to soften the tin lining to such a degree as to alloy it with the tin even clear to the inner surface of the tube. A suggestion of mine overcame this difficulty. A separate hollow cylinder of tin was placed in a surrounding cylinder of lead of such size as to leave nearly a quarter of an inch of space between the two. Then melted solder was poured between the two cylinders; they were perfectly united without melting the tin perceptibly, and a perfect tin-lined pipe was produced. I used this pipe throughout my country house at West Hampton, and one of the spring companies at Saratoga employed it for a deep spring, using a very large sized pipe, 2 in. or more. A test of the proper condition of the pipe was easily made by cutting off a section about an inch long, holding it in forceps, and carefully heating it over a Bunsen burner. If it was in good shape the solder would first melt, as could be seen by the eye, and the tin tube could be shaken out in a sound condition. If, on the contrary, the lead had alloyed the tin the entire lining sloughed off on heating. Special joints were devised and the invention was a complete success. But the cost of plumbing was considerably increased, both for material and labor, and the invention never came into general use.

### POISONOUS COSMETICS

Before I leave the subject of lead poisoning I must say a word with regard to the poisonous cosmetics which I examined in 1869. Hair tonics, washes, and restoratives were much advertised and sold. The following are the results of my examinations of those sold in New York City. Only one was free from lead, that was Hoyt's Hiawatha Hair Restorer, which was an ammoniacal solution of nitrate of silver, and harmless. Here are the others:

GRAINS OF LEAD IN ONE FLUID OUNCE

| | |
|---|---|
| Clark's Distilled Restorative for the Hair | 0.11 |
| Chevalier's Life for the Hair | 1.02 |
| Circassian Hair Rejuvenator | 2.71 |
| Ayer's Hair Vigor | 2.89 |
| Prof. Wood's Hair Restorative | 3.08 |
| O Brien s Hair Restorer America | 3.28 |
| Gray's Celebrated Hair Restorative | 3.39 |
| Phalon's Vitalia | 4.69 |
| Ring's Vegetable Ambrosia | 5.00 |
| Mrs. S. A. Allen's World's Hair Restorer | 5.57 |
| L. Knittel's Indian Hair Tonique | 6.29 |
| Hall s Vegetable Sicilian Hair Renewer | 7.13 |
| Dr. Tebbett's Physiological Hair Regenerator | 7.44 |
| Martha Washington Hair Restorative | 9.80 |
| Singer s Hair Restorative | 16.39 |

These fluids consist of an aqueous solution of acetate of lead, generally containing a sediment of flowers of sulfur. They are to be well shaken before use and when applied at intervals to the hair are said to "gradually restore the original youthful beauty and color." Six lotions or washes for the complexion were examined, one contained corrosive sublimate and sulfate of zinc. Seven enamels for the skin were examined. Three contained oxide of zinc, and three others carbonate of lead.

### THE PLUMBING SYSTEM

I should have been very glad to have had time to explain the improved system of plumbing which resulted from the experimental set of plumbing arrangements which I erected at the Board of Health building, where with a kitchen sink, butler's pantry sink above it, a wash bowl above that, and a bath tub above that, all with glass traps for ready observation, it was easy to demonstrate the absolutely unsafe condition of the plumbing, not only in New York, but everywhere else in this country.

The result of this was an improvement resulting in carrying the soil pipe through the roof, of undiminished caliber; the back-airing of all traps by means of a separate pipe running through the roof; the running trap between the house and the street sewer; and the inlet for fresh air between the house and this trap. This system was approved by the plumbers and fixed by law, and was placed under the control of the Board of Health. It was generally adopted throughout the country, and there was no more talk about sewer gas as a cause of disease. Microbes took its place. Patent traps were not accepted as substitutes for good old-fashioned S-traps. By the way, I have just learned from Mr. A. E. Hansen, hydraulic and sanitary engineer, who is advisor to the Master Plumbers' Association, that an effort is now being made to force the plumbers to adopt a "patent trap." To pass such a regulation would be a crime against the inhabitants of this city.

### CONCLUSION

There are many other topics to which I would delight to call your attention such as:

My connection with the first production of oleomargarine, that cheap, wholesome article of food which has been so handicapped by the Government; the introduction of cheap water gas in New York and in Boston, and the sustaining of the Lowe process for its manufacture; my study of sugar refining in Europe in 1869; and the Hunters Point nuisance.

I should also enjoy telling you of the splendid work of Miss Louisa Lee Schuyler in rescuing 2500 pauper insane from the State poor-houses and placing them in State insane asylums where they had some chance of recovery; and of Mrs. Kinnicutt's very successful campaign to secure an efficient Street Cleaning Department. In both of these enterprises I was honored with the responsibilities of president of the Associations which the ladies organized, but the credit of these great reforms belongs entirely to them.

I must also call attention to the lion's share of the work in my report on the air of the subway, published when that public utility was first opened and certain individuals erroneously pronounced the air therein so unwholesome. Dr. Floyd J. Metzger performed the laborious portion of the investigation.

I wish I could take the time to tell you how much certain members of this Chemists' Club have contributed to the success of the City and State Health Departments: Elwyn Weller, Samuel A. Goldsmith, Edward G. Love, Arthur H. Elliott, Charles E. Munsell, and others whose names I do not just now recall.

In conclusion let me express my appreciation and warmest thanks to the members of your committee, who have considered me deserving of this Medal.

# SCIENTIFIC SOCIETIES

## SPRING MEETING AMERICAN CHEMICAL SOCIETY

The Spring Meeting of the American Chemical Society will be held in St. Louis, Mo., during the week of April 12, 1920, with headquarters at the Hotel Statler, Ninth Street and Washington Avenue.

The following committee has charge of the local arrangements:

*Executive:* Dr. Chas. E. Caspari, St. Louis College of Pharmacy, 2108 Locust Street.

*Program:* Dr. Chas. E. Caspari.

*Finance:* Dr. F. W. Frerichs, Herf and Frerichs Chemical Co., Pierce Building.

*Hotels:* Dr. H. A. Carlton, The Mallinckrodt Chemical Works, 3600 North Second Street.

*Registration and Information:* Dr. T. R. Ball, Washington University, Skinker Road and Lindell Blvd.

*Excursions:* Gaston du Bois, Monsanto Chemical Works, 1800 South Second Street.

*Transportation:* Dr. A. C. Boylston, The Mallinckrodt Chemical Works, 3600 North Second Street.

*Entertainment and Smoker:* F. W. Sultan, Sultan Drug Co., 112 North Second Street.

*Banquet:* E. J. Sheppard, National Lead Co., Manchester and Subette Avenues.

*Publicity:* Dr. L. F. Nickell, Monsanto Chemical Works, 1800 South Second Streets.

The University of Missouri Section, at Columbia, Mo., has agreed to act with the St. Louis Section of the Society as hosts at the Spring Meeting.

## AMERICAN CHEMICAL SOCIETY'S SERIES OF TECHNOLOGIC MONOGRAPHS

At the meeting of the Society in Buffalo, in April 1919, the Committee on Publication of Compendia of Chemical Literature, etc., presented a report[1] in part as follows:

Your committee recommends that the American Chemical Society undertake to have two series of monographs prepared and published under its supervision. To give effect to this general recommendation, it would recommend that the following specific steps be taken:

(A) That three trustees be appointed, two, including the chairman, by the president of the American Chemical Society, and one by the president of the National Research Council, to organize and control the business side of the undertaking. These trustees shall be named to serve for one year and shall be eligible for reappointment. Subject to the approval of the directors of the American Chemical Society, in all matters leading to expense, the trustees shall have the power to enter into negotiations with publishing houses for the publication of the series or to develop any other plan of financial administration. In particular, it is urged that the trustees should attempt to raise funds from which advance payments of royalties (say of $500) may be made to each author (selected under B) invited to prepare a monograph and second payments of the same amount to each author when his monograph has been accepted. The trustees in return will receive all royalties accruing on the sale of a given monograph until the sums paid to an author of the monograph have been liquidated (without interest); later royalties are to go to the author. Royalties received in this way by trustees shall serve for the endowment of further monographs.

(B) That two control committees be organized, one for a series of technological monographs, another for a series of scientific monographs. Each committee is to consist of five members to be elected by the Council of the Society (as in the case of the editors of our journals). The chairman of each committee shall be the editor of the corresponding series, and shall receive compensation of the same nature as the editor of the *Journal of the American Chemical Society.* The committee shall select men who are to be invited to prepare monographs on selected topics and shall pass on the final acceptance of such monographs as may be offered for publication. Decisions as to the business arrangements for publication will rest with the trustees rather than with the scientific control committees.

The report was adopted by the Council, which authorized the Advisory Committee to elect the chairman of each board of editors. In June the Advisory Committee recommended W. A. Noyes and John Johnston as chairmen of the board of editors of the scientific and technologic series, respectively, and voted that the chairman should nominate the other members of the

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[1] Reprinted in This Journal, 11 (1919), 415.

board. They also voted to recommend to the Directors that the salary of the chairman of each board be $1,000 a year, and that "royalties not to exceed $500 be paid in advance to each author chosen by the Committee to write a monograph, and that an additional sum of like magnitude be paid to him upon the completion and acceptance of his monograph, the amount so paid to be deducted from any royalties received until such time as the amounts advanced are returned to the SOCIETY or its agent; that thereafter any royalties received should be paid one-third to the AMERICAN CHEMICAL SOCIETY and two-thirds to the author of the monograph."

On November 28 the Advisory Committee appointed as associate editors of the scientific series:

G. N. LEWIS (California) A. A. NOYES (Throop Inst.)
L. B. MENDEL (Yale) J. STIEGLITZ (Chicago)

and as associate editors of the technologic series:

C. G. DERICK, National Aniline and Chemical Company, Buffalo, N. Y.
WILLIAM HOSKINS, Consulting Chemist, Chicago, Ill.
F. A. LIDBURY, Oldbury Electro-Chemical Company, Niagara Falls, N. Y.
A. D. LITTLE, Consulting Chemist, Cambridge, Mass.
C. L. REESE, du Pont de Nemours and Company, Wilmington, Del.
C. P. TOWNSEND, Union Carbide and Carbon Corp., New York City.

They also approved a suggestion designed to insure a rotation of interests upon the Board.[1] The trustees in charge of the financial arrangements for both series are now C. L. Parsons, chairman, Gellert Alleman, and J. E. Teeple.

The board of editors of the Technologic Monographs have had considerable correspondence and have held a meeting at which the following general policy was agreed upon:

> The ideal monograph is a critical presentation of the topic which it treats, and gives the reader the present status of the knowledge of that topic in such a way that he need not consult prior literature except for details; it should show clearly which points are still uncertain and require further investigation, and so act as an incentive to research by suggesting problems. The preparation of such a monograph implies that the author has first-hand knowledge of the topic treated, and this implies in turn, particularly in the case of technologic monographs, that the topic chosen must not be too large. In other words, instead of a book dealing with a very broad general topic, we would prefer a number of more specific smaller topics, each written by a man thoroughly conversant with that particular phase. The Board wishes to emphasize that the proposed series will aim to be critical in character, rather than mere compilations; and takes this ground because a number of existing monographs cover a field broader than the author was really familiar with, the result being that the book contains one or two good chapters but is largely a somewhat uncritical compilation of material.

Before authorizing monographs the Board wishes to review the whole field carefully; to ascertain what topics have already been treated adequately in readily available monographs; and to prepare a systematic well-balanced scheme covering the area of desirable effort, indicating the relative importance of subjects or the relative need of treatment. However, where an author is available who is uniquely qualified to treat a particular subject within our scheme, we should get a monograph from that man while he is available and not run the risk of losing the benefit of his special knowledge, and should do so without much reference to the order in which we would otherwise take up the subject if it were one in which a reasonable number of fully qualified men were available.

It is realized that the main difficulty is likely to be to secure the author best qualified to write on a particular topic—especially in view of the policy of secrecy which has prevailed in so many instances—and that the selection of topics will be largely determined by the availability of an appropriate author. The difficulty likely to be encountered in securing a good monograph dealing with a specific manufacture inclines the Board to the belief that it might well give preference to monographs dealing with general operations, such as drying, roasting, grinding, mixing, filtration, etc., until these unit operations, which constitute the elements of technologic chemical processes, have been fairly well covered. Among the topics already suggested as desirable, the following may be mentioned: industrial hydrogen, corrosion of metals, resistant alloys, water softening, pyrometry, liquefaction of gases, catalytic and electrolytic oxidation and reduction of organic compounds. In all cases it is proposed that the manuscript, before it is accepted for publication, shall be reviewed by at least one man who is thoroughly conversant with the particular topic.

It is hoped that a definite program may be formulated within the next two months, so that the books may begin to appear in the fall. In the meantime the Board invites the membership of the SOCIETY to coöperate by favoring it with comments and suggestions, particularly with specific suggestions of desirable topics and competent authors. All correspondence relative to the technologic series should be addressed to John Johnston, Yale University, New Haven, Conn.

## THE A. C. S. NEWS SERVICE REPORT

The remarkable interest and coöperation which the press of the United States has shown in the work of the A. C. S. News Service of the AMERICAN CHEMICAL SOCIETY are indicated in the analysis of the newspaper clippings which we received in the last year.

There were issued in 1919, 35 bulletins, from which 893 clippings were received, as compared with the 54 bulletins issued in 1918, from which 455 clippings resulted. The space occupied by the clippings received in 1919 amounts to 7,768 inches as compared with the 3,319 inches of the previous year. These returns indicate only in a general way the extent to which the Service has been received, as there is no method by which an absolute check can be made on the volume of publicity of this character.

The Service now supplies popular information on chemistry to 650 newspapers and magazines, for in August of last year the publicity list was practically doubled. Of the newspapers in the United States, 205 print our bulletins with the regularity of clockwork, while others select from time to time those which are of special interest in their localities.

The most significant development of last year was in connection with the meetings of the SOCIETY. As the two meetings of the year constitute the most important news points with which our Service has to deal, an effort was made to bring them especially to the attention of the press. The Cleveland meeting, held in the fall of 1918, had practically no publicity—possibly not more than 10 or 15 notices in all. Although our resources did not permit a full program in connection with the Buffalo meeting, held in 1919, we obtained a limited amount of notice for that gathering in American newspapers. The Buffalo papers printed 67 news items concerning the spring meeting of 1919, and 35 appeared in other newspapers throughout the United States.

The fall meeting of 1919, held in Philadelphia, gave an opportunity to test the value of a national publicity program—the first ever undertaken by this SOCIETY. This was possible through the enterprise of the Philadelphia Section, which paid the entire expenses. The Associated Press, the United Press, the International News Service, the Western Newspaper Union and various agencies coöperated with the A. C. S. News Service in distribution. The result was that every newspaper of importance in the United States gave adequate reports, and 20 publications sent special representatives to cover the meeting. A press room was established at the Hotel Bellevue-Stratford and every facility was placed at the disposition of reporters and correspondents. The matter distributed there was equal in words to 30 of our weekly bulletins.

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[1] THIS JOURNAL, **12** (1920), 84.

A preliminary publicity campaign of six weeks, undertaken to stimulate the interest of the American people, reached its climax on the first of September 1919. The clipping book now in the possession of the Philadelphia Section shows 700 notices of the meeting of last autumn, exclusive of those obtained from the regular bulletins.

Success of the pre-publicity has caused the Director of the Service to continue the policy of having an extensive advance campaign.

Another important development of the A. C. S. News Service was the coöperation which it received from the local sections. The secretaries of a number of the sections have been in close touch with the newspapers of their localities, and from that policy has developed important auxiliary publicity. The clippings containing accounts of meetings of local sections form very gratifying evidence of the increased popular interest in chemistry which has been stimulated by this means throughout the United States.

In addition to the bulletins and other matter, clip sheets were sent out in 1919 for the first time, on which were important articles from the *Journal of Industrial and Engineering Chemistry* and also its editorials. The ten sheets mailed were well received by the newspapers—so much so as to lead us to extend this Service in 1920 by re-writing some of the articles into popular form, and making a general revision of the clip sheet along newspaper lines.

In view of the progress made by the A. C. S. News Service, the Directors decided to increase the appropriation made for the year 1919; to generally increase the facilities; and to provide for systematic programs covering the spring and fall meetings.

The policy of national publicity inaugurated at the Philadelphia meeting in September 1919 will be continued and developed at the New York office, with the assistance of the local sections.

The bulletins will be increased so that, besides a general one each week, there will be also issued, from time to time, special bulletins applying to definite parts of the country or of interest to groups of newspapers and magazines.

As some of the newspapers have already availed themselves of our offer to advise them on the scientific accuracy of articles on chemistry in advance of publication, we shall extend this method of serving them for the coming year.

From small beginnings the Publicity Service of the American Chemical Society has now grown to large proportions and is recognized by the journalistic world as a valuable source of news and information.

John Walker Harrington,
*Technical Manager*

New York, N. Y.
January 1, 1920

## ROCHESTER SECTION, AMERICAN CHEMICAL SOCIETY

At a recent meeting of the Rochester Section, at which Secretary C. L. Parsons was present, the local membership committee had made a careful canvass of the chemists around Rochester and presented to the Secretary at one time forty-two new members. Most of these new members were present at the time their names were read, and the Secretary signed their applications as each one stood up in the audience.

## CALENDAR OF MEETINGS

American Ceramic Society—Annual Meeting, Hotel Bellevue-Stratford, Philadelphia, Pa., February 23 to 26, 1920.

American Electrochemical Society—Spring Meeting, Boston, Mass., April 8 to 10, 1920.

American Chemical Society—Fifty-ninth Meeting, Hotel Statler, St. Louis, Mo., April 12 to 17, 1920.

# NOTES AND CORRESPONDENCE

## EXPLAINS DANGER OF WOOD ALCOHOL[1]

Dr. Reid Hunt, Eminent American Authority on Effects of Alcohol, Shows Difficulties of Detecting Poison Drink and Explains Facts concerning It Unknown to the General Public

New York, December 31, 1919—Facts concerning the dangers of wood alcohol which are scarcely known to the general public were given to-day by Dr. Reid Hunt, a leading American authority on the effects of alcohol, whose researches in this line are regarded as having been more extensive than have those of any other American scientist.

Dr. Hunt is the head of the Department of Pharmacology of the Medical School of Harvard University, was formerly at Johns Hopkins, and several years ago was chief of the Division of Pharmacology of the United States Health Service, in which position he advised the Government in the regulation of the sale of drugs, poisons, and intoxicating liquors. He is the author of the standard work, "Studies in Experimental Alcoholism." At the request of the American Chemical Society, of which he is a member, Dr. Hunt prepared a bulletin on wood alcohol. To-day this was given out for publication.

"Wood alcohol," writes Dr. Hunt, "has become known as the American poison on account of the frequency with which cases of poisoning have been traced to it in the United States. Despite this fact, there is still a lack of appreciation of its dangers and of an understanding of its nature. It is on this account that I am glad to comply with the request of the American Chemical Society to prepare this bulletin. The misconception of the dangers of wood alcohol evidently exists not only among those who drink or sell 'alcoholic' beverages of unknown origin, but also to those who prepare drinks containing wood alcohol for sale and perhaps also to those who sell wood alcohol to the latter class. No other explanation of the recent accidents is thinkable; for, however sordid the motives and however reckless of human life the manufacturers of spurious 'alcoholic' beverages may be, it is unreasonable to suppose that anyone would knowingly incur the legal and other responsibilities for such a wholesale slaughter as has recently taken place."

### POPULAR MISCONCEPTIONS

"Among the misconceptions prevalent," said Dr. Hunt, "the following may be mentioned:

"Many consumers and perhaps some of those who sell such drinks seem to think that wood alcohol has such characteristic properties that its presence can be readily detected by the odor or taste. On the other hand, those who make such drinks know that this is not the case, but believe either that the poisonous action has been exaggerated or that the chances of detection are relatively slight.

"Moreover, testimony was offered in a court a number of years ago to the effect that the manufacturers of flavoring extracts had been approached by dealers in wood alcohol and urged to make their preparations with it. The fact that already at that time the bottles bore the label 'poison' was explained as a ruse to prevent the Government from placing an internal revenue tax upon wood alcohol.

"It cannot be too strongly emphasized," he added, "that there is not a single property of wood alcohol, except its poisonous effects, by which anyone but a chemist can distinguish between purified wood and ordinary or 'grain' alcohol. The appearance, odor, and taste of the two are so strikingly alike, that even chemists who have had much experience with them are unable by these properties to distinguish between them with certainty. The difficulty is, of course, greatly increased when essences, flavors or coloring matters are added, as is the case in the spurious drinks now being offered for sale. Not only can the consumer, however great his familiarity with alcoholic beverages may be, not trust his own judgment in this matter

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[1] A. C. S. News Service Bulletin issued to the press for release on January 1, 1920.

but he cannot trust the judgment of an experienced bar or saloon keeper.

### HOW WOOD ALCOHOL POISONS

"Now, as regards the question of the poisonous properties of wood alcohol," added the expert:

"It is inconceivable that any ordinarily intelligent person can now be in doubt on this subject, in view of the hundreds of cases of death and blindness resulting from its use. Twenty years ago when such cases first began to be reported there was some reason for a little uncertainty on this subject, not only on the part of the public, but of chemists and of those physicians who were not familiar with certain pharmacological experiments on dogs. The odor, taste, and other properties of pure wood alcohol are so like those of ordinary alcohol that chemists were inclined to attribute the bad effects from the former to the presence of impurities in the commercial samples. But none of the impurities in the latter are as poisonous or cause the same effects as the absolutely pure wood alcohol itself.

"Pharmacologists, moreover, from experiments on dogs, had, years before, shown that the action of wood alcohol upon the animal organism is fundamentally different from that of ordinary alcohol. This difference may be briefly summarized. When ordinary alcohol is taken into the body it is rapidly converted into water and carbonic acid gas which are harmless substances, always present in the body, and any excess of which is promptly eliminated by the kidneys and lungs. Wood alcohol, on the other hand, instead of being changed into harmless substances which are easily eliminated, remains in the body as such for a considerable time and is then slowly converted into another poison—formic acid—the acid which is found in ants. These poisons and perhaps a third formed from the wood alcohol, formaldehyde, attack the brain and other organs and cause death or blindness.

"Poisonousness is an inherent quality of wood alcohol," continued Dr. Hunt. "It is as impossible to prepare nonpoisonous wood alcohol as it is to prepare nonpoisonous prussic acid.

### HOW MUCH IS A FATAL DOSE

"Individuals vary considerably in their susceptibility to wood alcohol; some die or become blind from amounts which seem to do no harm to others. This is true, however, of all poisons. Death or blindness has resulted from two teaspoonfuls and from one or two tablespoonfuls of the poison. Sixty to seventy-five per cent of those taking four ounces, that is, a quarter of a pint or half a 'glassful,' have died or become permanently blind. That wood alcohol is properly placed in the list of 'deadly poisons' is evident from the fact that the mortality from arsenic poisoning is only fifty to seventy-five per cent and that from bichloride of mercury even less. Of a group of 130 men who drank a mixture of wood and grain alcohol all but 32 died or became blind.

"At the present time when the manufacture and sale of genuine alcoholic beverages are illegal the only safe course to pursue is to refrain from buying, drinking, or dealing in anything purporting to be such a beverage.—[*Bulletin* 251]

## REGISTRATION OF STILLS

A question has been raised as to whether the law requiring registration of stills applies to distilling apparatus used in chemical work.

A notice issued by the Commissioner of Internal Revenue reads in part as follows:

*To Collectors of Internal Revenue, Revenue Agents, and Others Concerned:*

* * * * All persons, firms or corporations thus manufacturing a still or worm to be used in distilling are deemed manufacturers of stills. This applies to all stills capable of the production of distilled spirits but does not apply to small laboratory stills (usually glass) for legitimate laboratory purposes, or to water stills which are not capable of and intended for the production of distilled spirits. Ordinarily, laboratory stills are small, constructed of glass, and not adapted to the production of distilled spirits in commercial quantities, and many water stills are also of such construction that they are not adapted to the commercial production of distilled spirits.

Any stills or worms adapted to the production of distilled spirits for commercial or beverage purposes are presumed to be intended for such use. * * * In order to remove such presumption in the case of stills and worms intended to be used in the manufacture of essential oils, vinegar, and like products, and in purification of water (other than small glass laboratory stills), the person for whom such still is made will be required to submit to the Collector evidence under oath showing that the still is not to be used for the production of spirits and setting forth specifically the actual purposes for which it is to be used.

* * * *

All stills set up, whether intended for use or not, must be registered with the Collector of the district on Form 26 in duplicate. This applies to all stills of whatever size or for whatever purpose intended, whether for distillation of spirits or for pharmaceutical or other purposes, except as to small glass laboratory stills.

Copies of Form 26 may be obtained from the Collector of Internal Revenue for the district in which the stills are to be set up, and instructions will be given as to filling out such forms. Failure to register such still or distilling apparatus will be a violation of Section 3258 R. S.

## EXTRACT FROM THE FEDERAL LAW RELATING TO THE REMOVAL OF THE "COUNTRY OF ORIGIN" FROM IMPORTED ARTICLES

UNITED STATES TARIFF ACT OF 1913, SEC. 4, PAR. F, SUBSECTION 2

If any person shall fraudulently violate any of the provisions of this act relating to the marking, stamping, branding, or labeling of any imported articles or packages; or shall fraudulently deface, destroy, remove, alter, or obliterate any such marks, stamps, brands, or labels with intent to conceal the information given by or contained in such marks, stamps, brands, or labels, he shall upon conviction be fined in any sum not exceeding $5,000, or be imprisoned for any time not exceeding one year or both.

## DISAPPEARANCE OF DR. ARTHUR LACHMAN

The disappearance, on December 11, 1919, of Dr. Arthur Lachman, of San Francisco, was noted in the last number of THIS JOURNAL. The causes suggested are foul play or temporary dementia.

The accompanying description and photograph are printed here in the hope of developing some clue.

ARTHUR LACHMAN

ADDRESS: 358 Holbrook Building, San Francisco, Cal.—Sutter 4653; 143–14th Avenue—Pacific 3926.
HEIGHT: 5 ft. 7 in.
WEIGHT: 170 lbs.
COMPLEXION: Fair
EYES: Light blue
HAIR: Very bald—gray. Reddish mustache, turning gray
GLASSES: Wore eye glasses
CLOTHING: Gray-green suit, small plaid
  Black vici kid shoes
  Dark gray, knee-length overcoat
  Dark fedora hat
EFFECTS: Pipe; curve cut old English tobacco
  Illinois watch
  Black silk vest chain, initial slide, letter "L" set in pearls
  Gold cuff buttons each set in one diamond and one ruby
  "Lefax" memorandum book

## ADVANCED WORK FOR HIGH SCHOOL CHEMISTRY TEACHERS

*Editor of the Journal of Industrial and Engineering Chemistry:*

From time to time articles have appeared in various chemical journals advocating more thorough training for men in chemical professions. A great deal has been said about chemists doing advanced work and in a number of instances provision has been made whereby men with certain companies have been provided with means for development along research lines.

I feel that something should be said in regard to the teachers of chemistry in the various high schools over our country. A university professor of national reputation made the remark at a scientific meeting not long ago that some of the best material available for replenishing the staffs of various universities was to be found in the men who are teaching in the high schools. If this is the case, why not give these men a chance to earn a doctor's degree, which is now required to hold a position with most, if not all, of the foremost colleges and universities? Men in high schools who are heads of departments, especially in large cities, receive salaries ranging from $3,000 to $4,000 per year of 10 mos. In most cases they have their bachelor's and master's degrees, have done graduate work beyond this, and very often keep in touch with the chemistry department of some good university.

These men would like to go on and obtain the doctor's degree, but such a thing is impossible under present conditions, unless the applicant for the degree resigns his position in his school and spends a year or more at the university. Some compensation indeed may be obtained by instructing part time and devoting the remaining time to the problem at hand, but they have assumed responsibilities for which such compensation is inadequate, and few are going to relinquish salaries of $3,000 a year and spend $2,000 more per year to keep their families, in order to obtain the degree.

Why not offer some alternative? Permit them to use their spare time during the academic year in their own laboratories on some assigned problem, especially where library and laboratory facilities are quite complete, and then have them come to the university during the summer to continue the work and so on for the following years until all requirements for the degree are fulfilled. This suggestion, if followed, would eliminate some of the longer graduate courses, but certainly not all of the graduate courses.

If this, or some other plan, be adopted it would enable these men to go into college or university work when the degree was obtained, and there is no reason to believe that they would fall short of what is expected of them. When, in this way, they have become eligible for positions in a university at a salary even somewhat less than they are now receiving, the university would be able to replenish its corps with experienced teachers, instead of graduate students with no teaching experience. It is not necessary, however, that these men go into university work. They may remain where they are. It is a well-known fact that a great deal of research work has been done in other countries by men in secondary schools. Let it be so in this country. All that is needed is a little encouragement.

Personally, I feel that the time is coming when universities will make provision for these science men. When they do it certainly will stimulate every red-blooded man to put forth the best that is in him and will open a field rich in scientific workers which at present is practically inactive.

SOLDAN HIGH SCHOOL
ST. LOUIS, MO.
January 5, 1920

W. R. TEETERS

## THE QUESTION OF THE IDENTITY OF BALATA AND GUM CHICLE

*Editor of the Journal of Industrial and Engineering Chemistry:*

With reference to my paper on "Industrial and Agricultural Chemistry in British Guiana, with a Review of the Work of Prof. J. B. Harrison" [THIS JOURNAL, 11 (1919), 874], I have received several inquiries as to balata and whether or not it is the same substance as gum chicle. My impression had always been that the two substances were derived from different trees but to be certain I referred the query to Professor Harrison, who writes as follows:

> Balata and true gum chicle are not identical. Your impression that they are derived from different trees, the *Mimusops balata* and the *Sapota zapotilla*, respectively, is correct. But quite recently an export trade has arisen from Venezuela in what the Creoles call "white hya-hya" and the Venezuelans term "white balata," the impissated latex of the "milk" tree. This is being used either directly as chewing gum or else as an adulterant of chicle. The latex of certain ficus trees termed locally *douchallibalti* and *kumatraballi* is probably also being used as adulterants of chicle.

Balata and gum chicle are treated as synonymous terms in the Decennial Index of *Chemical Abstracts*, but as pointed out by Professor Harrison the two substances are not identical and they should, therefore, have been treated in the Index under separate headings.

C. A. BROWNE

NEW YORK SUGAR TRADE LABORATORY, INC.
80 SOUTH STREET, NEW YORK, N. Y.
January 6, 1920

## PLATINUM THEFT

On Monday morning, December 22, 1919, it was discovered that the vault of the Department of Agricultural Chemistry at the University of Missouri had been entered and the entire stock of platinum crucibles, amounting to some 2500 g., had been taken. The following list is a fairly accurate inventory of the material taken:

| | Grams |
|---|---|
| 18 plain crucibles | 780.38 |
| 6 J. Lawrence Smith crucibles | |
| 11 Gooch crucibles | |
| 27 dishes | 1212.72 |
| Foil | 26 |
| Wire | 17 |
| 5 small, flat, sugar dishes | 77 |
| 17 Gooch crucible caps | 41.5 |
| 6 small caps | 10.5 |
| 21 seamless filter cones | 73 |
| 18 covers for crucibles | 96 |
| 6 covers for dishes | 43 |
| 2 spatulas | 12.5 |
| 2 spoons | 6.5 |
| Scrap | 22.2 |

## FIRE CAUSED BY YELLOW PHOSPHORUS

In the rubbish from a fire which occurred in the chemical stock shelves of the Organic Research Laboratory, a can was found partly filled with yellow phosphorus. This had been in stock for approximately five years. The cover had been forced open about one-sixteenth of an inch, and the bottom had numerous pinholes. Presumably these had been formed by corrosion with the result that the water leaked out very slowly. A slow oxidation of the phosphorus then took place, becoming more rapid as the temperature rose. Finally sufficient pressure was developed to force open the cover and the phosphorus then burst into flames. A close watch should be kept on stocks of yellow phosphorus in cans, or else the contents transferred to glass bottles and covered with water, the bottles then being securely stoppered. The manufacturers should attempt to find some better method of packing the substance.

HARRY LEB. GRAY

ORGANIC RESEARCH LABORATORY
EASTMAN KODAK COMPANY, ROCHESTER, N. Y.
December 23, 1919

## RESEARCH ON METALLO-ORGANIC COMPOUNDS AT NORTHWESTERN UNIVERSITY

Northwestern University's Department of Chemistry has received a grant of $3,500 from the Interdepartmental Social Hygiene Fund of the United States Government. This fund is for the purpose of supporting research leading to the development of new metallo-organic compounds which may prove of therapeutic value in the treatment of syphilis of the central nervous system.

A plan of coöperation has been worked out between the Universities of Wisconsin, Minnesota, Illinois, and Northwestern, whereby all pharmacological work will be done by the first-named institution and the synthesis of new compounds by Minnesota, Illinois, and Northwestern in coöperation.

# WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

The middle of January finds the fight in the Senate over the protection of the American dye and coal-tar chemical industry still unsettled. The Longworth dye bill which was passed by the House and which will serve as the basis for whatever measure the Senate passes, is before the subcommittee of the Senate Finance Committee, which has not yet agreed as to just what shall be the provisions of the measure it finally will frame.

Members of the committee say they probably will have a measure ready for the Senate within the next fortnight. A meeting of the dyes subcommittee will be called some time next week to consider the measure in the light of hearings which have been held, and a report is expected soon thereafter.

Faced with a strong opposition from some members of the Senate to the licensing system as embodied in the Longworth bill, the dye men have drafted a substitute for this section and the licensing system, as such, is discarded. The committee now has before it this substitute; another offered ostensibly by John P. Wood, of Philadelphia, one of the leading opponents of the Longworth bill both before the House and Senate committees, and other tentative suggestions from various quarters. These two are the most important and from them probably will come the measure which the committee will decide on.

The substitute which was drawn up by a committee of the American Dyes Institute and submitted to the committee by Joseph H. Choate, Jr., counsel, provides in brief:

> That the United States Tariff Commission shall prepare two lists, one list of dyes and coal-tar chemicals covered by the act, to be known as the importable list, and a second to be known as the conditionally importable list. Products not on either of these lists could not be imported. The provisions would remain in effect for a period of ten years.

The proposed substitute, as submitted to the committee, follows:

> Sec. 503. (*a*) During 10 years after the taking effect of this act, no product covered by the dutiable list in Section 500 hereof which is manufactured in the United States in quantity sufficient to meet the demand for domestic consumption, and in quality substantially equal to the standard for such product, prevailing in the industry on August 1, 1914, and no product having substantial usefulness only as a substitute for a product so manufactured in the United States, shall be admitted to import. All questions of fact as to which of such products are entitled to admission to import shall be determined by the United States Tariff Commission as hereinafter provided.
>
> The said Tariff Commission shall forthwith proceed to prepare after investigation, a list to be known as the importable list of such products as may be found by it to fulfill the above requirements for admission to import. The said list shall be revised from time to time, and except as hereinafter provided no product not named thereon shall be admitted to import.
>
> Before any of the products named on said list shall be admitted to entry, the importer shall file with the Tariff Commission a notice containing sworn statements by the importer that the proposed import is either for current use or consumption by him and will not, either alone or in conjunction with previous notice, or any other supply from whatever source derived, suffice to provide him with a quantity greater than his actual requirements for such current use or consumption for the ensuing six months, or that the proposed import is desired in order to fill an actual *bona fide* order from a named domestic consumer for such consumer's like current use or consumption, in which event there shall be annexed to the notice proof by affidavit of such consumer that the proposed import will not either alone or in conjunction with previous orders or any other supply from whatever source derived, suffice to provide him with a quantity in excess of his actual requirements for such current use or consumption for the ensuing six months. Said sworn statement of the importer shall also state the name, chemical identification, strength and quantity of the proposed import, together with the name of the port of entry at which it is to be brought in. A copy of such notice shall be transmitted by the commission to the collector of said port, and no import shall be admitted to entry unless found to correspond with such notice. The collectors of all ports shall promptly notify the Commission of the admission of all such imports. The phrase "use or consumption" as used herein shall, in the case of products customarily used for medical or photographic purposes only, include sale for such purposes only. The Commission may suspend, pending investigation by it, the operation of any notice which may appear to it to be calculated to provide any consumer with a supply of any product in excess of his actual requirement for current use of consumption during six months after the date of such notice. If upon such investigation the Commission shall determine that any such notice covers any such excess, it shall forthwith cancel the said notice and notify the person by whom the same was filed.
>
> When at any time the Commission shall find that notices received by it, of which copies have been transmitted to the collectors, cover a quantity of any product sufficient in the aggregate to constitute an excess over current consumption equal to a six-months' supply for the ordinary requirements of such product for domestic consumption, no copies of notices covering such product shall be transmitted to the collectors until the commission shall determine that the unused quantity of such product in the United States is less than such six months' supply. The Commission shall promptly notify of such action all persons who have filed notices the operation of which is thus suspended.
>
> The Commission shall also prepare a second list to be known as the conditionally importable list comprising all products which, while mainly useful as substitutes for domestic products, have special uses for which a domestic equivalent is not available. The said conditionally importable list shall state opposite the name of each product the special uses. Any product named in such list may be imported, subject to the conditions hereinbefore provided, when and only when the notice covering the proposed import contains a sworn statement by an actual consumer that the proposed import will be used by him solely for one or more of the special uses stated in said list for said product.
>
> Notices received by the Commission shall not be open to public inspection.
>
> If at any time complaint shall be made of the Tariff Commission that the price of any domestic product covered by the dutiable list of Section 500, of this act, is unreasonably high, the Commission shall investigate and if upon such investigation the Commission shall, after a hearing, determine that such price is sufficient to yield an unreasonable profit to every domestic manufacturer, it shall place such product on the importable list during the continuance of such unreasonable prices. Two weeks' notice of such determination shall be given all domestic manufacturers of such product known to the Commission before such product shall be placed on the importable list.
>
> Notwithstanding anything herein contained, any product covered by this act may be imported and stored in a United States bonded warehouse. No product so imported shall be released from such bonded warehouse or admitted to entry except as hereinbefore provided.
>
> Sec. 503. (*b*) The United States Tariff Commission in executing the duties imposed upon it by this act may regulate its own practice and procedure, but shall so regulate the same as to prevent all avoidable delay.
>
> Sec. 503. (*c*) Any product covered by Section 500 of this act, which shall be imported into the United States or any of its possessions, otherwise than as provided herein, shall be forfeited and shall be destroyed whenever and wherever found.
>
> Sec. 503. (*d*) Any person subject to the jurisdiction of the United States who shall, either as principal or as accessor, import or attempt to import or aid in importing any product covered by Section 500 of this act, otherwise than as herein provided, or who in making any sworn statement required by this act shall willfully misstate or misrepresent any facts shall be fined not exceeding $5,000 or the value of such product at the time of importation, whichever shall be greater, or shall be imprisoned for not more than one year, or both.
>
> Sec. 504. Except as otherwise herein specially provided, this act shall take effect on the day following its passage.

Committee members who have expressed themselves as being opposed to the licensing system agree that the substitute quoted above is an improvement, and some have expressed the opinion that with modifications this will be written into the bill in place of the licensing provision. Objection is found to the length of time—ten years—it is proposed to continue the law in effect. This very probably will be reduced.

Another objection which has been raised is that under its provisions American manufacturers may be exporting products which consumers are not permitted to import. Some dissatisfaction has been expressed with the six-months' supply provision, also.

An attempt to forecast just what the committee will do is futile. Frankly, members of the committee do not know themselves. The plan offered by John P. Wood has found some favor. This is not actually Mr. Wood's plan but was drawn up by an official of the Tariff Commission. As first drafted it was rather lengthy and when submitted to one of the influential members of the committee it was suggested that it be rewritten, much of the lengthy definitions contained in it eliminated, and the proposal be boiled down.

This was done and the plan was submitted to the committee by Mr. Wood at the hearings which were reopened for a day on January 12.

The products of any firm or individual who engaged in full line forcing, tying contracts, or unfair competition, could be prohibited from import by the customs officials under this plan. The first paragraph is as follows:

> Sec. 504. Whenever it shall appear to the satisfaction of the United States Tariff Commission (*a*) that any person is commonly and systematically importing, selling, or causing to be imported and sold any products enumerated in Section 500 of this act under any agreement, understanding, or conditions that any persons shall not use, purchase, or deal in, or shall be restricted in his using, purchasing, or dealing in such products of any persons, or (*b*) that any person is guilty of any other unfair method of competition in importation of products enumerated in Section 500 of this act, said Commission shall certify that fact to the Secretary of the Treasury, and entry into the United States shall thereupon be refused to any such products, sold, shipped, consigned, or manufactured by such person: PROVIDED, That such act or acts shall be done with the intent, tendency, or result of destroying or injuring any industry in the United States or of preventing the establishment of an industry in the United States or of restraining or monopolizing trade and commerce in the United States.

The substitute amendment offered by the dyes committee aims to prevent the possibility of harm being done to the American coal-tar chemical industry by restricting imports. That offered by the Tariff Commission through Mr. Wood is designed to punish those who do harm to the industry. The former anticipates and moves to prevent; the latter waits until harm is done and then seeks to punish.

These two proposed amendments were discussed at the brief hearing held by the committee on January 12, at which Mr. Choate testified for the dye industry; while Mr. Wood, Herman A. Metz, and several other consumers and importers also were present.

The Tariff Commission discusses the various methods of protecting the industry which have been suggested in a report on the Longworth bill which it has submitted to the Senate Finance Committee. This report deals with administrative difficulties foreseen if some of the proposals before the committee are enacted and seeks to perfect them, urging the wisdom of Congress fixing "the governing rules" so that the administrative body enforcing the law will not be required to initiate policies.

Attention also is directed to "the exceedingly complex administrative problems connected with undertaking to determine, as the bill requires, what will be reasonable terms as to prices, quality and delivery of domestic dyes, in the absence of which the importation of foreign dyes may be licensed." The report deals largely with the licensing system, and many of the difficulties pointed to in it are removed in the substitute offered through Mr. Choate. The report suggests:

> It is further suggested that the proposed legislation does not at present take account of the fact that many licenses which may be granted by the license authority may be rendered inoperative through the control of numerous German patents, sold by the Alien Property Custodian during the war to the Grasselli Chemical Company, of Cleveland, Ohio, and to the Chemical Foundation. The Tariff Commission suggests that Congress may find it possible before enacting the legislation to secure from these corporations binding agreements to issue licenses under their patents, without discrimination and at definitely stated rates, to all recipients of import licenses.

Francis P. Garvan, president of the Chemical Foundation, Inc., told your correspondent that the Foundation would immediately comply with any request which may be made of it along this line, when informed of the suggestion of the Tariff Commission.

The measure for the protection of the dye and coal-tar chemical industry which seems most likely to be decided on by the committee at this time, is a compromise between the two substitutes. The dye industry is having a harder fight in the Senate than in the House. It needs a Longworth in the Senate. What the outcome will be is still a secret of the future.

While some members of Congress have expressed opposition to the proposal to establish the Chemical Warfare Service as a separate unit of the War Department, the majority sentiment among committee members who have the reorganization measures in charge, seems to be in favor of such a proposal, recognizing the extreme importance of this branch in future warfare.

Reports reaching here from abroad state that the German chemical trust is taking steps to double its capital. Belief is expressed in England, it is said, that in spite of all difficulties, Germany is in better position as regards this industry than ever before.

January 15, 1920

# INDUSTRIAL NOTES

On January 1, 1920, The Norvell Chemical Corporation of Perth Amboy, N. J., was incorporated in Delaware with an authorized capital of $1,000,000 of preferred stock and 20,000 shares of common stock, no par value. The company has taken over from McKesson & Robbins, Inc., property near Perth Amboy, N. J., consisting of 350 acres of land and a number of factory buildings, and will operate the plant, supplying the medical profession and the drug trade with pharmaceutical chemicals and the industries with chemicals useful in the manufacture of a variety of products. The company has a staff of highly trained chemists for research work. At a stockholders' meeting the following directors and officers were elected: President, Donald McKesson; Vice President and Treasurer, Saunders Norvell; Second Vice President, Francis J. McDonough; Secretary, William S. Gray, Jr.; Assistant Treasurer and Assistant Secretary, James J. Crawford; General Manager, George Simon.

The Bureau of the Mint and the Geological Survey have issued the following preliminary estimate of the production of gold and silver in the United States during the calendar year 1919: Gold, 2,829,395 oz., valued at $58,488,800; silver, 55,285,196 oz., valued at $61,966,412. These figures, compared with those for 1918, show a reduction in the output of gold of $10,157,900, and in that of silver of 12,524,943 oz.; compared with those for 1917 they show a reduction in gold of $25,261,900, and in silver of 16,455,166 oz.

Platinum and gold worth $75,000 were stolen on December 28, 1919, from the plant of the Roessler & Hasslacher Chemical Co., Perth Amboy, N. J. Burglars drilled the safe.

The Director of Sales of the War Department has announced that the Ordnance Department Salvage Board, through the District Office, 1107 Broadway, New York City, is offering for sale land, buildings, and equipment of the sulfuric acid plant at Mount Union, Pa. The plant consists of two brick buildings and several frame buildings, and the land comprises $20^1/_2$ acres. Among the facilities are 784 yards of railroad siding, 1,887 ft. of 8-in. water main, sewers, electric lights, and roads. The equipment includes 4 improved rotary burners, 2 sulfur elevators, 4 Boston type gas pumps, and a 100-ton, 50-foot Howe truck scale, all ready for immediate shipment.

A test case brought by the United States Department of Agriculture against the Monsanto Chemical Works for shipping saccharin has ended in a disagreement of the jury. The case has been pending since 1916. The Monsanto Chemical Works requested another trial immediately, but the government attorneys refused to try the case again until the next term of court, some months from now.

The Engineering Experiment Station of the University of Illinois has sixteen research graduate assistantships open to graduates of approved universities and technical schools for research work in engineering, physics, and applied chemistry. Appointment must be accepted for two consecutive collegiate years, at the end of which the Master of Science degree will be conferred if all requirements have been met. Assistantships carry $500 stipends and are free from all fees except matriculation and diploma fees. Application must be made to the Director not later than the first day of March, to become effective the following September.

Announcement has just been made of a contribution of $5,000,000 by the Carnegie Corporation of New York for the use of the National Academy of Science and the National Research Council. A part of the fund will be used for erecting in Washington a home for the two beneficiary organizations. The remainder will be placed in the hands of the Academy, which possesses a federal charter, to be used as a permanent endowment for the National Research Council.

The Bureau of Chemistry of the U. S. Department of Agriculture has announced the production of malt sugar sirup on a commercial scale as a substitute for sugar. Both the raw materials and the machinery formerly used in the manufacture of beer can now be used for the production of malt sugar sirup, and up to a certain point the process is the same. Malt sugar sirup has a flavor very like honey and can be used wherever cane sugar is used.

The *Journal of Commerce* reports the development in England of a new process for the extraction of commercial alcohol, which though still in the experimental stage, is said to be a perfect motor spirit. Ethylene, alcohol and derivatives have been extracted from coke oven gas by the sulfuric acid contact process on a commercial scale, at the Skinningrove Iron and Steel Works, giving an average yield of 1.6 gallons of alcohol per ton of coal carbonized. According to calculations, all the coal reduced to coke in England in 1918 would have produced over 23,000,000 gallons of alcohol, had this process been applied.

The United States Civil Service Commission announces a competitive examination for research chemist for work in connection with iron and steel or refractories and gases, at a salary of $2,200 to $2,500. Applications must be filed with Civil Service Commission, Washington, D. C., by February 10, 1920.

The United States Civil Service Commission announces an examination for pyrotechnic engineer at a salary of $2,400 to $3,600. Applicants must have graduated in mechanical, electrical, or chemical engineering from a college of recognized standing and have at least one year's experience in engineering and aviation work. Applications must be filed with the Civil Service Commission, Washington, D. C., by February 17, 1920.

The Duane Sugar Refining Co., of Connecticut, recently incorporated with capital stock of $500,000, has bought the plant at Waterside, Conn., formerly occupied by the Synthetic Color Company and later by the Edgewood Arsenal, and will equip a sugar refinery for the Stollwerck Company and allied industries.

New trade names have arisen for vat dyes in England. The vat dyes of British Dyes, Ltd., are called chloranthrene colors; those of Levinstein, Ltd., duranthrene colors; those of L. B. Holliday & Co., hydranthrene colors; while Scottish Dyes, Ltd., has affixed the name of caledon to its products.

Among the corporations recently formed for the production of chemical products are the following: Egyptian Chemical Co., Boston, Mass., capital $90,000; Shawinigan Products Corporation, Manhattan, capital $200,000—carbide, acetic acid and chemicals; California Chemical Co., Dover, Del., capital $1,000,000; Dura Chemical Co., Philadelphia, Pa., capital $100,000—dyestuffs and chemicals; Exidol Laboratories, Inc., Dover, Del., capital $100,000; The Yardley Chemical Corporation, Manhattan, capital $450,000.

During the first nine months of 1919 about 40,400 oz. of platinum were imported. According to James M. Hill, of the United States Geological Survey, Department of the Interior, there seems to be little hope of any marked increase in the output of platinum in the United States or Canada over the small output heretofore made.

The Iowa Corn Products Company has been reorganized with an initial capital of $1,000,000, which will be increased, and has effected a permanent organization with the following officers: President, O. J. Meredith; Vice President, A. N. Higgins; Treasurer, F. T. Fogarty; Secretary, R. B. McConologue. T. C. Cessni will be chairman of the board of directors.

In its third annual report submitted to Congress with the close of 1919 the United States Tariff Commission outlines the work of the Commission on acids dutiable under paragraph 1 of the tariff act of 1913, as well as the raw materials from which such acids are made, and several closely allied commodities which are duitable under other paragraphs. This report will soon be available for distribution. The list includes formic, oxalic, citric, tannic, gallic, pyrogallic, and tartaric acids, which present tariff problems of a most varied character. In several cases there were notable developments of the industry in the United States during the war. This was particularly true with reference to formic, oxalic, and gallic acids. These acids, formerly secured almost entirely from Germany, are now being made in the United States in substantial amounts.

The dye plant of the National Aniline and Chemical Co., located on Jamaica Bay, Brooklyn, N. Y., has been transferred to a new corporation, and will hereafter be known as the Hilwalkal Corporation. This property was formerly the plant of the W. Becker Aniline and Dye Works, and the Beckers Company.

The Atlantic Dyestuffs Company has purchased the L. H. Shattuck Company's shipyard at Portsmouth, N. H., and also considerable of the equipment and material that was in the yard, and will use the site for a plant for the manufacture of dyes. The yard comprises twelve shipways and covers about 100 acres, with a waterfront of about 2,000 ft. along the Piscataqua River, four and a half miles upstream from Portsmouth, N. H.

The General Chemical Co., New York, has purchased the Western Chemical Co., of Denver, Colorado. The capitalization of the Western Chemical Company is $2,000,000.

The experimental paper mill of Arthur D. Little, Inc., Cambridge, Mass., is working on the commercial production of acid-washed filter paper for quantitative chemical analysis, which was formerly imported. The mill will be able to meet the entire American demand with the highest quality product. For some time the mill has been demonstrating the paper-making quality of linters and cotton hull fiber which were used for smokeless powder during the war.

The suit in the U. S. District Court against the Cassett Bros. Company to enjoin them from selling salvarsan, brought by the Chemical Foundation, Inc., the Dermatological Research Laboratories, the Takamine Laboratories, the Diarsenol Company, and the H. A. Metz Laboratories, is to be dropped on the understanding that the Cassett Bros. Company will discontinue the sale.

The Butterworth-Judson Corporation announces that it has under construction new plants for the production of Gamma acid, H acid and J acid, and that preparations are being made to market a great many colors of this line as soon as the intermediate plants have been completed. The research department has also been doing considerable work on cyanthrol.

The War Trade Board Section of the Department of State has announced that general import license PBF No. 37, War Trade Board Ruling 837, issued December 1, 1919, has been revised and extended, effective January 10, 1920, so as to permit the importation thereunder without individual import licenses, of salvarsan, neosalvarsan, arsphenamine and all substitutes therefor and equivalents thereof, and narcotics, from all countries, excepting those parts of Russia under control of the Bolshevik authorities. The War Trade Board Section has extended to February 15, 1920, the time during which applications for Allocation Certificates allowing the importation of German dyes will be considered.

The Marentay Varnish Company has been organized at Detroit, Mich., with $150,000 capital, to manufacture and sell varnishes, chemicals, and paints.

The Sherwin-Williams Company have moved their general sales and executive departments from 116 West 32d Street to larger quarters at 115 Broadway, New York City.

The Northwestern Turpentine Company is to extract rosin by a new process from a tract of Douglas fir timber of 160 acres, near Disston, Oregon.

The Chemical Foundation, Inc., has recently issued two pamphlets, one describing the present status of vat dye patents held by the Foundation, the other covering metallurgical patents. These pamphlets may be secured at a price of 30 cents each by addressing the Chemical Foundation, Inc., 81 Fulton St., New York City.

The General Chemical Co., 25 Broad St., New York, and the Solvay Process Co., of Syracuse, N. Y., have organized the Atmospheric Nitrogen Corporation, for the development of nitrogen fixation, with $5,000,000 capital. According to R. L. Pierce, president of the Solvay Process Co., it is contemplated to erect a development plant at Syracuse, N. Y., at an approximate cost of $1,000,000. The following officers have been elected: E. L. Pierce, president; A. W. Hudson, treasurer; Ernest Jones, secretary; directors — Mr. Pierce, H. H. S. Handy, E. L. Miller, W. H. Nichols, Jr., Henry Wigglesworth, and Harold Otis.

The Shipping Board has invited proposals to furnish 18,900,000 to 28,000,000 barrels of fuel oil at domestic ports for the year beginning April 1920. This is twice the amount consumed during 1919. Bids will close February 9, 1920.

# PERSONAL NOTES

**Dr. R. C. Maclaurin**, president of the Massachusetts Institute of Technology since 1908, an eminent scientist, lawyer, and executive, died at his home in Cambridge, Mass., January 15, of pneumonia.

**Mr. Oscar Evard Collenberg**, docent in the University of Upsala, has been elected as successor to the late Professor Farup in the Norges Techniske Höiskole.

According to a recent announcement, the following changes have been made in the personnel of the chemical laboratory at Frankford Arsenal: **Mr. Louis Hendler** has been promoted to the position of chief chemist-in-charge of the chemical research work; **Mr. George A. Miller, Jr.**, has been appointed metallurgist-in-charge of the metallurgical work, and **Mr. H. C. Pritham**, who was formerly with the explosives section of the Ordnance Department at Washington, D. C., has been retained as explosives chemist-in-charge of explosives and primer investigation.

**Mr. George D. McLaughlin** has resigned his position as chief chemist of Kullman, Salz & Co., tanners, of Benicia and San Francisco, Calif., to do research work in colloid chemistry, under Dr. Martin H. Fischer, at the University of Cincinnati, Cincinnati, Ohio.

**Mr. Paul O. Powers**, formerly with the Atlantic Dyestuff Co. of Burrage, Mass., where he was employed after being discharged from the Chemical Warfare Service, is now in the azo department of the U. S. Color and Chemical Co., of Ashland, Mass.

**Mr. R. E. Andrew**, formerly First Lieutenant in the Sanitary Corps, food and nutrition section, U. S. A., A. E. F., recently joined the staff of the Connecticut Agricultural Experiment Station, New Haven, Conn., as assistant chemist in the food and drug laboratory.

**Mr. Charles H. Chandler** has accepted the position of special investigational chemist for the Preston and Banes Bay Divisions of the United Fruit Company, in connection with their cane sugar factories and plantations. Mr. Chandler is located at Preston, Oriente, Cuba.

According to a recent announcement in the *New York Commercial*, **Mr. A. H. Jacoby** has been appointed, at the instance of officials in the War Trade Board Section of the State Department, as technical adviser on dyes and pharmaceutical chemicals to the organization committee of the Reparations Committee at Paris. Mr. Jacoby will sail at once and remain abroad for about three months. He will represent this country in the distribution of the German dyes to be allocated to the United States.

**Mr. A. A. Bissiri**, formerly in the research department of Parke, Davis & Co., Detroit, Mich., has accepted the position of superintendent of the Guasti Chemical Co., Los Angeles, Cal.

**Dr. Arthur R. Hitch**, formerly chief chemist for the Ashland Iron and Mining Co., Ashland, Ky., is now research chemist with the E. I. du Pont de Nemours & Co., at their Jackson Laboratories, Wilmington, Del.

**Drs. E. V. McCollum, L. B. Mendel, John R. Murlin, Alonzo Taylor, Geo. H. A. Clowes, Lawrence J. Henderson, S. C. Prescott, W. D. Bancroft**, and **C. E. Mendenhall** have been appointed by the National Research Council as members of an Advisory Board for the American Institute of Baking at Minneapolis, Minn. It will be the purpose of this Board to advise and direct the problems of the Institute and to work with it in solving the fundamental problems which are concerned with baking fermentology, and with the production of bread that satisfies every need of human nutrition.

**Mr. James G. Vail**, chemical director of the Philadelphia Quartz Co., has been called to Europe under the direction of Mr. Herbert Hoover to assist in the distribution of food supplied by the Allied Relief Association European Children's Fund. He sailed for Germany last November and plans to be gone until the harvest of the 1920 German crops, returning to his duties with Philadelphia Quartz Co., probably in August 1920.

**Mr. Lawrence R. Taylor** and **Mr. Harry E. Bishop** have resigned from the staff of the State Board of Health Laboratories at Indianapolis, Indiana. Mr. Taylor has accepted the position as director of scientific work for the French Lick Springs Hotel Co., French Lick, Ind., while Mr. Bishop will do special research work in the laboratory of the National Association of the Manufacturers of Glass Containers, at Chicago.

A Chemists' Club has been organized by the members of the Chicago Section of the AMERICAN CHEMICAL SOCIETY for the purpose of having a place for chemists where science is not the only topic discussed and where they can get together for friendly visits, and where chemists from other cities can be entertained. The following officers have been elected: Wm. Hoskins, president; Frank M. DeBeers, first vice president; W. Lee Lewis, second vice president; Chas. C. Kawin, treasurer; and Paul Van Cleef, secretary. Trustees elected are as follows: H. O. Baker, E. F. Buchanan, R. E. Doolittle, Otto Eisenschiml, L. V. Redman, and F. W. Willard. The headquarters of the Club are at 315 Plymouth Court, Chicago.

According to a recent announcement the chemists and engineers of Savannah, Ga., have organized a Chemists' and Engineers' Club, with headquarters at 23 East Gordon St., Savannah. The officers of this club are as follows: Mr. J. H. Allen, president; Dr. V. H. Bassett, vice president; Mr. Baldwin Bridger, secretary, and Mr. P. McG. Shuey, treasurer. This club gives a cordial welcome to all visiting chemists, engineers, and technical men.

**Dr. C. von Egloffstein**, expert food chemist and pioneer in the malt extract business, passed away December 5, 1919, after a prolonged illness. Dr. von Egloffstein was for the past twelve years in the employ of the American Diamalt Co., of Cincinnati, Ohio. Previous to 1907, he was with the Malt Diastase Co., of Brooklyn, N. Y., and from 1887 to 1897 he was with the Maltine Mfg. Co., of Brooklyn. Dr. von Egloffstein was always a very interested member of the SOCIETY, being a member of the New York Section from 1890 to 1907, when he transferred to the Cincinnati Section.

**Mr. William L. Long** recently left the employ of Swan-Myers, of Indianapolis, Ind., where he was employed as bacteriologist, and has secured a position as chemist with the H. K. Mulford Co., of Philadelphia, Pa.

**Dr. Charles S. Palmer**, formerly of the Mellon Institute, Pittsburgh, has joined the United Fuel Gas Co., Charleston, W. Va., as chief chemist.

**Mr. John G. McLeod, Jr.**, has become research chemist in the Technical Service Department of the Brompton Pulp and Paper Co., Ltd., East Angus, Quebec, Canada.

**Prof. Herbert Spencer Woods**, assistant in the department of physiology, pharmacology and biochemistry of Baylor University, College of Medicine, Dallas, Texas, died January 4, 1919, following an operation. Professor Woods received the A.B. and A.M. degrees at the University of Missouri. He will be remembered for work done with the late Waldemar Koch on the quantitative estimation of the lecithins and other work done at various agricultural experiment stations of the United States.

**Mr. J. E. Toomer**, formerly research chemist with the Chino Copper Co., Hurley, N. M., has accepted a position as chief chemist with the Morris Fertilizer Co., Atlanta, Georgia.

**Mr. C. Luther Masser** has resigned as instructor of chemistry at Philadelphia Textile School, Philadelphia, Pa., to accept a position as supervising chemist with the New York Quinine and Chemical Works, Brooklyn, N. Y.

**Capt. W. E. Brophy**, formerly of the Barrett Co., and later of the Chemical Warfare Service, U. S. A., **Lieut. Robert F. LaBarron**, formerly of the U. S. Field Artillery, and **Mr. Chester G. Gilbert**, economic geologist and mining engineer, formerly of the Smithsonian Institution, have joined the engineering staff of Arthur D. Little, Inc., Cambridge, Mass.

**Mr. E. H. Leslie** has resigned his position as assistant to the vice president and general manager of the U. S. Industrial Alcohol Co., New York, N. Y., and has accepted a position as associate professor of chemical engineering in the University of Michigan, Ann Arbor, Michigan.

**Mr. H. P. Zeller**, formerly superintendent of the By-Product Coke Plant, of the Toledo Furnace Co., Toledo, Ohio, and later working in the Ordnance Department on the production of toluol, has for the past year been vice president and general manager of the Donner Union Coke Corp., Buffalo, N. Y.

**Dr. Allerton S. Cushman** will deliver the 1920 course under the Westbrook Foundation at the Wagner Free Institute of Science in Philadelphia. The lectures, four in number, on "Chemistry and Civilization," will be on successive Saturday evenings, beginning early in March. The lectures are freely open to the public.

# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**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. 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. **The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.**

### GEOLOGICAL SURVEY

**Gradations from Continental to Marine Conditions of Deposition in Central Montana during the Eagle and Judith River Epochs.** C. F. Bowen. Professional Paper 125-B. Shorter contributions to General Geology, 1919. 11 pp. Issued October 20, 1919.

**Geology and Ground Waters of the Western Part of San Diego County, California.** A. J. Ellis and C. H. Lee. Water Supply Paper 446. 321 pp. Paper, $1.00. This was prepared in coöperation with the Department of Engineering of the State of California and the City of San Diego.

**Slate in 1918.** G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1918, Part II. 16 pp. Issued October 23, 1919.

The value of the slate sold by the slate quarrymen of the United States in 1918 was $4,038,770. This shows a decrease of 30 per cent ($1,711,196) from the value for 1917. The total values for these two years cannot reasonably be compared, as the figures for 1918 do not include a considerable value of output for slate granules for patent roofing, which was used in large quantities in the construction of the government and other buildings necessitated by the war. Figures of slate granule production in 1918 are withheld so as not to disclose confidential information. The only slate product that showed increase in value in 1918 was mill stock, although the quantity sold showed a decrease.

**Antimony in 1918.** H. G. Ferguson. Separate from Mineral Resources of the United States, 1918, Part I. 25 pp. Issued October 18, 1919.

The United States is dependent upon three classes of material as sources of antimony or its alloys or compounds. (1) Antimony ore is imported from China (direct or via Japan), Bolivia (via Chile and Peru), and Mexico, and small quantities of ore are produced in the western United States. (2) Liquated antimony sulfide, also known as "crude antimony," "needle antimony," and antimony matte, is imported in small quantity from China. This material is produced by submitting the ores of the natural antimony sulfide, stibnite, to a red heat sufficient to melt but not to decompose it, and the metallic sulfide is then run into molds and allowed to cool. (3) Metallic antimony, known as antimony regulus, is imported from China, Japan, and Mexico, and during the war was produced in small quantity in the United States from both foreign and domestic ores. The metallic antimony imported from Japan is derived mainly from the refining of Chinese ore or "crude." A fourth class of material which should also be mentioned is antimonial lead, carrying from 12 to 18 per cent of antimony. Any of the three classes of materials noted above may enter into this product, but it is derived mainly from lead ores, most of them of the antimonial variety.

Domestic producers could not make a profit at the prices prevailing in 1918 and only about 190 tons of ore, containing about 50 tons of antimony, were mined. The antimony smelters continued production from imported ores until November, when all production of metallic antimony was temporarily suspended.

Most of the producers of antimony ore report that a price of 20 to 25 cents a pound for metal would be required to give ore prices sufficient to make the mining of domestic antimony ore profitable at the cost prevailing in 1918. It is probable, however, that antimony mining could be undertaken if there was assurance that a price of 16 or 17 cents would be continued over a considerable period, and according to one operator assurance of a steady price of 11 or 12 cents a pound would encourage production.

There is no reason to expect that prices of antimony will increase greatly during 1919, unless there should be a greatly increased tariff on antimony and antimony ores, as a surplus of antimony seems to be the condition over the entire world.

ANTIMONY ORE PRODUCED IN THE UNITED STATES, 1915–1918

| YEAR | Ore (Short tons) | Metal Content (Short tons) |
|---|---|---|
| 1915 | 5,000 | 2,100 |
| 1916 | 4,500 | 1,770 |
| 1917 | 1,060 | 390 |
| 1918 | 190 | 50 |

METALLIC ANTIMONY PRODUCED AT SMELTERS IN THE UNITED STATES 1917 AND 1918

| YEAR | From Domestic Ores (Short tons) | From Foreign Ores (Short tons) |
|---|---|---|
| 1917 | 258 | 2,182 |
| 1918 | 127 | 2,490 |

BY-PRODUCT ANTIMONIAL LEAD PRODUCED IN THE UNITED STATES FROM BOTH FOREIGN AND DOMESTIC ORES, 1916–1918

| YEAR | Gross Weight (Short tons) | Antimony Content (Short tons) | Value of Antimony Contents[1] |
|---|---|---|---|
| 1916 | 24,038 | 3,496 | $1,775,968 |
| 1917 | 18,646 | 2,759 | 1,142,226 |
| 1918 | 18,570 | 2,566 | 646,632 |

[1] Calculated on basis of average yearly price of 25.4 cents a pound, or $508 a short ton, in 1916, of 20.7 cents a pound, or $414 a short ton, in 1917, and of 12.6 cents a pound, or $252 a short ton, in 1918, for ordinary grades in the New York market.

ANTIMONY CONTENT OF SECONDARY ALLOYS RECOVERED FROM OLD ALLOYS, SCRAP, AND DROSS, 1913–1918

| YEAR | Quantity (Short tons) | Value[1] |
|---|---|---|
| 1913 | 2,705 | $401,963 |
| 1914 | 2,646 | 444,844 |
| 1915 | 3,102 | 1,811,568 |
| 1916 | 4,480 | 2,270,016 |
| 1917 | 4,961 | 2,061,700 |
| 1918 | 5,183 | 1,306,116 |

[1] Values calculated at average yearly price for ordinary brands of antimony as published by the *American Metal Market*.

**Fuller's Earth in 1918.** J. Middleton. Separate from Mineral Resources of the United States, 1918, Part II. 6 pp. Issued August 27, 1919.

There was a remarkable activity in the fullers' earth industry in 1918. Domestic fuller's earth is used chiefly in refining petroleum, and, as a result of the increase in the production of petroleum, the quantity, value, and average price per ton of fuller's earth sold in 1918 were by far the largest ever recorded by the United States Geological Survey, the increase in quantity being 11,901 short tons, or 16 per cent, and in value $374,267, or 48 per cent, compared with 1917. Although the demand was good, the conditions of labor, fuel, and transportation tended to restrict the output. The imports, on the other hand, on account of the scarcity of bottoms and of the increase in ocean freights, declined 4,387 tons, or 26 per cent. The value of imported fuller's earth (reported as at the foreign port of shipment) decreased $10,882, or 6 per cent. The apparent consumption—production plus imports—increased from 89,561 short tons in 1917 to 97,075 tons in 1918, an increase of 7,514 tons, or 8 per cent. On this basis the domestic production formed 87 per cent of the consumption in 1918, against 81 per per cent in 1917. Exports of fuller's earth, if any, were not separately classified.

**Deposits of Manganese Ore in New Mexico.** E. J. JONES. Bulletin 710-B. Contributions to Economic Geology, 1919, Part I. 24 pp. Issued October 21, 1919.

The total production in New Mexico of ores containing 35 per cent or more of manganese to December 31, 1918, was approximately 5,500 tons. A few deposits in the state are capable of yielding several thousand tons each of high-grade ore, but most of the deposits are small, containing from a few tons to several hundred tons each of high-grade ore. In view of the scanty developments on most of the deposits a close estimate of the ore reserves is not possible. The ores were shipped to furnaces in Chicago and other furnaces east of the Mississippi River. The minimum freight rate to Chicago is about $8 a long ton; the charges for mining and wagon transportation are high, and even at the high prices for manganese ores that prevailed during the summer of 1918 little profit was made.

### BUREAU OF STANDARDS

**A Comparison of the Heat Insulating Properties of Some of the Materials Used in Fire-Resistive Construction.** W. A. HULL. Technologic Paper 130. 40 pp. Paper, 10 cents. Issued November 12, 1919.

**An Apparatus for Measuring the Relative Wear of Sole Leathers, and the Results Obtained with Leather from Different Parts of a Hide.** R. W. HART AND R. C. BOWKER. Technologic Paper 147. 10 pp. Paper, 5 cents. Issued November 22, 1918.

**Location of Flaws in Rifle-Barrel Steel by Magnetic Analysis.** R. L. SANFORD AND W. B. KOUWENHOVEN. Scientific Paper 343. 12 pp. Paper, 5 cents. Issued October 3, 1919.

### COMMERCE REPORTS—DECEMBER 1919

Arrangements have been made in England for the distribution of the **dyestuffs** and **chemical drugs** to be furnished by Germany in accordance with the Peace Treaty. (P. 1219)

A plan has been proposed in England for charging consumers of gas for heat units furnished as computed from the volume of gas delivered, and its average calorific value. (P. 1333)

Government ownership of all the larger **electrical power plants** and transmission lines is being considered in Germany. (P. 1369)

The location and character of a large number of **chrome ore** mines in Asia Minor are described. (Pp. 1486–92)

The **nitrogen fixation** plants at Merseberg, Germany, are being enlarged to produce 300,000 tons of fixed nitrogen annually. (P. 1507)

Three large modern **cement** plants are now in operation in India. (Pp. 1526–8)

Among the important materials for the **paint industry** produced in Ireland are linseed oil, barytes, ochers, umbers, red oxide (obtained from iron sulfate produced by the oxidation of pyritiferous shales), white lead, zinc white, gypsum, and whiting. (Pp. 1570–2)

The indications are that the use of **fuel oil** will be greatly increased by Great Britain, especially for vessels. Efforts are being made to increase the oil output of the British Empire, especially in India, Trinidad, Egypt, and Canada. At present the British Empire furnishes only 2.5 per cent of the world's petroleum. (Pp. 1572, 1751–9)

Owing to the shortage of **petroleum** in Siberia, many substitutes are being used, such as wood distillation products for lighting, and coal tar for fuel. (P. 1581)

Among the **key industries** listed in the proposed Import and Export Regulation Bill in Great Britain, and for which importation will be permitted only under license, are: Coal-tar dyes and intermediates, synthetic drugs, chemicals and perfumes, analytical reagents and fine chemicals, optical glass, scientific glassware, illuminating glassware, laboratory porcelain, scientific and optical instruments, potassium compounds, tungsten and its alloys, zinc oxide and lithopone, arc lamp carbons and electrodes, magnetos and magnets, and gauges. (Pp. 1633–8)

A description is given of the **tungsten industry** of China. At present there is almost complete stagnation, due to reduced demands since the armistice. (P. 1657)

In a review of the **oil and fat** industry of Germany, it is pointed out that large importations will be necessary. Germany will prefer to import raw materials and press the oil in Germany; but there will be increased difficulty in obtaining foreign raw materials, due to the increased development of the oil milling industry in other countries, especially Japan and the United States. Efforts to obtain oil substitutes for the manufacture of soap, candles, and linoleum have not been successful. (Pp. 1687–9)

The **vegetable oil** industry of the Netherlands is described in detail. The oils produced are used largely in the margarine industry, the linseed oil in the paint and varnish industry, and other oils in soaps, candles, etc. The oil cake is used as cattle food in dairy farming. The principal oil seeds imported are almonds, copra, linseed, palm nuts, rape seed, peanuts, and soy beans. (Pp. 1780–91)

SPECIAL SUPPLEMENTS ISSUED DURING THE MONTH

FRANCE—5*b* and *c*
ITALY—8*c*
NORWAY—10*b*
SPAIN—15*f*
UNITED KINGDOM—19*g* and *h*
CANADA—23*b*
GUIANA—44*c*
JAPAN—55*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

HANKOW, CHINA—(P. 1514)
Antimony
Egg albumin
Gall nuts
Hides
Soy bean oil
Cottonseed oil
Sesame seed oil
Tea oil
Wood oil
Nut oil
Potassium sulfate
Rhubarb
Tallow

FRANCE—Sup. 5*b* and 5*c*
Calcium tartrate
Glue
Hides
Essential oils
Paper
Photographic goods
Sodium formate
Copper matte
Artificial silk

BIRMINGHAM, ENGLAND—Sup. 19*b*
Precipitated chalk
Ammonium carbonate
Ammonium chloride
Sulfur
Sodium bicarbonate
Diamond dust
Gelatin
Glass
Glue
Iridium
Chrome yellow
Indian red
Varnish
Artificial silk
Silver-plated ware
Soap

ITALY—Sup. 8*c*
Citric acid
Cork
Essences
Licorice
Mannite
Olive oil
Hides
Sumac
Crude tartar
Glue
Graphite
Pumice
Talc

SPAIN—Sup. 15*f*
Garnets
Iron ore
Beeswax
Aconite
Ergot
Licorice
Calcium tartrate
Potash
Thymol
Gelatin
Glue
Hides
Olive oil
Red oxide of iron
Paper stock

BRITISH GUIANA—Sup. 44*c*
Balata
Bauxite
Coconut oil
Copra
Gold
Hides

JAPAN—Sup. 55*a*
Aluminum leaf
Antimony
Bronze
Celluloid
Agar-agar
Camphor
Caffeine
Cutch extract
Sodium cyanide
Dextrin
Gambier
Glycerin
Gum arabic
Gutta jelutong
Iodine
Menthol
Creosote oil
Fusel oil
Phosphorus
Potassium salts
Quinine
Licorice
Shellac
Sodium potassium (carbonate)
Sulfur
Paraffin wax
Vegetable wax
Zinc oxide
Copper
Graphite crucibles
Soap fats
Fertilizers
Glass
Gold leaf
Hides
Rubber
Iridium
Matches
Fish oil
Vegetable oils
Manganese ore
Molybdenum ore
Tungsten ore
Paper
Platinum
Graphite
Porcelain
Oil seeds
Tin
Zinc dust

# NEW PUBLICATIONS

By Clara M. Guppy, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Boiler Feed Water: A Concise Handbook of Water for Boiler Feeding Purposes.** P. G. Jackson. 12mo. 102 pp. Price, $2.00. J. B. Lippincott Co., Philadelphia.

**Carbohydrates: The Simple Carbohydrates and the Glucosides.** E. F. Armstrong. 3rd Ed. 8vo. 239 pp. Price, $4.00. Longmans, Green & Co., New York.

**Catalysis in Industrial Chemistry.** G. G. Henderson. 202 pp. Price, $3.00. Longmans, Green & Co., New York.

**Chemical Industries of France: L'Essor des Industries Chimiques en France. Ressources et Avenir de ces Industries.** Eugène Grandmougin. 2nd Ed. Revised and Enlarged. 328 pp. Price, 16 fr.50. H. Dunod, Paris.

**Chemistry: Cours de Chimie.** R. DeForcrand. 2 Vol. 2nd Ed. 8vo. Price, Vol. 1, 14 fr. Vol. 2, 18 fr. Gauthier-Villars et Cie, Paris.

**Chemistry: Creative Chemistry; Descriptive of Recent Achievements in the Chemical Industries.** E. E. Slosson. 8vo. 311 pp. Price, $2.50. Century Co., New York.

**Chemistry: Handbook of Chemistry and Physics.** Hodgman, Coolbaugh, and Senseman. 7th Ed. 533 pp. Price, $2.50. Chemical Rubber Co., Cleveland, Ohio.

**Chemistry from the Industrial Standpoint.** P. C. Thorne. 8vo. 260 pp. Price, 4s. 6d. Hodder & Stoughton, London.

**Colloidal Chemistry and Its General and Industrial Applications.** 2nd Report. British Association for the Advancement of Science. 172 pp. Price, 1s. 6d. British Association for the Advancement of Science, London.

**Enzyme Action, Nature of.** W. M. Bayliss. 4th Ed. 8vo. 190 pp. Price, $2.50. Longmans, Green & Co., New York.

**Explosives: Manufacture and Testing of Military Explosives.** J. A. Marshall. 8vo. 257 pp. Price, $3.00. McGraw-Hill Book Co., New York.

**Heat and Heat Engines, Text-Book of.** Andrew Jamieson. 18th Ed. Revised by E. S. Andrews. 12mo. Vol. 1. 551 pp. Price, $3.00. J. B. Lippincott Co., Philadelphia.

**Industrial Research, Outlook for Research and Invention.** N. M. Hopkins. 256 pp. Price, $2.00. D. Van Nostrand Co., New York.

**Leather Chemistry: Practical Leather Chemistry; A Handbook of Laboratory Notes and Methods for the Use of Students and Works Chemists.** Arthur Harvey. 8vo. 207 pp. Price, 15s. C. Lockwood & Son, London.

**Metallography: Principles of Metallography.** R. S. Williams. 8vo. 155 pp. Price, $2.00. McGraw-Hill Book Co., New York.

**Mineral Industry, 1918.** *Edited* by G. A. Roush. Vol. 27. 8vo. 937 pp. Price, $10.00. McGraw-Hill Book Co., New York.

**Minerals and Ores of the Rarer Elements, Analysis of; For Analytical Chemists, Metallurgists and Advanced Students.** W. R. Schoeller and A. R. Powell. 8vo. 239 pp. Price, $5.00. J. B. Lippincott & Co., Philadelphia.

**Ore Analysis: Technical Methods of Ore Analysis.** A. H. Low. 8th Ed. Revised and Enlarged. 8vo. 388 pp. Price, $3.25. John Wiley & Sons, Inc., New York.

**Organic Chemistry: Handbuch der Organischen Chemie.** F. K. Beilstein. 4th Ed. 982 pp. Price, $15.00. G. E. Stechert & Co., New York.

**Physical and Chemical Constants: Tables of Physical and Chemical Constants and Some Mathematical Functions.** G. W. C. Kaye and T. H. Laby. 3rd Ed. 8vo. 153 pp. Price, $2.50. Longmans, Green & Co., New York.

**Physical Chemistry: Lecture Demonstrations in Physical Chemistry.** H. S. Van Klooster. 196 pp. Price, $2.00. The Chemical Pub. Co., Easton, Pa.

**Physiological Chemistry: Laboratory Manual of Physiological Chemistry.** E. W. Rockwood. 4th Ed. Revised and Enlarged. 12mo. 316 pp. Price, $2.00. F. A. Davis Co., Philadelphia.

**Steel: Forge-Practice and Heat Treatment of Steel.** J. L. Bacon. 3rd Ed. Revised and Enlarged by E. R. Markham. 12mo. 418 pp. John Wiley & Sons, Inc., New York.

**Stereo-Chemistry.** A. W. Stewart. 2nd Ed. 8vo. 277 pp. Price, $4.00. Longmans, Green & Co., New York.

**Strength of Materials.** Arthur Morley. 5th Ed. 8vo. 555 pp. Price, $5.40. Longmans, Green & Co., New York.

**Timber, Its Strength, Seasoning and Grading.** H. S. Betts. 234 pp. McGraw-Hill Book Co., New York.

## RECENT JOURNAL ARTICLES

**Alcohol as a Motor Fuel.** J. J. Meighs. *Chemical Age*, Vol. 1 (1919), No. 6, pp. 265–268.

**Asphaltum: Determination of the Softening Point of Asphaltum and Other Plastic Substances.** D. F. Twiss and E. A. Murphy. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 23, pp. 405*t*–406*t*.

**Black-Lead Pencils and Their Pigments in Writing.** C. A. Mitchell. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 22, pp. 383*t*–391*t*.

**Chemical Engineering: Some Developments in Chemical Engineering.** A. E. Marshall. *Chemical Age*, Vol. 1 (1919), No. 6, pp. 261–264.

**Dyestuff's Industry: Some Aspects of the Establishment of the American Dyestuffs Industry.** T. H. Norton. *Chemical Age*, Vol. 1 (1919), No. 6, pp. 235–240.

**Flotation: Use of Naphthylamine and Xylidine in Flotation.** E. H. Robie. *Engineering and Mining Journal*, Vol. 108 (1919), No. 18, pp. 730–732.

**Food Chemistry: Work of the Chemist in the Food Industries; A Summary of the Development of Chemical Control in the Manufacture of Food.** L. M. Tolman. *Chemical Age*, Vol. 1 (1919), No. 6, pp. 241–245.

**Forest Products Laboratory; A Government Institution Serving the Public Both Directly and through Valuable Data Furnished to Engineers, Architects and Industrial Concerns.** *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 15, pp. 757–764.

**Gasoline as Motor Fuel.** E. W. Dean. *Chemical Age*, Vol. 1 (1919), No. 7, p. 292.

**Leather Dyeing.** L. G. Hayes. *Journal of the American Leather Chemists' Association*, Vol. 14 (1919), No. 12, pp. 683–699.

**Melting of Some Nonferrous Metals and Their Electric Alloys in Electric Furnace.** E. F. Collins. *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 13, pp. 673–679.

**Molybdenum and Molybdenum Steel.** W. E. Simpson. *Mining and Scientific Press*, Vol. 119 (1919), No. 25, pp. 894–896.

**Organic Compounds: Commercial Possibilities in the Electrochemical Production of Organic Compounds; Description of Prospective Industrial Applications.** C. J. Thatcher. *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 13, pp. 663–666.

**Paraffins: Estimation of Paraffins and Unsaturated Compounds in Commercial Toluols.** H. G. Evans. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 23, pp. 402*t*–405*t*.

**Petroleum: Composition of Rectified Petroleum Spirit from Toluol-Petroleum Spirit Runnings of Asiatic Petroleum.** H. G. Evans. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 23, pp. 401*t*–402*t*.

**Portland Cement: Manufacture and Trade.** E. D. Boyer. *Chemical Age*, Vol. 1 (1919), No. 7, pp. 287–291.

**Potash Industry: Some Chemical Aspects of the Potash Industry in Great Britain.** E. C. Rossiter and C. S. Dingley. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 22, pp. 375*t*–383*t*.

**Potash Recovery from Blast Furnace Gases in England.** Harold Hibbert. *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 14, pp. 723–726.

**Potassium Permanganate from Ferromanganese by Electrolysis.** M. DeKay Thompson. *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 13, pp. 680–681.

**Pottery Industry of the United States. A Summary of the Production Work of the Ceramist for 1918.** Jefferson Middleton. *Chemical Age*, Vol. 1 (1919), No. 6, pp. 257–259.

**Refractive Indices of Fixed Oils: The Change of Refractive Indices of Fixed Oils with Temperature.** C. H. Wright. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 22, pp. 392*t*–394*t*.

**Shellac: Pure Gum Shellac.** C. H. Jones. *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 14, pp. 715–721.

**Sodium Cyanide Production: An Account of an American Plant Organized for War Purposes.** C. O. Brown. *The Chemical Age (London)*, Vol. 1 (1919), No. 25, pp. 656–658.

**Steel: The Hardening of Steel.** H. C. H. Carpenter. *Chemical News*, Vol. 119 (1919), No. 3111, pp. 248–251.

**Sulfuric Acid: Note on the De-Arsenication of Sulfuric Acid by Hydrogen Sulfide.** T. S. Moore. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 23, pp. 399*t*–400*t*.

**Tannins: Les Tannins Synthetiques et Leur Emploi en Tannerie.** Nihoul. *Chemie et Industrie*, Vol. 2 (1919), No. 9, pp. 1024–1034.

**Textile Industry and Its Oils. Treatment of Woolens and Worsteds, Silk and Shoddy, and the Products Adapted to Each Process.** C. V. Bacon. *Drug and Chemical Markets*, Vol. 5 (1919), No. 61, pp. 7–9.

**Thermal Expansions: Stretched Wire Apparatus for Measuring Thermal Expansions.** A. W. Gray. *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 13, pp. 667–671.

**Trinitrotoluene: Hygroscopicity of Trinitrotoluene.** W. J. Huff. *Chemical and Metallurgical Engineeering*, Vol. 21 (1919), No. 11, pp. 570–571.

**Vegetable Decolorizing Carbons.** A. B. Bradley. *Journal of the Society of Chemical Industry*, Vol. 38 (1919), No. 20, pp. 396*t*–398*t*.

**Wood and Chemistry.** L. F. Hawley. *Chemical Age*, Vol. 1 (1919), No. 6, pp. 247–248.

**Zinc Industry in Belgium.** M. F. Chase. *Chemical and Metallurgical Engineering*, Vol. 21 (1919), No. 11, pp. 571–573.

# MARKET REPORT—JANUARY, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

## INORGANIC CHEMICALS

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Acid, Boric, cryst., bbls. | lb. | .14½ | .14½ |
| Hydrochloric, com'l, 22° | lb. | .02 | .02 |
| Hydriodic | oz. | .19 | .19 |
| Nitric, 40° | lb. | .07 | .07 |
| Phosphoric, 50% tech. | lb. | .24 | .24 |
| Sulfuric, C. P. | lb. | .08 | .08 |
| Chamber, 66° | ton | 22.00 | 22.00 |
| Oleum | ton | 27.00 | 27.00 |
| Alum, ammonia, lump | lb. | .04 | .04 |
| Aluminum Sulfate (iron-free) | lb. | .03 | .03 |
| Ammonium Carbonate, pwd. | lb. | .13 | .13 |
| Ammonium Chloride, gran. | lb. | .15 | .15 |
| Ammonia Water, carboys | lb. | .10½ | .10½ |
| Arsenic, white | lb. | .10½ | .11 |
| Barium Chloride | ton | 95.00 | 95.00 |
| Nitrate | lb. | .11 | .11 |
| Barytes, white | ton | 25.00 | 25.00 |
| Bleaching Powd., 35%, Works, | 100 lbs. | 2.50 | 2.75 |
| Borax, cryst., bbls. | lb. | .09 | .09 |
| Bromine, tech., bulk | lb. | .60 | .60 |
| Calcium Chloride, fused | ton | 21.00 | 21.00 |
| Chalk, precipitated | lb. | .05½ | .05½ |
| China Clay, imported | ton | 18.00 | 18.00 |
| Copper Sulfate | 100 lbs. | 8.00 | 8.00 |
| Feldspar | ton | 8.00 | 8.00 |
| Fuller's Earth | 100 lbs. | 1.50 | 1.50 |
| Iodine, resublimed | lb. | 4.10 | 4.10 |
| Lead Acetate, white crystals | lb. | .14 | .14 |
| Nitrate | lb. | .15 | .15 |
| Red American | 100 lbs. | .10½ | .10½ |
| White American | 100 lbs. | .09½ | .09½ |
| Lime Acetate | 100 lbs. | 2.00 | 2.00 |
| Lithium Carbonate | lb. | 1.50 | 1.50 |
| Magnesium Carbonate, powd. | lb. | .19 | .19 |
| Magnesite | ton | 65.00 | 65.00 |
| Mercury flask | 75 lbs. | 85.00 | 93.00 |
| Phosphorus, yellow | lb. | .35 | .35 |
| Plaster of Paris | 100 lbs. | 1.50 | 1.50 |
| Potassium Bichromate | lb. | .30 | .28 |
| Bromide | lb. | .85 | .85 |
| Carbonate, calc., 80–85% | lb. | .24 | .24 |
| Chlorate, cryst. | lb. | .18 | .15 |
| Cyanide, bulk, 98–99% | lb. | .30 | .30 |
| Hydroxide, 88–92% | lb. | .28 | .28 |
| Iodide, bulk | lb. | 3.35 | 3.35 |
| Nitrate | lb. | .14 | .14 |
| Permanganate, U. S. P. | lb. | .60 | .70 |
| Salt Cake | ton | 17.00 | 17.00 |
| Silver Nitrate | oz. | .81½ | .82½ |
| Soapstone, in bags | ton | 12.00 | 12.00 |
| Soda Ash, 58%, bags | 100 lbs. | 2.25 | 2.25 |
| Caustic, 76% | 100 lbs. | 4.25 | 4.25 |
| Sodium Acetate | lb. | .25 | .25 |
| Bicarbonate | 100 lbs. | 2.25 | 2.25 |
| Bichromate | lb. | .22 | .18 |
| Chlorate | lb. | .15 | .12 |
| Cyanide | lb. | .30 | .30 |
| Fluoride, technical | lb. | .15 | .15 |
| Hyposulfite | 100 lbs. | 3.60 | 3.60 |
| Nitrate, 95% | 100 lbs. | 3.25 | 3.35 |
| Silicate, 40° | lb. | .02 | .02 |
| Sulfide | lb. | .05 | .05 |
| Bisulfite, powdered | lb. | .05 | .05 |
| Strontium Nitrate | lb. | .23 | .23 |
| Sulfur, flowers | 100 lbs. | 3.75 | 3.75 |
| Crude | long ton | 30.00 | 30.00 |
| Talc, American, white | ton | 20.00 | 20.00 |
| Tin Bichloride | lb. | .21½ | .21½ |
| Oxide | lb. | .60 | .60 |
| Zinc Chloride, U. S. P. | lb. | .22 | .22 |
| Oxide | lb. | .60 | .60 |

## ORGANIC CHEMICALS

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Acetanilid | lb. | .55 | .55 |
| Acid, Acetic, 28 p. c. | lb. | .02½ | .02½ |
| Glacial | lb. | .12 | .12 |
| Acetylsalicylic | lb. | 1.00 | 1.00 |
| Benzoic, U. S. P., ex-toluol | lb. | .85 | .85 |
| Carbolic, cryst., U. S. P., drs. | lb. | .15 | .15 |
| 50- to 110-lb. tins | lb. | .20 | .20 |
| Acid (*Concluded*) | | | |
| Citric, crystals, bbls. | lb. | .87 | .84 |
| Oxalic, cryst., bbls. | lb. | .32 | .35 |
| Pyrogallic, resublimed | lb. | 2.50 | 2.50 |
| Salicylic, bulk, U. S. P. | lb. | .55 | .55 |
| Tartaric, crystals, U. S. P. | lb. | .70 | .67 |
| Trichloracetic, U. S. P. | lb. | 4.40 | 4.40 |
| Acetone, drums | lb. | .14 | .14 |
| Alcohol, denatured, 190 proof | gal. | .75 | .78 |
| Ethyl, 190 proof | gal. | 4.75 | 5.25 |
| Wood, 95% | gal. | 1.75 | 2.00 |
| Amyl Acetate | gal. | 3.65 | 3.65 |
| Camphor | lb. | 3.50 | 3.40 |
| Carbon Bisulfide | lb. | .08 | .08 |
| Tetrachloride | lb. | .11 | .11 |
| Chloroform, U. S. P. | lb. | .30 | .30 |
| Creosote, U. S. P. | lb. | 1.15 | 1.00 |
| Cresol, U. S. P. | lb. | .17 | .17 |
| Dextrine, corn | lb. | .07 | .07 |
| Imported Potato | lb. | .17 | .17 |
| Ether, U. S. P., conc., 100 lbs. | lb. | .17 | .19 |
| Formaldehyde | lb. | .35 | .50 |
| Glycerin, dynamite, drums | lb. | .24 | .25 |
| Starch, corn | 100 lbs. | 5.35 | 5.35 |
| Potato, Jap. | lb. | .07½ | .07½ |
| Rice | lb. | .25 | .25 |
| Sago | lb. | .05 | .05 |

## OILS, WAXES, ETC.

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Beeswax, pure, white | lb. | .65 | .65 |
| Black Mineral Oil, 29 gravity | gal. | .22 | .22 |
| Castor Oil, No. 3 | lb. | .19 | .18 |
| Ceresin, yellow | lb. | .14 | .14 |
| Corn Oil, crude | lb. | .19 | .19 |
| Cottonseed Oil, crude, f. o. b. mill. | lb. | .19½ | .19½ |
| Menhaden Oil, crude (southern) | gal. | .95 | .95 |
| Neat's-foot Oil, 20° | gal. | 2.25 | 2.25 |
| Paraffin, 128–130 m. p., ref. | lb. | .10½ | .10½ |
| Paraffin Oil, high viscosity | gal. | .45 | .45 |
| Rosin, "F" Grade, 280 lbs. | bbl. | 18.25 | 18.25 |
| Rosin Oil, first run | lb. | .97 | .97 |
| Shellac, T. N. | lb. | 1.30 | 1.70 |
| Spermaceti, cake | lb. | .30 | .30 |
| Sperm Oil, bleached winter, 38° | gal. | 1.95 | 1.95 |
| Stearic Acid, double-pressed | lb. | .26 | .27 |
| Tallow Oil, acidless | gal. | 1.50 | 1.55 |
| Tar Oil, distilled | gal. | .60 | .60 |
| Turpentine, spirits of | gal. | 1.80 | 1.97 |

## METALS

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Aluminum, No. 1, ingots | lb. | .32½ | .32 |
| Antimony, ordinary | 100 lbs. | 9.87 | 9.87 |
| Bismuth | lb. | 2.70 | 2.52 |
| Copper, electrolytic | lb. | .21½ | .19 |
| Lake | lb. | .22 | .19½ |
| Lead, N. Y. | lb. | .09 | .09 |
| Nickel, electrolytic | lb. | .45 | .45 |
| Platinum, refined, soft | oz. | 160.00 | 160.00 |
| Silver | oz. | 1.32 | 1.36 |
| Tin | lb. | .62½ | .62½ |
| Tungsten Wolframite | per unit | 7.00 | 7.00 |
| Zinc, N. Y. | 100 lbs. | 8.75 | 9.75 |

## FERTILIZER MATERIALS

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Ammonium Sulfate | 100 lbs. | 7.00 | 7.00 |
| Blood, dried, f. o. b. N. Y. | unit | 7.50 | 7.50 |
| Bone, 3 and 50, ground, raw | ton | 48.00 | 48.00 |
| Calcium Cyanamide, unit of Ammonia | | 4.50 | 4.50 |
| Fish Scrap, domestic, dried, f. o. b. works | unit | 7.25 | 7.25 |
| Phosphate Rock, f. o. b. mine: | | | |
| Florida pebble, 68% | ton | Nom. | Nom. |
| Tennessee, 78–80% | ton | 11.00 | 11.00 |
| Potassium muriate, 80% | ton | 240.00 | 240.00 |
| Pyrites, furnace size, imported | unit | .18 | .18 |
| Tankage, high-grade, f. o. b. Chicago | unit | 7.50 | 7.50 |

## COAL-TAR CHEMICALS

### Crudes

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Benzol, C. P. | gal. | .27 | .27 |
| Cresol, U. S. P. | lb. | .17 | .17 |
| Naphthalene, flake | lb. | .08 | .08 |
| Phenol | lb. | .15 | .15 |
| Toluol, 90% | gal. | .28 | .28 |
| Xylol, water white | gal. | .40 | .48 |

### Intermediates

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Acids: | | | |
| Benzoic | lb. | .80 | .80 |
| Broenner's | lb. | 1.75 | 1.75 |
| Cleves | lb. | 2.00 | 2.00 |
| Cresylic, 95% | lb. | .75 | .75 |
| Gamma | lb. | 2.50 | 2.50 |
| H | lb. | 1.70 | 1.70 |
| Metanilic | lb. | 1.60 | 1.60 |
| Monosulfonic | lb. | .15 | .15 |
| Napthionic, crude | lb. | .65 | .65 |
| Neville & Winther's | lb. | 1.70 | 1.70 |
| Sulfanilic | lb. | .35 | .35 |
| Amido Azo Benzol | lb. | 1.15 | 1.15 |
| Aniline Oil | lb. | .33 | .35 |
| For Red | lb. | .65 | .65 |
| Aniline Salt | lb. | .42 | .42 |
| Anthracene, 80% | lb. | .65 | .65 |
| Anthraquinone | lb. | 5.50 | 5.50 |
| Benzaldehyde, tech | lb. | .75 | .75 |
| U. S. P. | lb. | 1.50 | 1.50 |
| Benzidene Base | lb. | 1.25 | 1.15 |
| Benzidine Sulfate | lb. | 1.00 | .90 |
| Diamidophenol | lb. | 6.00 | 6.00 |
| Dianisidine | lb. | 10.00 | 10.00 |
| *p*-Dichlorbenzol | lb. | .10 | .10 |
| Diethylaniline | lb. | 1.40 | 1.40 |
| Dimethylaniline | lb. | .90 | .90 |
| Dinitrobenzol | lb. | .26 | .26 |
| Dinitrotoluol | lb. | .38 | .38 |
| Diphenylamine | lb. | .65 | .65 |
| G Salt | lb. | .65 | .65 |
| Hydroquinone | lb. | 2.00 | 2.00 |
| Metol | lb. | 11.50 | 11.50 |
| Monochlorbenzol | lb. | .09 | .09 |
| Monoethylaniline | lb. | 2.15 | 2.15 |
| *a*-Naphthylamine | lb. | .33 | .33 |
| *b*-Naphthylamine | lb. | 1.15 | 1.15 |
| *b*-Naphthol, crude | lb. | .55 | .55 |
| *m*-Nitraniline | lb. | .95 | .95 |
| *p*-Nitraniline | lb. | 1.20 | 1.25 |
| *p*-Nitrobenzol, crude | lb. | .16 | .16 |
| Rectified (Oil Myrbane) | lb. | .18 | .18 |
| *p*-Nitrophenol | lb. | .80 | .80 |
| *p*-Nitrosodimethylaniline | lb. | .80 | .80 |
| *o*-Nitrotoluol | lb. | .17 | .17 |
| *p*-Nitrotoluol | lb. | 1.15 | 1.15 |
| *m*-Phenylenediamine | lb. | 1.10 | 1.10 |
| *p*-Phenylenediamine | lb. | 2.40 | 2.25 |
| Phthalic Anhydride | lb. | .60 | .60 |
| Primuline Base | lb. | 4.00 | 4.00 |
| R Salt | lb. | $.62^{1}/_{2}$ | $.62^{1}/_{2}$ |
| Resorcin, tech | lb. | 3.50 | 3.50 |
| U. S. P. | lb. | 6.00 | 6.00 |
| Schaeffer Salt | lb. | .55 | .55 |
| Sodium Naphthionate | lb. | 1.10 | 1.10 |
| Thiocarbanilid | lb. | .60 | .60 |
| Tolidine, Base | lb. | 1.65 | 1.65 |
| Toluidine, mixed | lb. | .44 | .44 |
| *o*-Toluidine | lb. | .25 | .25 |
| *m*-Toluylenediamine | lb. | 1.35 | 1.35 |
| *p*-Toluidine | lb. | 1.75 | 1.75 |
| Xylidene, crude | lb. | .50 | .50 |

## COAL-TAR COLORS

### Acid Colors

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Black | lb. | 1.15 | 1.15 |
| Blue | lb. | 3.00 | 3.00 |
| Fuchsin | lb. | 2.50 | 2.50 |
| Orange III | lb. | 1.00 | 1.00 |
| Red | lb. | 1.10 | 1.10 |
| Violet 10B | lb. | 6.50 | 6.50 |
| Alkali Blue, domestic | lb. | 4.75 | 4.75 |
| Imported | lb. | 8.00 | 8.00 |
| Azo Carmine | lb. | 4.00 | 4.00 |
| Azo Yellow | lb. | 2.00 | 2.00 |
| Erythrosine | lb. | 12.00 | 12.00 |
| Indigotine, conc. | lb. | 3.00 | 3.00 |
| Paste | lb. | 1.50 | 1.50 |
| Naphthol Green | lb. | 1.50 | 1.50 |
| Ponceau | lb. | 1.00 | 1.00 |
| Scarlet 2R | lb. | 1.00 | 1.00 |

### Direct Colors

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Black | lb. | .95 | .95 |
| Blue | lb. | 1.10 | 1.10 |
| Brown | lb. | 1.55 | 1.55 |
| Fast Red | lb. | 3.50 | 3.50 |
| Yellow | lb. | 2.00 | 2.00 |
| Violet, con't | lb. | 2.20 | 2.20 |
| Chryosophenine, domestic | lb. | 2.50 | 2.50 |
| Imported | lb. | 3.80 | 3.80 |
| Congo Red, 4B Type | lb. | 1.60 | 1.60 |
| Primuline, domestic | lb. | 3.00 | 3.00 |

### Oil Colors

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Black | lb. | .70 | .70 |
| Blue | lb. | 1.65 | 1.65 |
| Orange | lb. | 1.40 | 1.40 |
| Red III | lb. | 1.65 | 1.65 |
| Scarlet | lb. | 1.75 | 1.75 |
| Yellow | lb. | 1.70 | 1.70 |
| Nigrosine Oil, solution | lb. | .90 | .90 |

### Sulfur Colors

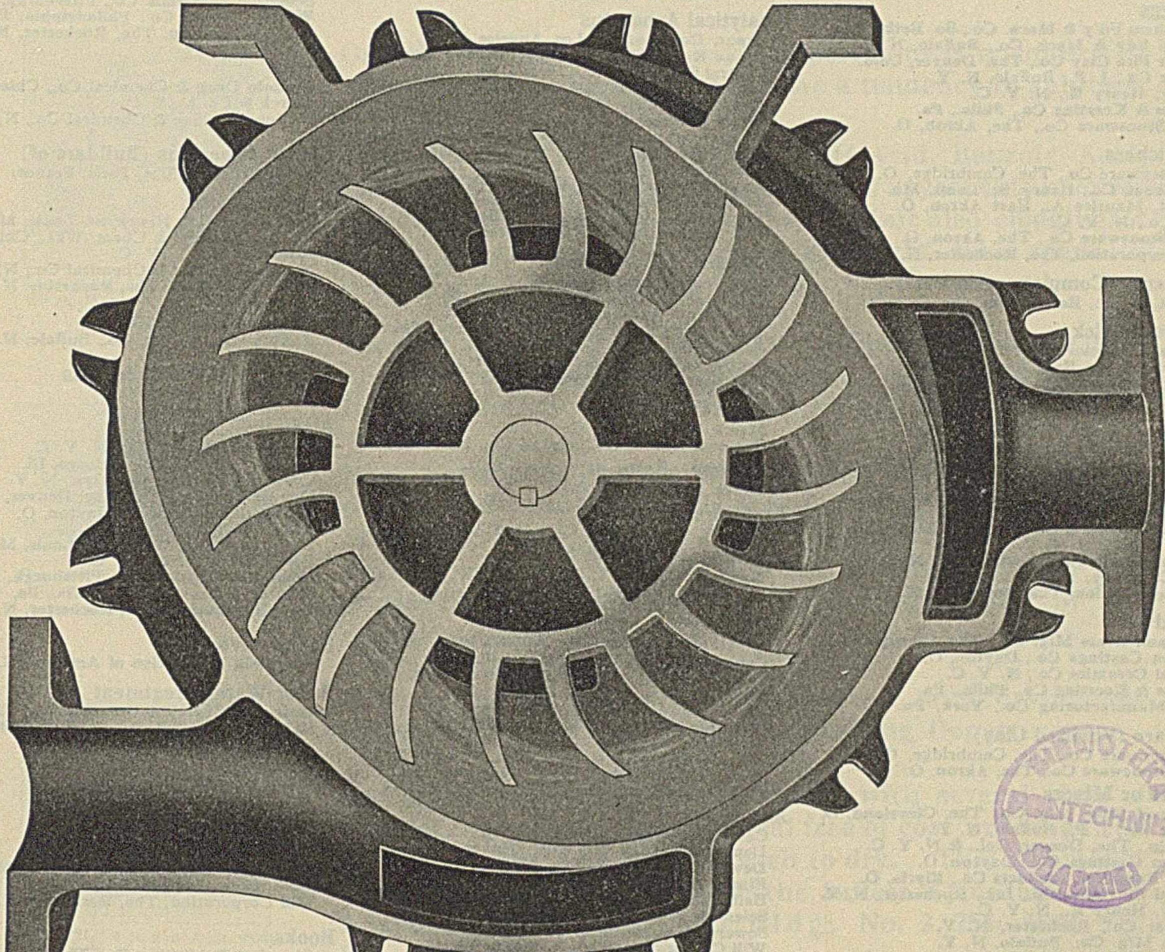
| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Black | lb. | .30 | .30 |
| Blue, domestic | lb. | .80 | .80 |
| Brown | lb. | .35 | .35 |
| Green | lb. | 1.00 | 1.00 |
| Yellow | lb. | .90 | .90 |

### Chrome Colors

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Alizarin Blue, bright | lb. | 7.75 | 7.75 |
| Alizarin Red, W. S. Paste | lb. | 5.00 | 5.00 |
| Alizarin Yellow R | lb. | 1.50 | 1.50 |
| Chrome Black, domestic | lb. | 1.25 | 1.25 |
| Imported | lb. | 2.20 | 2.20 |
| Chrome Blue | lb. | 2.50 | 2.50 |
| Chrome Green, domestic | lb. | 1.50 | 1.50 |
| Chrome Red | lb. | 2.00 | 2.00 |

### Basic Colors

| | | Jan. 1 | Jan. 15 |
|---|---|---|---|
| Auramine, O, domestic | lb. | 2.25 | 2.25 |
| Auromine, OO, imported | lb. | 3.50 | 3.50 |
| Bismarck Brown Y | lb. | .90 | .90 |
| Bismarck Brown R | lb. | 1.20 | 1.20 |
| Chrysoidine R | lb. | 1.00 | 1.00 |
| Chrysoidine Y | lb. | .90 | .90 |
| Green Crystals, Brilliant | lb. | 6.00 | 6.00 |
| Indigo, 20 p. c. paste | lb. | .75 | .75 |
| Fuchsine Crystals, domestic | lb. | 4.00 | 4.00 |
| Imported | lb. | 12.00 | 12.00 |
| Magenta Acid, domestic | lb. | 4.25 | 4.25 |
| Magenta Crystals, imported | lb. | 10.00 | 10.00 |
| Malachite Green, crystals | lb. | 4.50 | 4.50 |
| Methylene Blue, tech | lb. | 2.25 | 2.25 |
| Methyl Violet | lb. | 2.60 | 2.60 |
| Nigrosine, spts. sol | lb. | .85 | .85 |
| Water sol., blue | lb. | .65 | .65 |
| Jet | lb. | .90 | .90 |
| Phosphine G., domestic | lb. | 7.00 | 7.00 |
| Rhodamine B, ex-con't | lb. | 27.00 | 27.00 |
| Victoria Blue, base, domestic | lb. | 6.00 | 6.00 |
| Victoria Green | lb. | 6.00 | 6.00 |
| Victoria Red | lb. | 7.00 | 7.00 |
| Victoria Yellow | lb. | 7.00 | 7.00 |



# CLASSIFIED LIST OF CHEMICAL EQUIPMENT

**Absorption Towers**
Duriron Castings Co., Dayton, O.
General Ceramics Co., N. Y C.
Knight, Maurice A., East Akron, Ohio.
Lummus Co., The Walter E., Boston, Mass.
Thermal Syndicate, Ltd., The, N. Y. C.
U. S. Stoneware Co., The, Akron, O.

**Acid and Alkali Resistant Apparatus**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Cleveland Brass Mfg. Co., The, Cleveland, O.
Duriron Castings Co., Dayton, O.
Elyria Enameled Prod. Co., Elyria, O.
Jacoby, Henry E., N. Y. C.
Pfaudler Co., Rochester, N. Y.

**Acid Distillation Apparatus**
Thermal Syndicate, Ltd., The, N. Y. C.

**Acid Eggs**
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy & Mach. Co., Buffalo, N. Y.
Denver Fire Clay Co., The, Denver, Colo.
Devine Co., J. P., Buffalo, N. Y.
Jacoby, Henry E., N. Y. C.
Schutte & Koerting Co., Phila., Pa.
U. S. Stoneware Co., The, Akron, O.

**Acid Pitchers**
Guernseyware Co., The, Cambridge, O.
Heil Chem. Co., Henry, St. Louis, Mo.
Knight, Maurice A., East Akron, O.
Palo Co., N. Y. C.
U. S. Stoneware Co., The, Akron, O.
Will Corporation, The, Rochester, N. Y.

**Acid Plants (Complete or in Part)**
Knight, M. A., East Akron, O.

**Acid Proof Brick**
General Ceramics Co., N. Y. C.
Knight, M. A., East Akron, Ohio.
U. S. Stoneware Co., The, Akron, O.

**Acids**
Atlas Powder Co., Wilmington, Del.
Central Scientific Co., Chicago, Ill.
Dow Chemical Co., The, Midland, Mich.
Eimer & Amend, N. Y. C.
Gazzolo Drug & Chemical Co., Chicago, Ill.
Heil Chem. Co., Henry, St. Louis, Mo.
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co., N. Y. C.
National Aniline & Chemical Co., N. Y. C.
Palo Company, N. Y. C.
Will Corporation, The, Rochester, N. Y.

**Acid Valves**
Cleveland Brass Mfg. Co., The, Cleveland, O.
Duriron Castings Co., Dayton, O.
General Ceramics Co., N. Y. C.
Schutte & Koerting Co., Phila., Pa.
York Manufacturing Co., York, Pa.

**Acid Ware (Vitrified Clay)**
Guernseyware Co., The, Cambridge, O.
U. S. Stoneware Co., The, Akron, O.

**Agitators or Mixers**
Cleveland Brass Mfg. Co., The, Cleveland, O.
Devine Co., J. P., Buffalo, N. Y.
Dorr Co., The, Denver, Col., & N. Y. C.
Duriron Castings Co., Dayton, O.
Elyria Enameled Products Co., Elyria, O.
General Filtration Co., Inc., Rochester, N. Y.
Jacoby, Henry E., N. Y. C.
Pfaudler Co., Rochester, N. Y.
Sowers Mfg. Co., Buffalo, N. Y.
Stevens Brothers, N. Y. C.
Werner & Pfleiderer Co., Saginaw, Mich.

**Air Compressors**
Abbé Engineering Co., N. Y. C.
Crowell Engineering Co., Brooklyn, N. Y.
General Electric Co., Schenectady, N. Y.
Hubbard's Sons, Norman, Brooklyn, N. Y.
Nash Engineering Co., So. Norwalk, Conn.
Schutte & Koerting Co., Phila., Pa.

**Air-Diffusing Plates**
General Filtration Co., Inc., Rochester, N. Y.

**Air Washers**
Carrier Engineering Corp., N. Y. C.

**Alcohol Apparatus (Builders of)**
Egrot Co., Ltd., The, Paris, France.

**Alkalis**
Arnold Hoffman & Co., Inc., N. Y. C.
Lithflux Mineral & Chem. Wks., Chicago, Ill.
National Aniline & Chemical Co., N. Y. C.

**Alundum Ware**
Denver Fire Clay Co., The, Denver, Colo.
Heil Chem. Co., Henry, St. Louis, Mo.
Norton Co., Worcester, Mass.
Scientific Materials Co., Pittsburgh, Pa.
Will Corporation, The, Rochester, N. Y.

**Ammeters**
Brown Instrument Co., Philadelphia, Pa.
General Electric Co., Schenectady, N. Y.

**Ammonia**
Atlas Powder Co., Wilmington, Del.
Heil Chem. Co., Henry, St. Louis, Mo.

**Ammonia Fittings and Supplies**
York Manufacturing Co., York, Pa.

**Ammonia—Salts of**
Merck & Co., N. Y. C.

**Analysis—Gas**
Sarco Co., Inc., N. Y. C.

**Analysis—Gas Apparatus**
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Emil Greiner Co., The, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sarco Co., Inc., N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H. Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Analytical Apparatus**
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Analytical Laboratories**
Chemical Laboratories of N. Y., Inc., N. Y. C.
Columbus Laboratories, Chicago, Ill.
Dearborn Chemical Co., Chicago, Ill.
Fort Worth Laboratories, Fort Worth, Texas.
General Chemical Laboratories, N. Y. C.
Sadtler & Son, Samuel P., Philadelphia, Pa.
Westport Mill, Westport, Conn.

**Aniline Oil—Salts of**
Merck & Co. N Y C.
National Aniline & Chemical Co., N. Y. C.

**Antimony—Salts of**
Merck & Co., N. Y. C.

**Arresters (Dust)**
Sly Mfg. Co., W. W., Cleveland, O.

**Arsenic—Metallic & Salts**
Merck & Co., N. Y. C.

**Arsenic Plants (Acid Proof Stoneware)**
Knight, M. A., East Akron, O.

**Asphalt & Tar Testing Apparatus**
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N Y C.
Heil Chem. Co., Henry, St. Louis, Mo.
Scientific Materials Co., Pittsburgh, Pa.
Standard Scientific Co., N. Y. C.
Thermo-Electric Instrument Co., Newark, N. J.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Autoclaves**
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo
Devine Co., J. P., Buffalo, N. Y.
Eimer & Amend, N Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Scientific Materials Co., Pittsburgh, Pa
Sowers Manufacturing Co., Buffalo, N. Y
Will Corporation, The, Rochester, N. Y.

**Autoclaves (Glass Enameled Steel)**
Pfaudler Co., Rochester, N. Y.

**Autoclaves (High and Low Pressure)**
Buffalo Fdy. & Mch Co., Buffalo, N. Y
Devine Co., J. P., Buffalo, N Y.

**Automatic Pressure Regulators**
Brown Instrument Co., The., Phila., Pa.
Taylor Instrument Cos., Rochester, N. Y.

**Automatic Temperature Regulators**
Brown Instrument Co., The, Phila., Pa.
Engelhard, Charles, N. Y. C.
Taylor Instrument Cos., Rochester, N. Y.

**Bakelite**
General Bakelite Co., N. Y. C.

**Balances and Weights**
Becker Inc., Christian, N. Y C.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Standard Scientific Co., N. Y. C.
Thomas Co., Arthur H., Philadelphia, Pa.
Whitall Tatum Co. Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Barium—Salts of**
Dow Chemical Co., The, Midland, Mich.
Heil Chem. Co., Henry. St. Louis, Mo.
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co., N. Y. C.
Will Corporation, The, Rochester, N. Y.

**Barometers**
Brown Instrument Co., The, Phila., Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Standard Scientific Co., N. Y C.
Taylor Instrument Cos., Rochester N. Y.
Will Corporation, The, Rochester, N. Y.

**Beakers**
Braun-Knecht-Heimann Corp., San Francisco
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend N Y. C
Guernseyware Co., The, Cambridge, O.
Heil Chem. Co., Henry, St. Louis, Mo.
Herold China & Pottery Co., Golden, Col.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y

**Benzol**
Gazzolo Drug & Chemical Co., Chicago, Ill.
Merck & Co. N Y C
National Aniline & Chemical Co., N. Y. C.

**Benzol Apparatus (Builders of)**
Egrot Co. Ltd., The, Paris, France.

**Betanaphthol**
Heil Chem. Co., Henry, St. Louis, Mo.
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co. N Y C.
National Aniline & Chemical Co., N. Y. C.
Will Corporation, The, Rochester, N. Y.

**Betanaphthol Apparatus**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.

**Bismuth—Metallic & Salts**
Merck & Co., N. Y. C.

**Blowers**
Abbé Engineering Co., N. Y. C.
Central Scientific Co., Chicago, Ill.
Crowell Mfg. Co., Brooklyn, N. Y.
Denver Fire Clay Co., The, Denver, Colo.
Duriron Castings Co., Dayton, O.
Eimer & Amend, N Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C
Scientific Materials Co., Pittsburgh, Pa.
Schutte & Koerting Co., Phila., Pa.
Will Corporation, The, Rochester, N. Y.

**Boiler Coverings**
Magnesia Association of America, N. Y. C.

**Boiler Water Treatment**
Dearborn Chemical Co., Chicago, Ill.
Heil Chem. Co., Henry, St. Louis, Mo.
Merck & Co., N. Y. C.

**Bolting Cloth**
Abbé Engineering Co., N. Y. C.
Multi Metal Co., Inc., N. Y. C.

**Bone Black**
Heil Chem. Co., Henry St. Louis, Mo.
Toch Bros., N Y. C.
Will Corporation, The, Rochester, N. Y.

**Books**
Chemical Publishing Co., The, Easton, Pa.
Stechert & Co., G. E., N. Y. C.
Van Nostrand Co., D., N. Y C.
Wiley & Sons, Inc., John, N. Y. C.

**Bottles (Glass)**
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend N Y. C
Heil Chem. Co., Henry, St. Louis, Mo.
Scientific Materials Co., Pittsburgh, Pa.
Wheaton Co., T C., Millville N J.
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

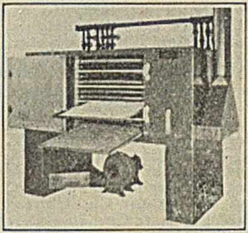
**Brinell Machines**
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Will Corporation, The, Rochester, N. Y.

**Burner Guards**
Heil Chem. Co., Henry, St. Louis, Mo.
Knight, M. A., East Akron, O.
Will Corporation, The, Rochester, N. Y.

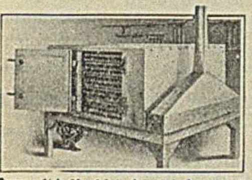
**Burners—Gas and Oil**
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill
Denver Fire Clay Co., The, Denver, Colo.
Detroit Heating & Lighting Co., Detroit, Mich.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.

# Avoid Sublimation

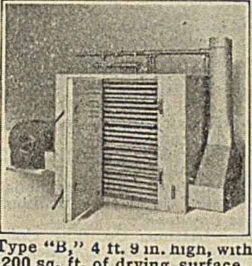
## and other material losses



Type "AA," 4½ ft. high, with 50 sq. ft. of drying surface.



Type "A," 4½ ft. high, with 100 sq. ft. of drying surface.



Type "B," 4 ft. 9 in. high, with 200 sq. ft. of drying surface.

One of the most difficult drying operations is encountered when handling chemicals that have a tendency to sublime.

Products such as Beta Naphthol, H Acid, Benzoic Acid, etc., sublime easily. In many forms of dryers this involves not only considerable loss of material, but also clogging of the apparatus and consequent loss of the time spent in taking apart and cleaning.

Each of these drawbacks adds considerably to the cost and uncertainty of the drying process, besides demanding frequent shut-downs and interruptions.

In a Gordon Dryer the construction and the system of temperature and air control make such a condition practically impossible. The money saving thus caused will soon pay the entire cost of the Gordon installation, over and above the advantages of continuous operation of the apparatus at full capacity.

If you have such a drying problem—or any drying—we invite you to submit it to our Engineering Department.

Our extensively equipped laboratory with several sizes of Gordon Dryers is at your disposal free of cost or obligation for tests of any material you wish to dry. This laboratory has been built for you—take the fullest advantage of it. Address Bush Terminal Bldg. No. 3, 253—36th St., Brooklyn, N. Y.

Write to the GORDON DRYER CORPORATION, 39 Cortland Street, N. Y., Manufacturers of all Gordon Dryers

# Gordon Dryers

For Chemicals, Colors, Dyes, Pharmaceuticals and similar materials.

## CLASSIFIED LIST OF CHEMICAL EQUIPMENT—(*Continued*)

Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill
Schutte & Koerting Co., Phila., Pa.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

### Burners—Sulphur
Schutte & Koerting Co., Phila., Pa.

### Burnishing Pots and Baskets (Acid Proof)
Knight, M. A., East Akron, Ohio.

### By-Product Machinery
Devine Co., J. P., Buffalo, N. Y.
Swenson Evaporator Co., Chicago, Ill.

### Cabinets (Laboratory, Chemical, Sample and Specimen)
Schwartz Sectional System, Indianapolis, Ind.

### Cable & Wire
General Electric Co., Schenectady, N. Y.

### Cadmium—Salts of
Dow Chemical Co., The, Midland, Mich.
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co., N. Y. C.

### Calcium—Salts of
Dow Chemical Co., The, Midland, Mich.
Merck & Co., N. Y. C.

### Calorimeters—Fuel and Gas
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sarco Co., Inc., N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

### Capsules
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y C.
Engelhard, Charles, N. Y. C. ("Impervite")
Heil Chem. Co., Henry, St. Louis, Mo.
Norton Co., Worcester, Mass.
Thermal Syndicate, Ltd., The, N. Y. C.
Will Corporation, The, Rochester, N. Y.

### Carbon Bisulfide
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co., N. Y. C.
National Aniline & Chemical Co., N. Y. C.

### Carbon Tetrachloride
Dow Chemical Co., The, Midland, Mich.
Gazzolo Drug & Chemical Co., Chicago, Ili.
Merck & Co., N. Y. C.

### Carboys
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

### Carboy Inclinators
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo
Will Corporation, The, Rochester, N. Y.

### Carboy Stoppers (Acid Proof)
Knight, M. A., East Akron, O.
Whitall Tatum Co., Philadelphia, Pa.

### Casseroles
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Duriron Castings Co., Dayton, O.
Eimer & Amend, N. Y. C.
Guernseyware Co., The, Cambridge, O.
Heil Chem. Co., Henry, St. Louis, Mo.
Herold China & Pottery Co., Golden, Colo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Will Corporation, The, Rochester, N. Y.

### Castings (Acid and Heat Resisting)
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Cleveland Brass Mfg. Co., The, Cleveland, O.
Devine Co., J. P., Buffalo, N. Y.
Duriron Castings Co., Dayton, O.
Jacoby, Henry E., N. Y. C.

### Castings (Chemical, Acid and Caustic)
Bethlehem Fd'y & Mach. Co., So. Beth., Pa
Buffalo Fdy. & Mach. Co., Buffalo, N. Y.
Cast Iron Pipe Publicity Bureau, N. Y. C.
Cleveland Brass Mfg. Co., The, Cleveland, O.
Devine Co., J. P., Buffalo, N. Y.
Duriron Castings Co., Dayton, O.
Ferguson & Lange Foundry Co., Chicago, Ill
Garrigue & Co., William, Chicago, Ill.

### Castings (Chilled)
Jacoby, Henry E., N. Y. C.
Sowers Mfg. Co., Buffalo, N. Y.

### Castings—Evaporator & Vacuum Pan
Buffalo Fdy. & Mch. Co., Buffalo, N Y.
Devine Co., J. P., Buffalo, N. Y.
Garrigue & Co., William, Chicago, Ill.
Sowers Manufacturing Co., Buffalo, N. Y.

### Castings (Machinery)
Ferguson & Lange Foundry Co., Chicago, Ill.

### Castings (Semi-steel)
Ferguson & Lange Foundry Co., Chicago, Ill.

### Caustic Potash
Gazzolo Drug & Chemical Co., Chicago, Ill.
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co., N. Y. C.

### Caustic Pots
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.

### Caustic Soda
Arnold, Hoffman & Co., Inc., N. Y. C.
General Chem. Co., N. Y. C.
Merck & Co., N. Y. C.
National Aniline & Chemical Co., N. Y. C.

### Caustic Soda Dissolvers—Automatic
Lummus Co., The Walter E., Boston, Mass.

### Cement Filler
Toch Bros, N. Y. C.

### Cement Refractory
Heil Chem. Co., Henry, St. Louis, Mo.
Norton Co., Worcester, Mass.

### Cement Testing Apparatus
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago. Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

### Centrifugals
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Cal.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago Ill.
DeLaval Separator Co., N. Y. C.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Fletcher Works, Philadelphia, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.
International Equipment Co., Boston, Mass.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Sharples Specialty Co., The, West Chester, Pa.
Tolhurst Machine Works, Troy, N. Y.
Will Corporation, The, Rochester, N. Y.

### Centrifugal Dryers
Fletcher Works, Philadelphia, Pa.

### Centrifugal Engineers
Fletcher Works, Philadelphia, Pa.
Sharples Specialty Co., The, West Chester, Pa.
Tolhurst Machine Works, Troy, N. Y.

### Cerium Oxalate
Merck & Co., N. Y. C.

### Charcoal
Booth Apparatus Co., Syracuse, N.Y.
Heil Chem. Co., Henry, St. Louis, Mo.

### Chemical Apparatus
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Detroit Heating & Lighting Co., Detroit, Mich.
Devine Co. J. P., Buffalo, N. Y.
Eimer & Amend, N. Y. C.
Fletcher Works, Philadelphia, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Kauffman-Lattimer Co., The, Columbus, Ohio.
Laboratory Materials Co., Chicago, Ill.
Schaar & Co., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Sowers Manufacturing Co., Buffalo N. Y
Standard Scientific Co., N. Y. C.
Werner & Pfleiderer Co., Inc., Saginaw, Mich.
Will Corporation, The, Rochester, N. Y.

### Chemical Glass Tubing
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C
Heil Chem. Co., Henry, St. Louis, Mo.
Will Corporation, The, Rochester, N. Y

### Chemical Glassware
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.
Kauffman-Lattimer Co., The, Columbus, Ohio.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Standard Scientific Co., N. Y. C.
Thomas Co., Arthur H., Philadelphia, Pa.
Wheaton Co., T. C., Millville, N. J.
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y

### Chemical Plants (Complete Installation)
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.
Garrigue & Co., William, Chicago, Ill.
Hercules Engineering Corp., N. Y. C.
Knight, M. A., East Akron, O.
Lummus Co., The Walter E., Boston, Mass.
Mantius Engineering Co., N. Y. C.
Swenson Evaporator Co., Chicago, Ill.
Technical Products Co., Inc., N. Y. C. (used equipment)

### Chemical Plants (Erected and Supervised)
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Egrot Co. Ltd., The, Paris, France.
McNamara, M., Everett, Mass.
Swenson Evaporator Co., Chicago, Ill.

### Chemical Reagents
Baker Chem. Co., J. T., Phillipsburg, N. J.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
General Chemical Co., Baker & Adamson Works, Easton, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.
Merck & Co., N. Y. C.
National Aniline & Chemical Co., N. Y. C.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Will Corporation, The, Rochester, N. Y.

### Chemicals
Atlas Powder Co., Wilmington, Del.
Baker & Adamson Chemical Co., Easton, Pa.
Baker Chemical Co., J. T., Phillipsburg, N. J.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill
Dearborn Chemical Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Dow Chemical Co., The, Midland, Mich.
Eastman Kodak Co., Rochester, N. Y.
Eimer & Amend, N. Y. C.
Gazzolo Drug & Chemical Co., Chicago, Ill
General Chemical Co., N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.
Hercules Powder Co., N. Y. C.
Kauffman-Lattimer Co., The, Columbus, O.
Laboratory Materials Co., Chicago, Ill.
Lithflux Mineral & Chem. Wks., Chicago, Ill
Merck & Co., N. Y. C.
Monsanto Chemical Works, St. Louis, Mo.
National Aniline & Chemical Co., N. Y. C.
Newport Chemical Works, Inc., N. Y. C.
Palo Company, N. Y. C.
Pfizer & Co., Charles, N. Y. C.
Roessler & Hasslacher Chemical Co., N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Schaar & Co., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Standard Scientific Co., N. Y. C.
Thomas Co., Arthur H., Philadelphia, Pa.
Toch Bros., N. Y. C.
Will Corporation, The, Rochester, N. Y.

### Chlorine Generators—Acid Proof
Knight, M. A., East Akron, O.

### Chlorine—Liquid
Arnold, Hoffman & Co., Inc., N. Y. C.
Electro Bleaching Gas Co., N. Y. C.

### Chromel Metal
Hoskins Mfg. Co., Detroit, Mich.

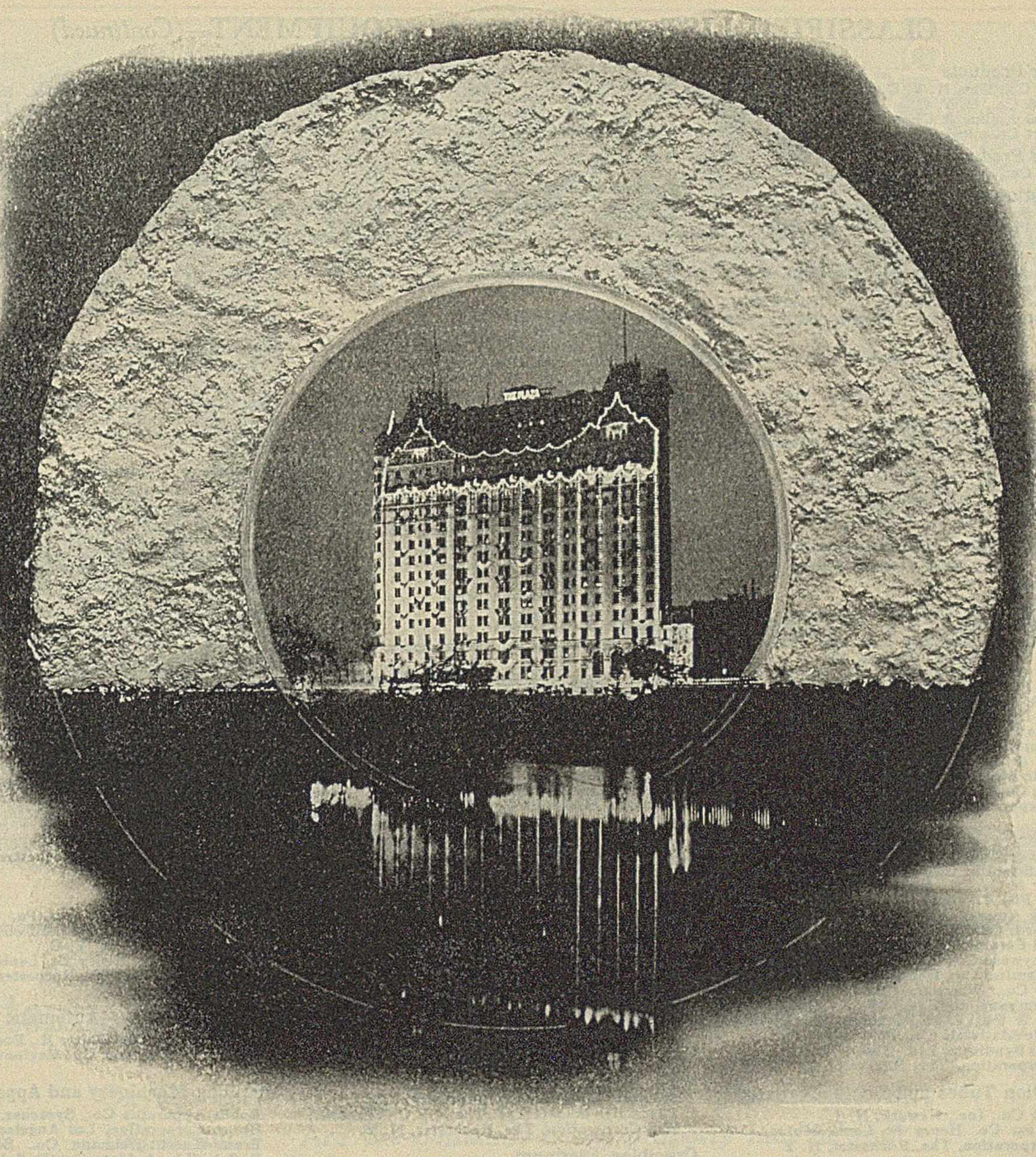
### Chromium (Metal & Salts)
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co., N. Y. C.

### Circuit Breakers and Switches
General Electric Co., Schenectady, N. Y.

### Clarifiers
Sharples Specialty Co., The, West Chester, Pa

### Classifiers
Dorr Co., The, Denver, Colo., & N. Y. C.

### Classifiers or Washers
Dorr Co., The, Denver, Colo., & N. Y. C.



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## CLASSIFIED LIST OF CHEMICAL EQUIPMENT—(*Continued*)

### Coal-Tar Products
Barrett Co., The, N. Y. C.
Merck & Co., N. Y. C.
National Aniline & Chemical Co., N. Y. C.
Newport Chemical Works, Inc., N. Y. C.

### Coal-Tar Products (Plants for)
Devine Co., J. P., Buffalo, N Y.

### Coal Testing Apparatus
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Engelhard, Charles, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Scientific Materials Co., Pittsburgh, Pa
Thermo-Electric Instrument Co., Newark, N. J.
Will Corporation, The, Rochester, N. Y

### Coating Sprays
Eureka Machine Co., Cleveland, O.

### Cobalt—Metal & Salts
Merck & Co., N. Y. C.

### Cocks—Plug (Acid Proof)
Cleveland Brass Mfg. Co., The, Cleveland, O.
Duriron Castings Co., Dayton, O.
Knight, M. A., East Akron, O.
U. S. Stoneware Co., The, Akron, O.

### Cocks—Laboratory (Brass)
Mueller Mfg. Co., H., Decatur, Ill.

### Coils or Worms (Acid Proof Stoneware)
Knight, M. A., East Akron, Ohio.

### Colorimeters
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

### Combustion Tubes and Boats
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Engelhard, Charles, N. Y. C. ("Impervite")
General Ceramics Co. N. Y. C.
Guernseyware Co., The, Cambridge, O.
Heil Chemical Co., Henry, St. Louis, Mo.
Norton Co., Worcester, Mass.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thermal Syndicate, Ltd., The, N. Y. C.
Will Corporation, The, Rochester, N. Y.

### Combustion Tubes and Boats (Platinum)
Baker & Co., Inc., Newark, N. J.
Heil Chem. Co., Henry, St. Louis, Mo.
Will Corporation, The, Rochester, N. Y

### Compressors, Rotary
Crowell Mfg. Co., Brooklyn, N. Y.
Devine Co., J. P., Buffalo, N. Y.
Heil Chem. Co., Henry, St. Louis, Mo.

### Concentrators—Sulphuric Acid
Thermal Syndicate, Ltd., The, N. Y. C.

### Condensers (Barometric and Surface)
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y
Duriron Castings Co., Dayton, O.
Jacoby, Henry E., N. Y. C.
Lummus Co., The Walter E., Boston, Mass.
Schutte & Koerting Co., Phila., Pa.
Stevens Brothers, N. Y. C.

### Condensers—Nitric Acid
Thermal Syndicate, Ltd., The, N. Y. C.

### Conductivity Measuring Apparatus
Central Scientific Co., Chicago, Ill.
Leeds & Northrup Co., The, Philadelphia, Pa.

### Consulting Chemists & Chemical Engineers
Abbott, W. G., Jr., Wilton, N. H.
Andrews, A. B., Lewiston, Me.
Booth Apparatus Co., Syracuse, N. Y.
Brickenstein, John H., Washington, D. C.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y
Carlitz & Co., J. S., Philadelphia, Pa
Columbus Laboratories, Chicago, Ill.
Ellis-Foster Co., Montclair, N. J.
Fort Worth Laboratories, The, Ft. Worth, Tex.
Foster, A. B., Washington, D. C
Gorzo, Julius, Pittsburgh, Pa.
Levin, Isaac H., Newark, N. J.
Maas, Arthur R., Los Angeles, Cal.
McNamara, M., Everett, Mass
Mantius Engineering Co., N. Y. C.
Marvin-Davis Laboratories, Inc., N. Y. C.
Mount, W. D., Roanoke, Va.
National Laboratories, The, Washington, D.C
Parker, C. L., Washington, D. C.
Pease Laboratories, N. Y. C.
Rutherford Laboratories, Rutherford, N. J.
Sadtler & Son, Samuel P., Philadelphia, Pa.
Schwarz Laboratories, N. Y. C.
Sieck & Drucker, Chicago, Ill.
Singer-Perlstein Co., Milwaukee, Wis.
Stillwell Laboratories, N. Y. C.
Sutton, Frank, N. Y. C.
Swenson Evaporator Co., Chicago, Ill.
Townsend, Clinton P., Washington, D. C.
Westport Mill, The (Dorr Co.), Westport, Conn.
Wheeler & Woodruff, N. Y. C.
Wiley & Co., Inc., Baltimore, Md.

### Contracting Engineers
Swenson Evaporator Co., Chicago, Ill.

### Controlling Instruments
Brown Instrument Co., The, Phila., Pa.
Engelhard, Charles, N. Y. C.
Taylor Instrument Cos., Rochester, N. Y.
Will Corporation, The, Rochester, N. Y.

### Converters—Booster
Westinghouse Elec. & Mfg. Co., E. Pittsburgh, Pa

### Converters—Rotary
General Electric Co., Schenectady, N. Y.

### Copper—Salts of
Lithflux Mineral & Chem. Wks., Chicago, Ill.
Merck & Co., N. Y. C.

### Cores
Norton Co., Worcester, Mass.

### Counters—Revolution
Brown Instrument Co., Philadelphia, Pa.

### Critical Point Determination Apparatus
Brown Instrument Co., Philadelphia, Pa.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Engelhard, Charles, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Hoskins Mfg. Co., Detroit, Mich.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Thwing Instrument Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

### Crucibles
Braun Corporation, Los Angeles, Cal.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Duriron Castings Co., Dayton, O. (Acid proof.)
Eimer & Amend, N. Y. C.
Engelhard, Charles, N. Y. C. ("Impervite")
Guernseyware Co., The, Cambridge, O.
Heil Chemical Co., Henry, St. Louis, Mo.
Herold China & Pottery Co., Golden, Col.
Norton Co., Worcester, Mass. (Alundum.)
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thermal Syndicate, Ltd., The, N. Y. C. (Vitreosil.)
Will Corporation, The, Rochester, N. Y.

### Crucibles, Platinum
American Platinum Works, Newark, N. J.
Baker & Co., Inc., Newark, N. J.
Bishop & Co., J. Malvern, Pa.
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Scientific Materials Co., Pittsburgh, Pa.
Will Corporation, The, Rochester, N. Y.

### Crushers & Grinders (Ind. & Lab'y)
Abbé Engineering Co., N. Y. C.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Raymond Bros. Impact Pulv. Co., Chicago, Ill.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.
Williams Patent Crusher & Pulv. Co., Chicago.

### Crystallizers—Ammonia Nitrate
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.

### Crystallizing Pans (Acid Proof)
Knight, M. A., East Akron, Ohio.

### Cupels
Braun Corporation, Los Angeles, Cal.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chemical Company, Henry, St. Louis, Mo
Hoskins Mfg. Co., Detroit, Michigan.
Norton Company, Worcester, Mass.

### Cylinders (Glass)
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

### Decanting Pots—Acid Proof
Knight, M. A., East Akron, O.
Will Corporation, The, Rochester, N. Y.

### Denitrating Apparatus
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.

### Diaphragms—Acid Proof
General Filtration Co., Inc., Rochester, N. Y
Herold China & Pottery Co., Golden, Colo.

### Dictionary—Chemical
Chemical Catalog Co., The, N. Y. C.

### Diffusion Apparatus
Devine Co., J. P., Buffalo, N. Y.
General Filtration Co., Inc., Rochester, N. Y.
Lummus Co., The Walter E., Boston, Mass.
Swenson Evaporator Co., Chicago, Ill.

### Dipping Baskets & Jars—(Acid Proof)
Knight, M. A., East Akron, Ohio.

### Dishes (Crystallizing)
Will Corporation, The, Rochester, N. Y.

### Dishes (Glass)
Will Corporation, The, Rochester, N. Y.

### Dishes ("Imperite")
Engelhard, Charles, N. Y. C.

### Dishes (Petri)
Will Corporation, The, Rochester, N. Y.

### Dishes (Platinum)
Bishop & Co., J., Malvern, Pa.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Will Corporation, The, Rochester, N. Y.

### Dissolving Tanks—Automatic
Lummus Co., The Walter E., Boston, Mass.
Werner & Pfleiderer Co., Saginaw, Mich.

### Distilling Machinery and Apparatus
Booth Apparatus Co., Syracuse, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Central Scientific Co., Chicago, Ill.
Cleveland Brass Mfg. Co., The, Cleveland, O.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Detroit Heating & Lighting Co., Detroit, Mich
Devine Company, J. P., Buffalo, N. Y.
Duriron Castings Co., Dayton, O.
Egrot Co., The, Paris, France.
Eimer & Amend, N. Y. C.
Electric Heating Apparatus Co., N. Y. C.
Elyria Enameled Prod. Co., Elyria, O
Garrigue Co., Wm., Chicago, Ill. (Fatty Acids)
General Ceramics Co., N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Jacoby, Henry E. N. Y. C.
Lummus Co., The Walter E., Boston, Mass
Palo Company, N. Y. C.
Pfaudler Co., Rochester, N. Y.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Sowers Mfg. Co., Buffalo, N. Y.
Stevens Bros., N. Y. C.
Stokes Machine Company, F. J., Phila., Pa.
Swenson Evaporator Co., Chicago, Ill.
Thomas Co., Arthur H., Philadelphia, Pa.
Wheeler Condenser & Eng. Co., Carteret, N. J.
Will Corporation, The, Rochester, N. Y.
Zaremba Company, Buffalo, N. Y.

### Draft Gauges
Braun-Knecht-Heimann Co., San Francisco
Brown Instrument Co., Philadelphia, Pa.
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.

### Drum Dryers—Vacuum and Atmospheric
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.

### Dry Blast Plants
Carrier Engineering Corp., N. Y. C.

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A high grade Black coal-tar Paint

Acid Vapors eat up metal:
Eternium saves it.

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U. S. A.

## CLASSIFIED LIST OF CHEMICAL EQUIPMENT—(*Continued*)

**Dryers—Atmospheric**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.
Gordon Dryer Corp., N. Y. C.

**Dryers—Centrifugals**
Fletcher Works, Philadelphia, Pa.
Tolhurst Machine Works, Troy, N. Y.

**Dryers—Vacuum**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Company, J. P., Buffalo, N. Y.
Jacoby, Henry E., N. Y. C.
Sowers Mfg. Co., Buffalo, N. Y.
Stokes Machine Co., F. J., Philadelphia, Pa.
Werner & Pfleiderer Co., Saginaw, Mich.

**Drying Apparatus and Machinery**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Central Scientific Co., Chicago, Ill.
Devine Co., J. P., Buffalo, N. Y.
Eimer & Amend, N. Y. C.
Engelhard, Charles, N. Y. C.
General Electric Co., Schenectady, N. Y.
Gordon Engineering Corp., N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Jacoby, Henry E., N. Y. C.
Palo Company, N. Y. C.
Sowers Mfg. Co., Buffalo, N. Y.
Tolhurst Machine Works, Troy, N. Y.
Werner & Pfleiderer Co., Saginaw, Mich.
Will Corporation, The, Rochester, N. Y.

**Duriron—Acid-Proof**
Duriron Castings Co., N. Y. C.

**Dyestuffs**
du Pont de Nemours & Co., E. I., Wilmington, Del.
Gazzolo Drug & Chem. Co., Chicago, Ill.
Lithflux Mineral & Chem. Co., Chicago, Ill.
Merck & Co., N. Y. C.
Metz & Co., H. A., N. Y. C.
National Aniline & Chemical Co., N. Y. C.

**Dynamos and Motors**
General Electric Co., Schenectady, N. Y.

**Efficiency Instruments**
Braun-Knecht-Heimann Co., San Francisco, Cal.
Brown Instrument Co., Philadelphia, Pa.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Engelhard, Charles, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Hoskins Mfg. Co., Detroit, Mich.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Thwing Instrument Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Electric Heating Devices**
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Heil Chem. Co., Henry, St. Louis, Mo.
Will Corporation, The, Rochester, N. Y.

**Electric Locomotives—Industrial**
General Electric Co., Schenectady, N. Y.

**Electrical Instruments**
Brown Instrument Co., Philadelphia, Pa.
Central Scientific Co., Chicago, Ill.
General Electric Co., Schenectady, N. Y.
Engelhard, Charles, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Hoskins Mfg. Co., Detroit, Mich.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Thwing Instrument Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Electrical Measuring Instruments**
Brown Instrument Co., Philadelphia, Pa.
Central Scientific Co., Chicago, Ill.
Engelhard, Charles, N. Y. C.
General Electric Co., Schenectady, N. Y.
Heil Chem. Co., Henry, St. Louis, Mo.
Leeds & Northrup Co., Phila., Pa.
Palo Company, N. Y. C.
Will Corporation, The, Rochester, N. Y.

**Electrical Supplies**
General Electric Co., Schenectady, N. Y.

**Electrodes—Platinum**
American Platinum Works, Newark, N. J.
Baker & Co., Inc., Newark, N. J.
Bishop & Co., J., Platinum Works, Malvern, Pa.
Braun Corporation, Los Angeles, Cal.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Engelhard, Chas., N. Y. C.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Will Corporation, The, Rochester, N. Y.

**Electrolytic Apparatus—Acid Proof**
Knight, M. A., East Akron, O.

**Enameled Apparatus (Acid Resistant)**
Elyria Enameled Prod. Co., Elyria, O., & N. Y. C.
Jacoby, Henry E., N. Y. C.
Pfaudler Co., Rochester, N. Y.

**Essential Oils**
Gazzolo Drug & Chem. Co., Chicago, Ill.
Lithflux Mineral & Chem. Co., Chicago, Ill.
Merck & Co., N. Y. C.
National Aniline & Chemical Co., N. Y. C.

**Ether Apparatus (Builders of)**
Egrot Co. Ltd., The, Paris, France.

**Evaporating Machinery**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Company, J. P., Buffalo, N. Y.
Electric Heating Apparatus Co., N. Y. C.
Hercules Engineering Co., N. Y. C.
Jacoby, Henry E., N. Y. C.
Lummus Co., The Walter E., Boston, Mass.
Sowers Mfg. Co., Buffalo, N. Y.
Sperry & Co., D. R., Batavia, Ill.
Stokes Mach. Co., F. J., Philadelphia, Pa.
Swenson Evaporator Co., Chicago, Ill.
Werner & Pfleiderer Co., Saginaw, Mich.
Wheeler Condenser & Eng. Co., Carteret, N. J.
Zaremba Company, Buffalo, N. Y.

**Evaporating Pans and Dishes**
Braun-Knecht-Heimann Co., San Francisco, Cal.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Devine Co., J. P., Buffalo, N. Y.
Duriron Castings Co., Dayton, O. (Acid Proof.)
Eimer & Amend, N. Y. C.
Elyria Enameled Prod. Co., Elyria, O., & N. Y. C.
Engelhard, Charles, N. Y. C. ("Impervite")
General Ceramics Co., N. Y. C.
Guernseyware Co., The, Cambridge, O.
Heil Chemical Co., Henry, St. Louis, Mo.
Herold China & Pottery Co., Golden, Colo.
Knight, Maurice A., East Akron, Ohio.
Palo Company, N. Y. C.
Pfaudler Co., Rochester, N. Y.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Sowers Manufacturing Co., Buffalo, N. Y.
Thermal Syndicate, Ltd., The, N. Y. C.
U. S. Stoneware Co., The, Akron, O.
Will Corporation, The, Rochester, N. Y.

**Evaporators—Crystallizing**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.

**Evaporators—Single and Multiple Effects**
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Chemical Equipment Co., Chicago, Ill.
Devine Co., J. P., Buffalo, N. Y.
Wheeler Condenser & Eng. Co., Carteret, N. J.

**Exhaust and Ventilating Fans**
General Electric Co., Schenectady, N. Y.

**Exhaust and Ventilating Fans—Acid-Proof**
Duriron Castings Co., Dayton, O.

**Extracting Apparatus**
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Devine Co., J. P., Buffalo, N. Y.
Eimer & Amend, N. Y. C.
Egrot Co., The, Paris, France.
Fletcher Works, Philadelphia, Pa.
Heil Chem. Co., Henry, St. Louis, Mo.
Lummus Co., The Walter E., Boston, Mass.
Scientific Materials Co., Pittsburgh, Pa.
Tolhurst Machine Works, Troy, N. Y.
Will Corporation, The, Rochester, N. Y.

**Extraction Cylinders**
Lummus Co., The Walter E., Boston, Mass.

**Extraction Thimbles**
Angel Co., Inc., H. Reeve, N. Y. C.
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Engelhard, Charles, N. Y. C. ("Impervite")
Heil Chem. Co., Henry, St. Louis, Mo.
Norton Co., Worcester, Mass.
Will Corporation, The, Rochester, N. Y.

**Extraction Thimbles (Greens)**
Eimer & Amend, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Extractors—Centrifugal**
Fletcher Works, Philadelphia, Pa.
International Equipment Co., Boston, Mass.
Tolhurst Machine Works, Troy, N. Y.

**Fabroil Gears & Pinions**
General Electric Co., Schenectady, N. Y.

**Faucets (Stoneware—Acid Proof)**
General Ceramics Co., N. Y. C.
Knight, Maurice A., East Akron, Ohio.
U. S. Stoneware Co., The, Akron, O.

**Filter-Cel**
Celite Products Co., N. Y. C.

**Filter Cloth**
United Filters Corp., N. Y. C.

**Filter Cloth (Metallic)**
Multi-Metal Co., Inc., N. Y. C. (Monel Metal)
United Filters Corp., N. Y. C.

**Filtering Media**
General Filtration Co., Inc., Rochester, N. Y.
Herold China & Pottery Co., Golden, Colo.

**Filter Paper**
Angel Co., Inc., H. Reeve, N. Y. C.
Braun-Knecht-Heimann Co., San Francisco.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Gazzolo Drug & Chem. Co., Chicago, Ill.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Filter Paper Clippings**
Angel Co., Inc., H. Reeve, N. Y. C.

**Filter Presses (Laboratory & Industrial)**
Abbé Engineering Co., N. Y. C.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Central Scientific Co., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Johnson Co., Inc., John, Brooklyn, N. Y.
International Filtration Corp., N. Y. C.
Jacoby, Henry E., N. Y. C.
Kelly Filter Press Co., Salt Lake City, Utah.
Lungwitz, E. E., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Shriver & Co., T., Harrison, N. J.
Sperry & Co., D. R., Batavia, Ill.
Sweetland Filter Press Co., N. Y. City.
United Filters Corp., N. Y. C.
Will Corporation, The, Rochester, N. Y.

**Filter Pulp**
Angel Co., Inc., H. Reeve, N. Y. C.

**Filters**
Engelhard, Charles, N. Y. C. ("Impervite")
General Filtration Co., Inc., Rochester, N. Y.
Norton Co., Worcester, Mass.
United Filters Corp., N. Y. C.
Will Corporation, The, Rochester, N. Y.

**Filters—(Acid Proof)**
General Filtration Co., Inc., Rochester, N. Y.
Knight, Maurice A., East Akron, Ohio.
United Filters Corp., N. Y. C.

**Filters (Bone Black)**
Colwell, Lewis, Chicago, Ill.

**Filters, Folded**
Angel Co., Inc., H. Reeve, N. Y. C.
Central Scientific Co., Chicago, Ill.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Thomas Co., A. H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Filters—Vacuum**
American Continuous Suction Filter
(See United Filters Corp., N. Y. C.)
Devine Co., J. P., Buffalo, N. Y.
General Filtration Co., Inc., Rochester, N. Y.
United Filters Corp., N. Y. C.

**Filters—Water**
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Booth Apparatus Co., Syracuse, N. Y.
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
General Ceramics Co., N. Y. C.
Griebel Instrument Co., Carbondale, Pa.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Schutte & Koerting Co., Phila., Pa.
Thomas Co., Arthur H., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Filtros**
General Filtration Co., Inc., Rochester, N. Y.

**Filtros—Vacuum**
Devine Company, J. P., Buffalo, N. Y.

**Fire Brick and Clay**
Denver Fire Clay Co., The, Denver, Colo.

**Flasks**
Braun-Knecht-Heimann Co., San Francisco
Central Scientific Co., Chicago, Ill.
Daigger & Co., A., Chicago, Ill.
Denver Fire Clay Co., The, Denver, Colo.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Scientific Materials Co., Pittsburgh, Pa.
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.

**Foamite Firefoam**
Foamite Firefoam Co., N. Y. C.

**Fuel Gas Plants**
Detroit Heating & Lighting Co., Detroit, Mich.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.

**Funnels**
Denver Fire Clay Co., The, Denver, Colo.
Heil Chem. Co., Henry, St. Louis, Mo.
Knight, M. A., East Akron, Ohio.
Whitall Tatum Co., Philadelphia, Pa.
Will Corporation, The, Rochester, N. Y.