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EDITORIAL OFFICES:
One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613–0614

Cable Address: JIECHEM

ADVERTISING DEPARTMENT:
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TELEPHONE: Gramercy 3880

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CONTENTS

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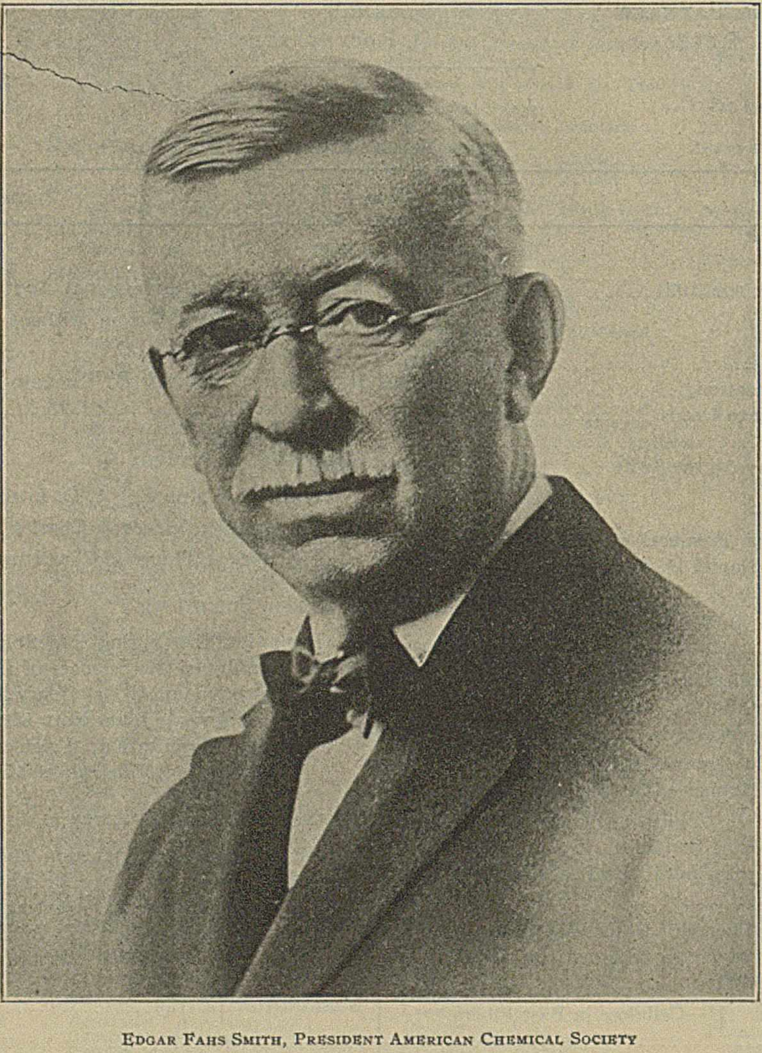
THE SOCIETY'S PRESIDENT FOR 1921

EDGAR FAHS SMITH

Forty-five years ago the AMERICAN CHEMICAL SOCIETY was founded, and just a quarter of a century has passed since Edgar Fahs Smith was its president. The SOCIETY gives expression to its appreciation of his labors by choosing him once more for the highest office in its gift, and in doing so it places in tried and worthy hands the leadership of its fortunes.

Few remain now who can recall the struggles and discouragements of those early years. So faint was the breathing at times that it seemed almost as if the patient was at his last gasp. There were chemists scattered here and there over the land, but most of them were kept too busy to give time to investigation. The teacher had little assistance with his classes, and the practical side of building up our infant industries was all-absorbing. Besides, the SOCIETY'S *Journal* had to enter the field of publication with first one, then two other journals. All honor, then, to those who had heart of hope and, with vision of the future, kept up the struggle. In these days of leadership in many fields of investigation it is well to pause a while and think of the sturdy pioneers who blazed the way and made this progress possible.



EDGAR FAHS SMITH, PRESIDENT AMERICAN CHEMICAL SOCIETY

Among these pioneers none stands higher than our new president, and no one has such a host of friends nor is so well-beloved. A kindlier soul has never walked among us. Counselor and friend to all who needed him, lover of the truth whether it lay hidden in the nature around him or in his fellow man, with deep, abiding faith in all that was fine and noble and true, he has stood throughout the years four-square to every wind that blew. His friendship has been an inspiration and a blessing to many.

It might seem unnecessary to recount the contributions of Dr. Smith in the building up of our science but, perhaps, there are some among our thousands of members who do not realize how much his labors have meant to all of us and how they have strengthened chemistry in America and kept fresh the story of its beginnings.

It is a somewhat striking coincidence that Dr. Smith began his life work as a teacher of chemistry in the University of Pennsylvania in 1876, the same year in which our SOCIETY was founded. Lifelong contemporaries they have been in the work. Starting as an instructor, he rose through the various grades to head of the department of chemistry, then vice provost, and lastly provost of the University, retaining throughout his devotion to his science and faithfully answering to the limits of his strength the calls that were made upon him. It is difficult to measure such an influence as he has exerted. The story is known to those who had the good fortune to study under him. They admire him, they love him, and happy are they if they pattern after him. In all these years he has been a wise and helpful counselor in the affairs of the SOCIETY, and has done much to promote its interests.

As a teacher, he has been helpful in introducing new methods and in providing excellent textbooks. At first these were translations from the most widely accepted foreign authors—as witness his several editions of Richter's "Organic Chemistry," and the "Electrochemistry" of Oettel. In this line he was one of the first to have a well-equipped electrochemical laboratory and to drill his students in this increasingly important branch, issuing several valuable guides and textbooks of his own. He devised new methods of analysis and greatly aided in introducing this valuable adjunct to the laboratory practice of the day. All of which was fitting on the part of one who held the chair of Robert Hare, who constructed the first American electric furnace.

The long list of his investigations helps to fill the pages of our *Journal* and need not be detailed here. Suffice it to say that his interests and his work lie in many fields. Chief among them are electrochemistry, the complex inorganic acids, the rare earths, and the revision of those constants, if constants they be, the atomic weights. In this latter field he has covered about one-fourth of the known elements, and his work ranks high. This is a monumental work in itself. His latest work on the atomic weights of boron and fluorine is a fine example of how such work should be done.

The many-sided interests of this man are shown by the caretaking, accurate, and very valuable work which he has done as a historian. His activities in this line may have been aroused by the fact that he occupied the chair which had been held by Benjamin Rush, the first professor of chemistry in America, and lives in the historic city of Philadelphia, where in 1792 was "instituted" the first chemical society in the world, antedating by a half century the London Chemical Society, the first to be established in Europe. Also, he is a member and for some years was president of the American Philosophical Society, which was founded by Benjamin Franklin.

Surrounded by such historic memories he has made the past live over again in a series of books for which those of us who do honor to the men who paved the way for our feet cannot be too grateful. Hare performs over again for us his surprising experiments with the oxyhydrogen blowpipe which he invented, and Woodhouse, Cooper, and others tell of their discouragements and achievements. And now in the account of Priestley in America, which he has just published, we catch an insight into the character of that great discoverer, his limitations offset by his surprising vision, which some of us who have read much about him had never gained before.

To such tried and approved leadership we intrust the reputation and future of the SOCIETY.

CHAPEL HILL, N. C. FRANCIS P. VENABLE

EDITORIALS

ELEMENTARY ECONOMICS

Some are arguing that duty-free importation of scientific apparatus by educational institutions will mean a great saving in dollars and cents. But to discuss the economic aspect of this question it is necessary to shake one's self loose from memories of pre-war conditions and remember that to-day we are dwelling in a very much changed world. Before the war Germany, thanks to an abundance of cheap, highly skilled labor, placed upon the market chemical wares at prices with which American manufacturers could not compete. To-day Germany is faced with the obligation of paying off during the next twenty-five or thirty years an enormous reparations debt. To do this Germany will sell goods in competition at absurdly low figures in order to destroy war-born industries in other lands, while charging exorbitant prices wherever she has a monopoly.

There is abundant evidence of the correctness of this statement. In *Science*, November 26, 1920, page 511, Professor James Lewis Howe complains that the file of a journal which had been offered him less than a year before for 3,000 marks has now risen in price to 25,000 marks (though the exchange value of the mark had meanwhile depreciated only 50 per cent). Monopoly:—exorbitant charge! But Professor Howe explains the situation in this same communication, for he quotes from a German firm's letter to an American customer:

> "A word about prices. I take it from your name and connections that you are of German family and am therefore prepared to make most liberal terms. As you doubtless know, it has been generally agreed in commercial circles here that all articles sold to *uitlanders*, and especially to Americans, shall be priced considerably higher than the same thing sold to our fellow-citizens, the idea being to in this way recuperate to some extent from our late overwhelming losses and to make our recent enemies aid us in paying our most outrageous and crushing war debt.
>
> "This policy has been adopted *en bloc* by our associated.... since some time. But as a fellow German, I am prepared to let you have these goods at the Berlin price, this of course being in all confidence, my most dear sir."

No camouflage about that—as long as it is in the family.

Now take the other side of the picture. England developed during the war a chemical glassware industry:—competition! The *London Morning Post* of November 24, 1920, quotes the following conditions of the British market at that time:

	German (Price to Retailer)	British (Cost to Manufacture)
1,000-cc. separating funnel	4s. 0d.	17s. 7d.
400-cc. flat bottom flask	0s. 6.5d.	0s. 11.5d.
500-cc. graduated flask	0s. 5d.	6s. 6d.
15-cc. bulb pipet	1s. 3.5d.	3s. 9d.
Potash bulb	1s. 9d.	3s. 6d.
Aneroid barometer	7s. 6d.	20s. 0d.
Chemical thermometer for testing acids	1s. 2d.	3s. 0d.
Clinical thermometer	0s. 8.5d.	2s. 4d.

Destructive competition! Do you believe those German prices will stand after the British industry is destroyed, say, four or five years, with that great reparation debt still having twenty or twenty-five years to run? We would be the veriest financial babes-in-the-woods if we deliberately shut our eyes to such a situation.

As further evidence, if it be needed, we quote from *The Chemical Age* (London), December 25, 1920, in summarizing the report of the Subcommittee on Chemical Glassware appointed by the Standing Committee on Trusts:

> "The nature of the foreign competition they have to meet may be gathered from the fact that, favoured by exchange rates

and other conditions, goods of the kind now being made in this country are being supplied by Continental manufacturers at prices less than the actual cost of manufacture here, whereas *for goods that are not yet being manufactured here prices are being charged by the Continental makers which mean to the consumer approximately five times the pre-war price of such goods.*"—[Italics ours.]

The U. S. Tariff Commission gives a new slant to the whole question. In its report on chemical glassware just submitted to the Ways and Means Committee (*Tariff Information Surveys*, Scientific Instruments and Apparatus, page 59), it says:

> "The great durability of domestic glassware makes it the cheapest in the final analysis. Institutions which sell at actual cost will no doubt find it to their advantage to use this material regardless of the price of foreign ware, because, although the first cost is high, the replacement cost is low and smaller reserve stocks can be carried. Those institutions, on the other hand, which plan on obtaining a profit from the sale of glassware to students will find it to their advantage to use the fragile foreign material. In this case heavy breakage increases the turnover and therefore the profit."

The Tariff Commission is not disposed to joke, nor to make charges without facts on which to base them.

Foster the American industry, then see that it plays the game fair!

THE ROAD TO DEMORALIZATION

Two German dye chemists, Dr. Otto Runger and Dr. Joseph Flachsländer, were officially released from Ellis Island and admitted into this country on January 5, 1921. This action followed a thorough investigation by the authorities of the port of New York based, according to press accounts, upon a protest from Germany. We don't blame Germany for protesting, but with this side of the matter we have no concern. The *herrschaften* proceeded immediately to Wilmington, Delaware, to take positions in the research laboratories of the du Pont Company. According to the newspapers, $25,000 each is the salary of these newcomers. Rumor has it that the amount is much larger. A high official of the Company informs us that these reports are greatly exaggerated. However, that matter is not important. But the changed policy of this Company, hitherto always considered 100 per cent American in every respect, is important, and unfortunate from whatever angle viewed.

An economic battle for the possession of the American market is in progress between the American and the German dye industry. In war information is obtained as far as possible from captured opponents, but renegades are not placed in positions of high command. Whatever tends to demoralization in the American ranks is a matter of national concern, and the gravest feature of this new policy is the lowered morale of the du Pont research staff which will result therefrom.

It is not difficult to imagine the feelings of American chemists who must take direction from men who a short while ago were busy in those plants whence came high explosives and poison gases, the latter accounting for a full third of our hospital casualties. Temperamentally that research staff now becomes a conglomeration of incompatibles, a hybrid mixture which has in it the elements of failure. At the outset of the building of the dye industry there were many laboratories where such a mixture was found to be thoroughly bad, and where the weeding-out process was put into operation and the staffs Americanized with consequent fine results.

It is easy to understand the feeling of discouragement which must possess the officials of the du Pont, as of every other American dye manufacturing company, over the failure of Congress to enact definite and adequate protective legislation. However, the pressure from consumers for a wider variety of dyes has been materially lessened through the constant licensing of imports by the War Trade Board and by the decreased demand for dyes during the present general industrial slump. Now is the time for developing an efficient research staff from among our ablest American chemists.

It is not too late to repair the damage. There are eastward-bound steamers constantly traveling across the Atlantic. Whatever the ability of these two chemists, however intimate their knowledge of special lines of manufacture may be—send them home and let the American industry proceed to its full development in an American way and by the force of American brains.

THOUGHTS TRANSLATED INTO DEEDS

Often we discuss, and plan, and build great air castles, and develop momentary boundless enthusiasm —and then, with the peak of the curve reached, enthusiasm wanes, interest subsides or becomes diverted to other matters, and the result is nothing. Happily for progress this is not always the case.

At the meetings of the Interallied Conference of Pure and Applied Chemistry which met in London and Brussels, in July 1919, it was determined seriously and comprehensively to set about the task of betterment of chemical literature. The AMERICAN CHEMICAL SOCIETY undertook for its share of this work the preparation and publication of two series of monographs, scientific and technologic, on chemical subjects. The announcement of the issuance of the first of the scientific series "The Chemistry of Enzyme Actions" by Dr. K. George Falk is an earnest that the AMERICAN CHEMICAL SOCIETY proposes to carry out promptly and to the full its part of this undertaking.

Congratulations to the three trustees, Drs. Charles L. Parsons, John E. Teeple, and Gellert Alleman, who so quickly finished the business arrangements connected with these publications; to the editors, Drs. W. A. Noyes and John Johnston, who already have announced progress in the preparation or printing of eleven other monographs; and to the Chemical Catalog Company, Inc., which has so excellently carried out the publication of this first of the series.

Clear a new space on your book shelves, there is a lot of fine material on the way to you!

SOWING GOOD SEED

There have been strange doings in Washington. In spite of the sentiment in Congress that the Chemical Warfare Service should be developed to the fullest extent, orders issued by high officials of the War Department have tended to restrict its activities, to cripple development, to prevent the training of troops in the methods of gas warfare, in short, to limit the Chemical Warfare Service solely to research.

Fortunately we are building for the future on better lines, and in this work the AMERICAN CHEMICAL SOCIETY is doing a fine part through the annual lectures given by distinguished members of the SOCIETY at the United States Military and Naval Academies. The first set of those lectures was given last winter, and it will interest all to learn that of the graduating class this year at West Point, 25 members requested assignment to the Chemical Warfare Service. The second series of lectures is now in progress.

Recently we asked for frank opinions of the value of these lectures. The Superintendent of the Military Academy, Brigadier General MacArthur, wrote in reply:

> Through the courteous coöperation of the AMERICAN CHEMICAL SOCIETY, following suggestions advanced in an editorial in the *Journal of Industrial and Engineering Chemistry* for March 1919, there were given last winter to the senior class of the Corps of Cadets of the U. S. Military Academy a series of lectures on important chemical processes. The lecturers and their subjects were:
>
> DR. W. H. NICHOLS, "Sulfuric Acid, the Pig Iron of Chemistry"
> DR. C. L. PARSONS, "The Fixation of Atmospheric Nitrogen"
> DR. W. H. WALKER, "The Manufacture of Toxic Gases"
> DR. C. L. REESE, "Smokeless Powders and High Explosives"
>
> Other lectures were planned but had to be omitted owing to reduction in time made necessary by the war-time schedule then being followed. These gentlemen, whose services were entirely voluntary, placed their subjects before the class in an extremely vivid, lucid and interesting manner, giving that personal touch not to be found in textbooks and arousing the keenest interest in their auditors, both by the subject matter and by the manner in which it was presented.
>
> The obvious benefit of these lectures has led to a continuation of the policy and in the coming spring a second series will be delivered, the lecturers and their proposed subjects being:
>
> DR. JOHN JOHNSTON, of Yale, "Industrial Research," March 23, 1921
> PROFESSOR WILLIAM MCPHERSON, of Ohio State University, "Large Scale Production of Munitions," March 30, 1921
> DR. G. A. RICHTER, of Berlin, N. H., "Rockets and Flares," April 6, 1921
> DR. G. W. GRAY, of New York, N. Y., "Fuel, Motor and Lubricating Oils," April 13, 1921
> DR. W. LEE LEWIS, of Northwestern University, "Toxic Gases," April 20, 1921

Rear Admiral Scales, Superintendent of the Naval Academy, was equally enthusiastic in his reply:

> The suggestion for a series of lectures to be given at the Naval Academy by members of the AMERICAN CHEMICAL SOCIETY first received public attention in an editorial entitled "The Soldier, the Sailor and the Chemist" which appeared in the *Journal of Industrial and Engineering Chemistry* for March 1919. The attention directed to this very important matter aroused the interest of all concerned. The cordial offer of the AMERICAN CHEMICAL SOCIETY, tendered by the President, Dr. William H. Nichols, to arrange for a series of lectures was much appreciated and the opportunity gladly made use of.
>
> During the academic year 1919–20, eight lectures in the general field of chemical engineering were delivered at Annapolis by members of the AMERICAN CHEMICAL SOCIETY. All of these lectures were heard by student officers attending the Naval Postgraduate School and four of them by the First (senior) Class of midshipmen. During the academic year 1920–21 a series of six lectures has been arranged, all of them to be heard by the student officers of the Postgraduate School and four of them by the First Class of midshipmen. The lecturers for the current session are:
>
> DR. JOHN JOHNSTON, "Industrial Research," December 4, 1920
> DR. A. S. CUSHMAN, "Preservation of Iron and Steel," January 8, 1921
> DR. G. W. GRAY, "Fuel, Motor and Lubricating Oils," February 4 and 5, 1921
> DR. WILDER D. BANCROFT, "Organized Research," March 4 and 5, 1921
> DR. W. LEE LEWIS, "Toxic Gases," April 1 and 2, 1921
> DR. CHARLES L. REESE, "Explosives," April 29 and 30, 1921
>
> The series of lectures of last year, and the current series, are proving both interesting and profitable to all who have the opportunity of hearing them, as they gain at least a perspective of what the profession of chemical engineering has done, and can do, in furnishing indispensable assistance to our military and naval forces in preparation for, and in conduct of, active operations calculated to carry into effect the requirements of our national views and aims.
>
> It is clear to us that the purpose contained in the original editorial suggestion is being accomplished. The ultimate benefits of the cordial coöperation of the AMERICAN CHEMICAL SOCIETY cannot be given a definite value, but it is certain that the movement now under way cannot fail to be productive of much good to the naval service.

Surely no more patriotic and fruitful work than the delivery of these lectures could be done by the members of the SOCIETY.

THE RACE IS NOT ALWAYS TO THE SWIFT

We hustling Americans are apt sometimes to poke good-natured fun at the slowness of the Britisher. But sometimes the shoe is on the other foot, witness the following chronological history of the British *ten-year* dye license bill in Parliament:

December 2, 1920	Bill introduced in House of Commons, first reading, ordered printed.
December 3, 1920	Bill printed, distributed and received endorsement of Colour Users Association.
December 7, 1920	*London Times* in a leading editorial said: "Attack is threatened from irreconcilable Free Traders [our Senator Thomas], out-and-out Protectionists [modified to straight-tariff-protectionists, our Senator Moses], and a section of the textile trade [our Mr. John P. Wood and his adherents]." Continuing, the *Times* said in comparing with other key industries: "There is justification for giving the dye industry preference on the ground that it is essential both from the economic and the military standpoints."
December 7, 1920	Bill moved to second reading. While a member was speaking in opposition, at eleven o'clock the *closure was moved* and carried by 280 votes to 74. The second reading was agreed to.
December 8–15, 1920	Bill considered in Committee.
December 17, 1920	Third reading of the bill and passage by 118 votes to 25.
December 17, 1920 (midnight)	First reading in the House of Lords.
December 21, 1920	Second reading, passed 83 to 36.
December 22, 1920	Passed Committee consideration.
December 23, 1920	Bill passed third reading in the House of Lords.
December 23, 1920 (midnight)	Bill received the royal assent.
January 15, 1921	Law became effective.

Nearly two years have elapsed since the Longworth bill was introduced in Congress. It is still there. What's the matter with us, anyhow?

Our correspondence basket is overflowing with a fine crop of "Tell-it-to-Herty" communications. Individual acknowledgment will eventually be made, meanwhile things are moving.

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

MEASUREMENT OF VAPOR PRESSURES OF CERTAIN POTASSIUM COMPOUNDS[1]

By Daniel D. Jackson and Jerome J. Morgan

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

Received December 9, 1920

Anderson and Nestell,[1]* in a report on "The Volatilization of Potash from Cement Materials," give the predominating factors affecting the recovery of potash in the furnace gases beyond the furnace, as follows:

> (1) The temperature prevailing in the kiln; (2) volume of gas passing; (3) the intimacy of contact between the furnace gases and the cement mix; (4) the vapor pressure of the potash salt or salts formed; (5) the possibility of dissociation under certain furnace conditions (oxidizing, neutral, or reducing atmosphere or changing temperature) to components of greater or less volatility than the original salt; (6) the degree of saturation of the gas in contact with the cement material; (7) the rate of diffusion both of the salt vaporizing in the interstices of the cement mix to the surface of contact with the gas stream, and of the saturated gas at the surface to the leaner gas areas beyond.

Of these seven factors, all may be more or less varied at will except the fourth, namely, *the vapor pressure of the potash salt or salts formed*. It was decided, therefore, that the fundamental thing in a study of the volatilization of potash is the determination of the vapor pressure of the potassium compounds involved. In the present work results of vapor pressure measurements are given for three natural silicates, leucite, orthoclase feldspar, and glauconite, which are sufficiently abundant to serve as sources of potash, and for four other potassium compounds, the chloride, carbonate, hydroxide, and sulfate, which are of particular interest on account of their connection with the recovery of potash from cement mill flue dust. The knowledge acquired in these vapor pressure measurements will later be applied to the study of the volatilization of potash from mixtures of silicates with releasing and volatilizing agents.

PREVIOUS WORK

In 1866, Bunsen[2] determined the relative volatility of certain salts by heating a centigram bead of the salt on a platinum wire in the hottest part of a Bunsen flame and measuring the time required for the salt to volatilize. In 1897, Norton and Roth[3] repeated and extended the work of Bunsen. The volatility of sodium chloride thus measured in each case was taken as unity. The results of these investigators, as far as they relate to potassium compounds, are given in Table I.

TABLE I—VOLATILITY OF POTASSIUM COMPOUNDS, TAKING THE VOLATILITY OF SODIUM CHLORIDE AS UNITY

COMPOUND	Results of Bunsen	Results of Norton and Roth
Iodide	2.828	2.362
Bromide	2.055	1.860
Chloride	1.288	1.083
Fluoride	...	0.329
Carbonate	0.310	0.277
Sulfate	0.127	0.149

Bergstrom,[4] in 1915, found the boiling points of the potassium halides to be as follows: potassium chloride 1500°, potassium bromide 1435°, and potassium iodide 1420°. Niggli[5] found that a mixture of potassium carbonate and silica heated for 60 hrs. at 900° to 1000° lost 15 mg. of K_2O. In addition, many of the recent articles dealing with processes for recovering potash from silicates contain statements as to the relative volatility of certain potassium compounds, but, with the exception of the work of Anderson and Nestell,[1] it is believed that there has been no previous quantitative study on the volatilization of potassium compounds.

METHOD OF VAPOR PRESSURE DETERMINATION

On account of the difficulty of finding a gastight material which would withstand the corrosive action of potassium compounds at high temperatures, and of measuring small pressures at these temperatures, it seemed useless to attempt to employ a static method for measuring the vapor pressure. Hence the dynamic method of von Wartenberg[6] was chosen.

In this method a measured volume of gas is passed over a weighed quantity of the substance whose vapor pressure is to be determined at the desired temperature. The amount volatilized is found by the loss of weight, and the partial pressure is calculated from the relation:

$$\text{Pressure of substance} = \frac{\text{Moles of substance} \times \text{total pressure}}{\text{Moles of gas} + \text{moles of substance}}$$

This partial pressure of the volatilized substance represents its vapor pressure only if the gas passed over the heated substance is saturated with the vapor of the substance at the given temperature, a condition which is never realized experimentally. However, the degree of saturation of the gas stream is inversely proportional to its speed. Hence by determining these partial pressures at three or more speeds of the gas stream, and plotting the partial pressures against the speeds, it is possible to obtain the slope of the line which shows the relation between partial pressures of the volatilized substance and speed of the gas stream. If this line is extended to zero speed it gives the partial pressure at saturation, which is the vapor pressure of the volatilized substance.

The application of this method presupposes a knowledge of the molecular weight in the gaseous state of

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[1] Part of a thesis presented in partial fulfilment of the requirement for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York, N. Y.

* Numbers refer to references at end of paper.

both the substance volatilized and the gas used, in order that the number of moles of each may be calculated. The number of moles of nitrogen, the gas passed through the reaction chamber, was easily found by weighing the water displaced by the nitrogen at a given temperature and pressure. In the case of the potassium compounds volatilized, the density in the gaseous state has been determined for only one of the compounds studied. Nernst[7] has shown that the molecular weight of potassium chloride at high temperatures corresponds to the simple formula KCl. In calculating the vapor pressures of the other compounds it was necessary to make certain assumptions regarding the molecular weight of the compound volatilized. The details of these assumptions are given under the discussion of the results for each compound. It can be pointed out here, however, that should later work show that the assumed molecular weight in any case is wrong, it will simply necessitate recalculation of the results and will not impair the usefulness of the experimental data. Furthermore, a vapor pressure here given, used in connection with the assumed molecular weight, will give practically the same result in calculation of the amount of potash necessary to saturate a given volume of gas at a given temperature and pressure as would a corrected molecular weight used with the recalculated vapor pressure. Nevertheless, to avoid misunderstanding special attention is called to the fact that, with the exception of the value for potassium chloride, the vapor pressures herein reported are based upon assumed molecular weights.

VAPOR PRESSURE APPARATUS

A general sketch of the apparatus is given in Fig. 1. It consisted of the gas container A, the purifying train B, the vapor pressure tube C, which was heated in an electric furnace, F, the absorbing train D, and the gas measuring apparatus E.

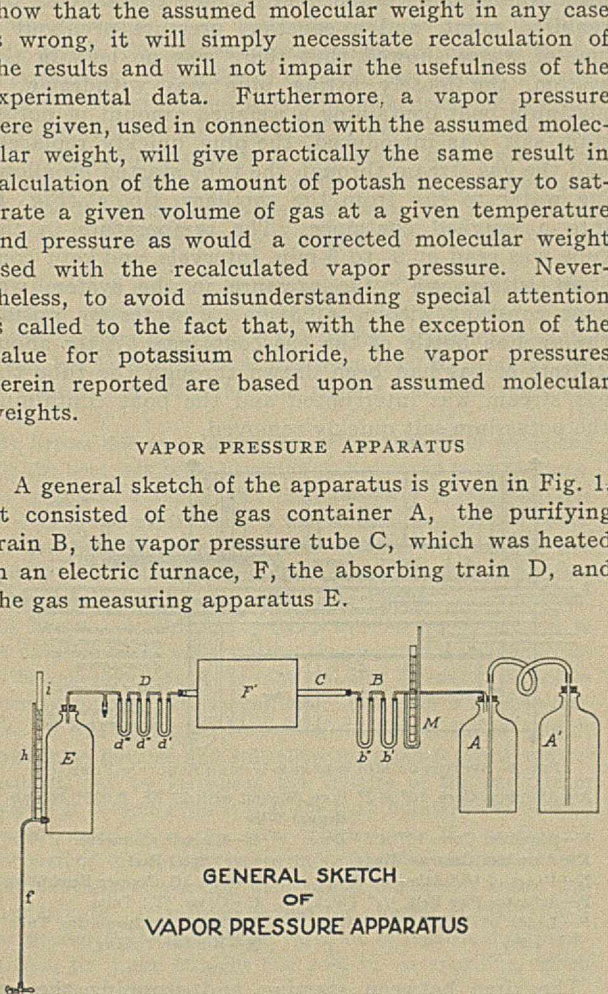

Fig. 1

The gas, nitrogen, which was to be passed through the vapor pressure tube was contained over water in a large bottle, A, which was connected by a syphon with another bottle, A′, containing a supply of water. This second bottle was suspended from a screw elevator so that the pressure of the gas in the apparatus could be kept constant within one centimeter of water pressure during the course of an experiment. A small manometer, M, filled with water showed the pressure in the apparatus.

After leaving the gas container and before entering the vapor pressure tube the gas was freed from any carbon dioxide which might be present by passing through the soda lime tube *b′*, and dried by passing through the calcium chloride tube *b″*, of the purifying train B.

After leaving the vapor pressure tube the gas passed through the absorbing train D, which consisted of three U-tubes filled as follows: *d′*, granular anhydrous calcium chloride; *d″*, soda lime in the first leg and bend and calcium chloride in the second leg; *d‴*, calcium chloride. The object of this purifying train was to prevent moisture from diffusing back into the vapor pressure tube and to absorb for weighing carbon dioxide set free by heating potassium carbonate in the determination of its vapor pressure.

The speed at which the gas was passed through the vapor pressure tube was regulated by the size of the capillary in the tip *g*, through which water was allowed to flow from the bottle E, and the volume of gas passed through the vapor pressure tube was determined by weighing the water displaced. By using a bottle with large cross-section and extending the outlet tube *f*, 2 liters of gas could be drawn into the measuring apparatus with a loss of only about 3 in. in a total head of 40 in. This is a change of 7.5 per cent, but experiments with different sizes of capillary tips showed an extreme variation of about 6 per cent in the speed of the water flowing during the first minute and during the last minute. The speed of the gas stream, therefore, varied during the course of an experiment not more than 3 per cent from the mean speed. The tube *h*, connected with the outlet tube, was open at the top and allowed the pressure in the measuring apparatus to be read upon the scale *i*. The rubber stopper of the bottle E had four holes and carried, besides the inlet tube shown in the figure, a tube by which water could be introduced and two thermometers, one to show the temperature of the gas and the other that of the water. In order to give as small variation as possible in the speed of the gas stream, before beginning an experiment a weighed quantity of water was run out and the level of the water brought below the shoulder of the bottle. The temperature of the gas at the beginning and end of the experiment was noted and correction made whenever necessary for the change of volume due to change of temperature.

A longitudinal section of the vapor pressure tube C is shown in Fig. 2. The tube was made of "Impervite" porcelain, 24 in. long and 1 in. bore, with walls about three-sixteenths inch thick. It was glazed on the outside and was found to be gastight at the temperatures employed. Into this tube was cemented with a grout of impervite body the fixed plug of impervite which was perforated with a one-sixteenth inch hole and had a recess for the Pt — Pt + Ir thermocouple as shown. The loosely fitting plug was also of impervite body, unglazed, and had embedded in it a piece of platinum wire by which it could be withdrawn from the tube. The diameter of this plug was about one-sixteenth inch less than the internal diam-

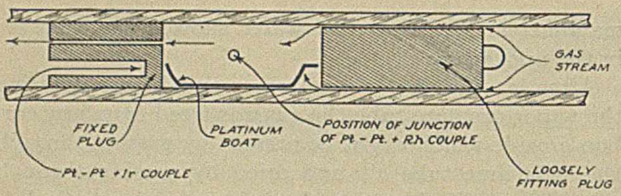

Fig. 2—Longitudinal Section of Central Portion of Vapor Pressure Tube

eter of the tube. Gas flowing through the vapor pressure tube was heated by passing through the space between the loosely fitting plug and the walls of the tube, and after passing over the substance contained in the platinum boat and taking up its load of vapor left the reaction chamber by the one-sixteenth inch hole in the fixed plug. The entrance end of the tube, which projected about 7 in. from the furnace, was closed by a rubber stopper carrying a glass tube through which the gas was introduced. The exit end of the vapor pressure tube, which projected from the furnace only about 1 in., was closed by a special stopper molded of a mixture of portland cement and asbestos. This was doubly perforated and carried an exit tube for the gas and a double-bored porcelain protecting tube for the platinum-iridium thermocouple. It was cemented into the tube by a mixture of sodium silicate and barium sulfate, and the joints were made gastight by coating with Bakelite varnish. At the higher temperatures the ends of the vapor pressure tube were cooled by strips of wet filter paper so that there was no decomposition of the rubber stopper or of the Bakelite varnish.

The vapor pressure tube was heated in a molybdenum-wound electric furnace, details of which are given in Fig. 3. The position of the tube in the furnace was such that the reaction chamber was in the central evenly heated portion of the furnace. Evidence that the reaction chamber was evenly heated is given by the fact that when the loosely fitting plug was withdrawn it was only after a few seconds that the outlines of the platinum boat became visible.

The temperature of the furnace was regulated by suitable resistances and was controlled by means of a platinum-iridium thermocouple connected with a Siemens and Halske millivoltmeter. The hot junction of the thermocouple was located in the recess in the fixed plug as shown in Figs. 2 and 3. The cold junction connections of the couple wires with the copper leads of the millivoltmeter were made in mercury, which was kept at a constant temperature by a water bath. The temperatures in the reaction chamber corresponding to readings on the millivoltmeter were determined at the beginning of each set of experiments by a platinum-rhodium couple and a Leeds and Northrup service potentiometer.

By substituting for the regular loosely fitting plug a perforated plug of the same size, the hot junction of the platinum-rhodium couple was supported over the empty platinum boat in the position indicated in Fig. 2. Gas was then run through the vapor pressure tube just as in a regular experiment. The cold junction connections of the platinum-rhodium couple with the leads of the service potentiometer were silver soldered and kept at 0° C. in a vacuum bottle packed with ice. The temperature was calculated from the electromotive force read on the potentiometer by Holman's formula,

$$e = mT^n,$$

using the values $m = 0.00275$ and $n = 1.18$, which were obtained for this particular thermocouple by calibration against the freezing points of zinc, antimony, and copper, by Mr. Roland P. Soule in the physics department of Columbia University. It is thought that these temperatures are correct within ±10° C., and the variation of the temperature during the course of an experiment was always well within these limits.

PROCEDURE

When the temperature in the tube, as shown by the platinum-iridium couple, had become constant at the required point, and a constant pressure of about 2 cm. of water showed that there was no leak in the system, the loosely fitting plug was withdrawn, a platinum boat containing a weighed amount of potassium salt was introduced, the plug quickly replaced, and the gas stream through the tube started by allowing water to run from the capillary tip *g* (Fig. 1) into a weighed container. The temperature in the tube was read at 3- to 5-min. intervals, and kept constant within ±5°; the pressure in the system was kept constant within ±0.5 cm. of water by raising the syphon bottle of the gas container. After about 2 liters of gas had been drawn through the tube the gas stream was interrupted and the boat containing the potassium salt quickly removed.

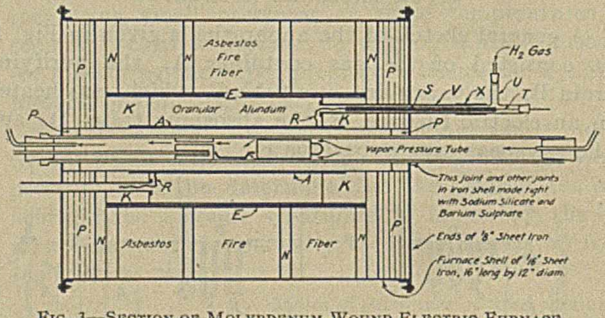

Fig. 3—Section of Molybdenum-Wound Electric Furnace

A—Alundum Core, 10" × 2" Bore, Wound with 27 Ft. 0.028" Molybdenum Wire
E—Alundum Core, 12" × 5" Bore
K—Alundum Cement Rings
N—Rings of 1/2" Asbestos Wood
P—Asbestos Fire Felt, 1/4" Thick
R—Leads of Molybdenum Wire, 4-Ply
S—Electric Connector of 5/16" Steel Rod
T—No. 10, Copper Feed Wire
U—Glass "T" Tube
V—Porcelain Insulating Tube
X—Rubber Tubing

The time between starting and stopping the gas stream was noted, as well as the temperature of the gas in the measuring apparatus and the pressure in the apparatus. The volume of gas at this temperature and pressure and saturated with water vapor was found by weighing the water displaced, its volume under standard conditions and dry was calculated, and from this the number of moles of gas passed through the vapor pressure tube was determined. The amount of potassium compound volatilized was found either by loss of weight or by analysis. All weighings were corrected to actual grams mass, and the total pressure, as read from the water manometer and a barometer, was reduced to millimeters of mercury at 0° C.

PROBABLE ERRORS

The sources and magnitudes of the errors in the vapor pressures of potassium chloride determined by this method may be classified as follows:

(1) Errors in measuring and controlling the temperature in the vapor pressure tube. It is believed that the temperature in the vapor pressure tube was determined correctly within ±10°, and that the variation of temperature during the course of an experiment was well within these limits. The maximum magnitude of these errors, therefore, varies from 9 per cent at 1044°, where a change of 10° in temperature makes a difference of 2.14 mm. in a total vapor pressure of 24.1 mm. of mercury, to 13 per cent at 801°, where a variation of 10° changes the vapor pressure 0.205 mm. in a total of 1.54 mm.

(2) Errors in determining the volume of gas passed through the vapor pressure tube. These errors may be due to (*a*) leaks in the system, (*b*) changes in temperature and pressure during the experiment, (*c*) inaccuracy in finding the amount of water displaced. The errors due to leaks in the system were carefully guarded against and are believed to be absent or at least negligible. Those due to changes in temperature of the gas in the measuring apparatus were always less than 0.5 per cent, and those due to changes in pressure not more than 0.2 per cent. The error in weighing the water displaced was 0.1 per cent, or less.

(3) Errors in determining the amount of potassium chloride volatilized varied from less than 0.2 per cent at 1044°, where the error was not more than 0.1 or 0.2 mg. in weighing and the amount lost by volatilization was from 110.0 to 131.3 mg., to 3 or 4 per cent at 801°, where the amount volatilized was 5.4 to 7.8 mg.

(4) Errors due to volatilization of the potassium compound while the boat was being placed in and removed from the tube. This error was never greater than the error in weighing, for whenever it was evident that a weighable amount of the potassium salt was being lost in this manner the amount was found by blank determinations and a correction applied. Hence this error is included in the errors in weighing.

(5) Excess volatilization of the potassium compound due to back diffusion of the vapor against the gas stream and condensation on cooler portions of the tube and plug in front of the vapor pressure chamber. The magnitude of this error is hard to estimate. It was kept small by having the loosely fitting plug fit as tightly as possible and still allow for rapid removal and replacement, and by increasing the velocity of the gas stream whenever it became evident that the back diffusion was causing material error. It is this error which limits the application of the method to vapor pressures under 25 or 30 mm., on account of the difficulty of working with gas-stream speeds above 200 cc. per minute. It is believed that the amount of this error is never greater than the extreme variation of a single determination from the mean straight line used in extrapolating, which is never over 5 per cent.

(6) Low volatilization due to partial saturation of the gas with potassium compounds volatilized from condensations in the tube during previous experiments. To avoid this error as far as possible, air was passed through the tube for some time between experiments. If allowed to accumulate, these condensations became a serious source of error, and when it became evident that they were seriously interfering, the tube was flushed out with air while heated at a temperature considerably higher than that at which the experiments were to be run, or else a new tube and new plugs were used. Owing to these precautions and the fact that this error is somewhat compensated for by the back diffusion mentioned in (5), it is thought that the magnitude of this error is never over 5 per cent.

(7) Errors due to uneven distribution of the vapor of the potassium compound in the gas stream over the boat. The direction and magnitude of these errors is difficult to estimate. Their presence was shown in some of the preliminary work on potassium chloride, where it was found impossible to get duplicates that checked using two different platinum boats, one of which happened to be deeper and narrower at the top than the other. The results using the narrow boat were invariably lower than those with the wider boat, due to the fact that a pocket of stagnant saturated gas was formed in the top of the narrow boat and hindered evaporation of the potassium compound. In the determinations reported, shallow wide boats were used and closely agreeing duplicates were obtained. It is believed that under these conditions the errors of this class are not serious.

(8) Errors due to reaction of the potassium chloride vapors with the impervite tube and plugs. Undoubtedly there was some reaction between the vapors and the material of which the tube and plugs were made, and this would tend to absorb the potassium chloride vapors and give high results. However, on account of the rapidity of the gas stream and the very small amount of vapor present in the gas, it is thought that the error due to this cause is entirely negligible.

(9) Errors in extrapolation. The partial pressures were plotted against the speeds of the gas stream on coördinate paper, and the straight line which agreed with the greatest number of points was extended to zero speed. To check the accuracy of this graphic method, the equations for the lines through pairs of mean results for different speeds were written and solved for the pressure (x) at zero speed ($y = 0$). The mean of the pressures thus found, which agreed very closely with the pressure found by the graphic method, was taken as the vapor pressure at the temperature in question. The extreme variation of the pressure values thus calculated from the mean value was about ±10 per cent, and it is believed that the vapor pressures here reported are reliable within these limits.

VAPOR PRESSURE OF POTASSIUM CHLORIDE

It has been shown by Nernst[7] that the vapor density of potassium chloride corresponds to the simple formula KCl. Hence in determining the vapor pressure of this compound the amount volatilized can be found directly by loss of weight. The salt used was from a 2-lb. bottle of J. T. Baker Chemical Company's C. P. Analyzed Potassium Chloride. According to the label it contained 0.001 per cent or less of each of the following impurities: iron, calcium oxide, magnesium oxide, and sulfuric anhydride, and also a trace of sodium. Qualitative tests for the above impurities showed that they were present only in extremely minute quantities. To expel moisture and avoid mechanical loss from decrepitation, the salt before being weighed for analysis or for use in a vapor pressure determination was fused in a weighed platinum boat. The total potassium present was determined both by the perchloric acid method, which separates any sodium which might be present, and by evaporating a weighed portion of the fused chloride with an excess of sulfuric acid in a platinum dish, igniting to constant weight and weighing as potassium sulfate. The results calculated as potassium chloride by the perchlorate method were 100.10 and 100.05 per cent, and by the sulfate method, 99.98 and 99.94 per cent. It is safe to conclude, therefore, that the fused salt is practically pure KCl. Analyses of the residues from the platinum boat after vapor pressure determinations showed that these also were pure potassium chloride. The potassium chloride left in the boat after Expts. 58 to 63, inclusive, weighed 0.2040 g., and yielded 0.2387 g. of potassium sulfate, which is equivalent to 0.2042 g. KCl; the residue from Expts. 67 to 71, weighing 0.5980 g., gave 0.6990 g. of K_2SO_4, equivalent to 0.5981 g. of KCl.

The results of the experiments with potassium chloride at three temperatures are given in Table II. In Fig. 4 these results are plotted, using the partial pressures of potassium chloride as abscissas and the speed of the gas stream in cubic centimeters per minute as ordinates. The values for the vapor pressures obtained by reading the partial pressures at zero speed are: 1.54 mm. at 801°, 8.33 mm. at 948°, and 24.1 mm. at 1044°.

TABLE II—VAPOR PRESSURE OF POTASSIUM CHLORIDE

Expt. No.	Cc. per Minute	Minutes	Nitrogen Millimoles	KCl Volatilized Grams	KCl Volatilized Millimoles	Partial Pressure Mm. Hg	° C.
46	78.2	23	80.3	0.0074	0.099	0.93	802
47	77.9	23	80.0	0.0078	0.105	0.99	801
50	100.1	18	80.5	0.0068	0.091	0.85	801
51	99.8	18	80.1	0.0065	0.087	0.82	803
53	108.8	16	77.7	0.0059	0.079	0.77	800
54	118.6	15	79.4	0.0054	0.072	0.69	800
55	118.7	15	79.5	0.0054	0.072	0.69	802
58	119.9	15	80.2	0.0337	0.452	4.24[1]	945
59	119.7	15	80.2	0.0338	0.453	4.25[1]	945
60	132.2	14	82.7	0.0318	0.426	3.88	948
61	132.9	13	77.1	0.0297	0.398	3.89	949
62	153.0	11	75.1	0.0244	0.327	3.28	948
63	153.5	11	75.4	0.0239	0.321	3.21	947
65	184.3	10	82.3	0.1146	1.54	13.9	1040
66	183.0	10	81.6	0.1110	1.49	13.6	1046
67	152.9	11	75.0	0.1162	1.56	15.5	1045
68	154.0	12	82.5	0.1268	1.70	15.3	1042
69	135.9	13	78.8	0.1313	1.76	16.6	1044
70	134.2	13	77.9	0.1285	1.72	16.4	1046

[1] In plotting the line to determine the vapor pressure, the values 4.36 and 4.37 corresponding to the temperature 948° were used.

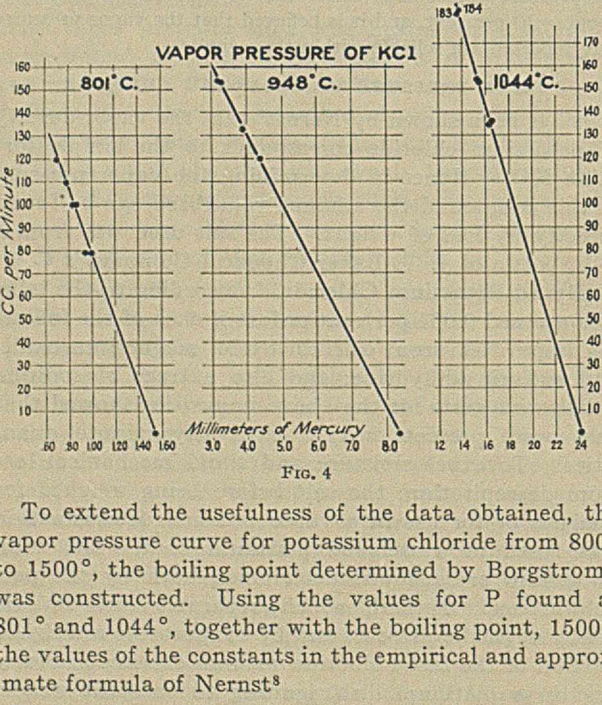

FIG. 4

To extend the usefulness of the data obtained, the vapor pressure curve for potassium chloride from 800° to 1500°, the boiling point determined by Borgstrom,[4] was constructed. Using the values for P found at 801° and 1044°, together with the boiling point, 1500°, the values of the constants in the empirical and approximate formula of Nernst[8]

$$\text{Log } P = \frac{\lambda_0}{4.571\,T} + 1.75 \log T - \frac{\epsilon}{4.571} T + C$$

were calculated. The simplified formula thus found for potassium chloride is:

$$\text{Log } P = \frac{-5326}{T} + 1.75 \log T + 0.000511\,T - 0.7064$$

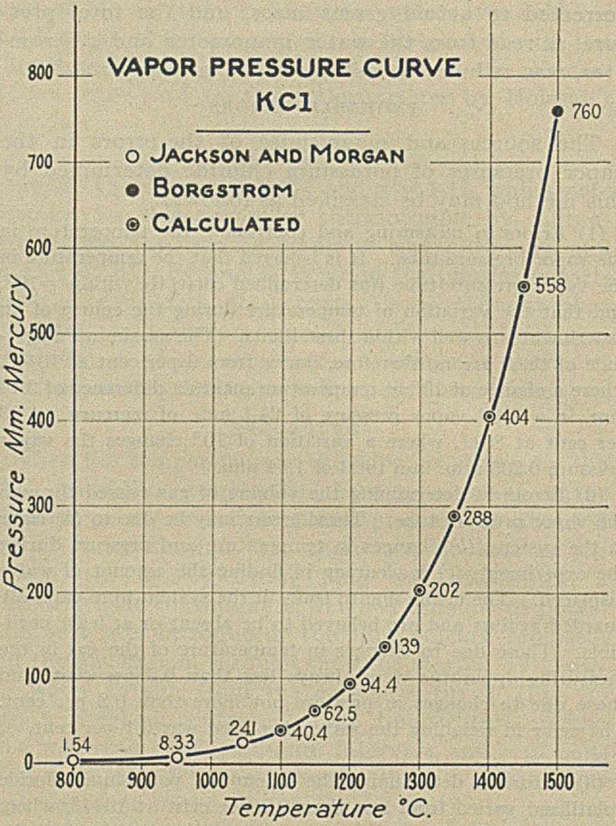

FIG. 5

TABLE III—VAPOR PRESSURES OF POTASSIUM CHLORIDE BETWEEN 800° AND 1500° C.

Temperature ° C.	Temperature ° Abs.	Pressure Calculated Mm. Hg	Pressure Observed Mm. Hg
801	1074	1.54	1.54
948	1221	9.06	8.33
1044	1319	24.1	24.1
1100	1373	40.4	..
1150	1423	62.5	..
1200	1473	94.4	..
1250	1523	139.0	..
1300	1573	202.0	..
1350	1623	288.0	..
1400	1673	404.0	..
1450	1723	558.0	..
1500	1773	760.0	760.0

The points on the vapor pressure curve calculated by this formula are given in Table III. The curve drawn through these points is shown in Fig. 5.

An approximate value for the latent heat of evaporation of potassium chloride can also be calculated from its vapor pressures by means of the van't Hoff equation written in the form:[9]

$$\text{Log } \frac{P_1}{RT_1} - \log \frac{P_2}{RT_2} = \frac{\lambda}{4.571}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The results of these calculations are given in Table IV.

TABLE IV—LATENT HEAT OF EVAPORATION OF POTASSIUM CHLORIDE CALCULATED FROM VAN'T HOFF'S EQUATION

Temperatures ° C.	Pressures Mm. Hg	Molecular Heat of Evaporation λ
801	1.54	
		—27,600
948	8.33	
		—32,800
1044	24.1	
		—32,000
1500	760.0	
MEAN VALUE	....	—30,800

VAPOR PRESSURE OF POTASSIUM CARBONATE

Potassium carbonate was the salt used in the first vapor pressure determinations made because it was thought that the conditions of volatilization of potash from potassium carbonate most nearly approach the condition of volatilization of potash from a cement mixture to which no special volatilizing or releasing reagent has been added. The salt used was a special grade of chemically pure potassium carbonate. When kept in a glass-stoppered bottle, which was nearly full and which was opened only as much as was necessary in removing the portions used, it did not seem to change in composition. The portions used for analysis or in the vapor pressure determinations were quickly transferred to a platinum boat and this at once placed in a glass-stoppered weighing bottle. The sample weighed in this manner gave on analysis by evaporating in platinum with an excess of sulfuric acid, heating over a Méker burner, and weighing as potassium sulfate, the following results:

	Per cent	
	K_2O	K_2CO_3
(*a*)	65.17	95.61
(*b*)	65.31	95.83
(*c*)	65.19	95.65
(*d*)	65.21	95.69
MEAN	65.22	95.70

The results by the perchlorate method which would separate any sodium present were:

	Per cent	
	K_2O	K_2CO_3
(*e*)	65.22	95.70
(*f*)	65.15	95.59
MEAN	65.19	95.65

The sample, therefore, is practically free from sodium, and qualitative tests showed it to be free from appreciable amounts of other impurities, except moisture and possibly bicarbonate. On account of the absence of nonvolatile impurities the amount of potassium oxide remaining after a vapor pressure determination was found by dissolving the residue from the platinum boat in a platinum dish, evaporating with an excess of sulfuric acid, and weighing the potassium sulfate formed.

After numerous unsuccessful attempts to obtain constant weight and constant composition by drying the salt at temperatures from 120° to 900° C., it was decided to use the sample as analyzed above. Attention is therefore called to the fact that the sample used contained about 4 per cent of moisture, and to the probability of the results as reported being slightly higher than the true vapor pressures of anhydrous potassium carbonate, due to the formation of a small amount of potassium hydroxide in heating the undried salt.

To calculate the partial pressure of the vapor of the potassium salt it is necessary to make an assumption regarding the molecular weight in the vapor state. In these experiments the amount of carbon dioxide absorbed by soda lime in the absorbing train agrees roughly with the amount of potassium oxide lost by volatilization. It seems probable, therefore, that potassium carbonate on volatilizing decomposes as follows:

$$K_2CO_3 \longrightarrow K_2O + CO_2$$

Hence the vapor pressures were calculated for K_2O, using the assumed molecular weight of 94.2. In the calculations the number of millimoles of carbon dioxide was included in the total number of millimoles whenever the amount of carbon dioxide evolved was sufficient to affect materially the final results.

The data and results of the experiments at two temperatures are given in Table V, and the plots of the results giving the vapor pressures at these temperatures are shown in Fig. 6. The vapor pressures thus obtained are: 1.68 mm. at 970° and 5.0 mm. at 1130° C.

TABLE V—VAPOR PRESSURE OF POTASSIUM OXIDE IN POTASSIUM CARBONATE

Expt. No.	Cc. per Min.	Minutes	Millimoles of			K_2O Lost		Partial Pressure of K_2O Mm. Hg	° C.
			N_2	CO_2	H_2O	Grams	Millimoles		
4	78	23	79.4	0.1	1.0	0.0068	0.072	0.68	970
5	79	22	76.8	0.1	0.9	0.0083	0.088	0.86	970
6	51	37	83.6	0.1	1.5	0.0109	0.116	1.03	970
7	51	36	81.6	0.1	1.1	0.0103	0.109	1.01	970
10	35	50	77.3	0.1	1.0	0.0119	0.126	1.21	970
11	35	50	77.7	0.1	0.7	0.0122	0.130	1.25	970
15	51	35	78.4	0.5	0.9	0.0390	0.414	3.9	1130
16	51	35	78.4	0.5	1.1	0.0471	0.500	4.7	1130
17	80	23	80.0	0.4	1.1	0.0311	0.330	3.1	1130
18	80	22	77.7	0.4	1.0	0.0309	0.328	3.1	1130
19	102	16	71.8	0.4	1.1	0.0243	0.258	2.7	1130

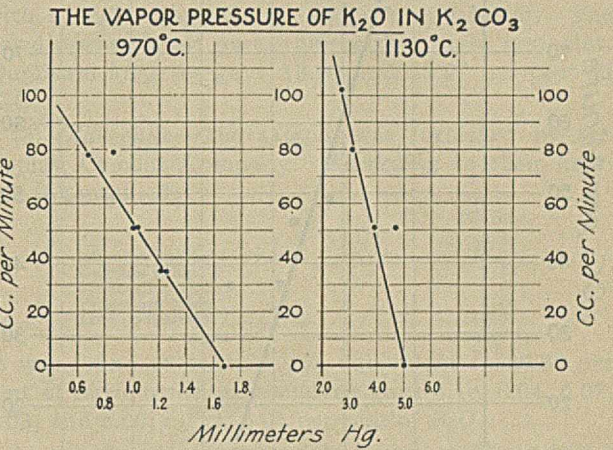

FIG. 6

VAPOR PRESSURE OF POTASSIUM SULFATE

On account of the impossibility of obtaining correct results in the determination of either the potassium or the sulfate radical in potassium sulfate by the ordinary methods of quantitative analysis, the salt used in these vapor pressure measurements was prepared by treating some of the same potassium chloride as was used in the vapor pressure determinations of that salt with pure sulfuric acid in a platinum dish, and heating the resulting potassium sulfate over a Méker burner to constant weight. Since this temperature was not high enough to melt the potassium sulfate, before using it in a determination it was melted in a platinum boat by being placed for 2 or 3 min. in the vapor pressure tube. It was found that no loss of weight resulted. An examination of the residue after a series of vapor pressure determinations by evaporating it in platinum with an excess of sulfuric acid and heating to constant weight showed that the residue also was pure potassium sulfate. Hence as there was no evidence of dissociation on heating and since the vapor density of potassium sulfate has never been determined, the assumption was made that the vapor corresponds to the formula K_2SO_4, molecular weight 174.4. The partial pressures of potassium sulfate were calculated on the basis of this assumption.

TABLE VI—VAPOR PRESSURE OF POTASSIUM SULFATE

Expt. No.	Cc. per Min.	Minutes	Millimoles N_2	K_2SO_4 Lost		Partial Pressure Mm. Hg	° C.
				Milligrams	Millimoles		
75	37	48	79.4	5.2	0.030	0.29	1129
76	37	48	79.6	6.7	0.038	0.36	1129
77	46	38	78.0	4.9	0.028	0.27	1127
78	65	27	78.5	3.5	0.020	0.19	1129
79	76	23	78.1	2.6	0.015	0.15	1127
80	76	23	77.5	2.5	0.014	0.14	1126
81	49	38	82.6	4.1	0.024	0.22	1131

The results of the experiments with potassium sulfate are given in Table VI, and the plot showing the vapor pressure is given in Fig. 7.

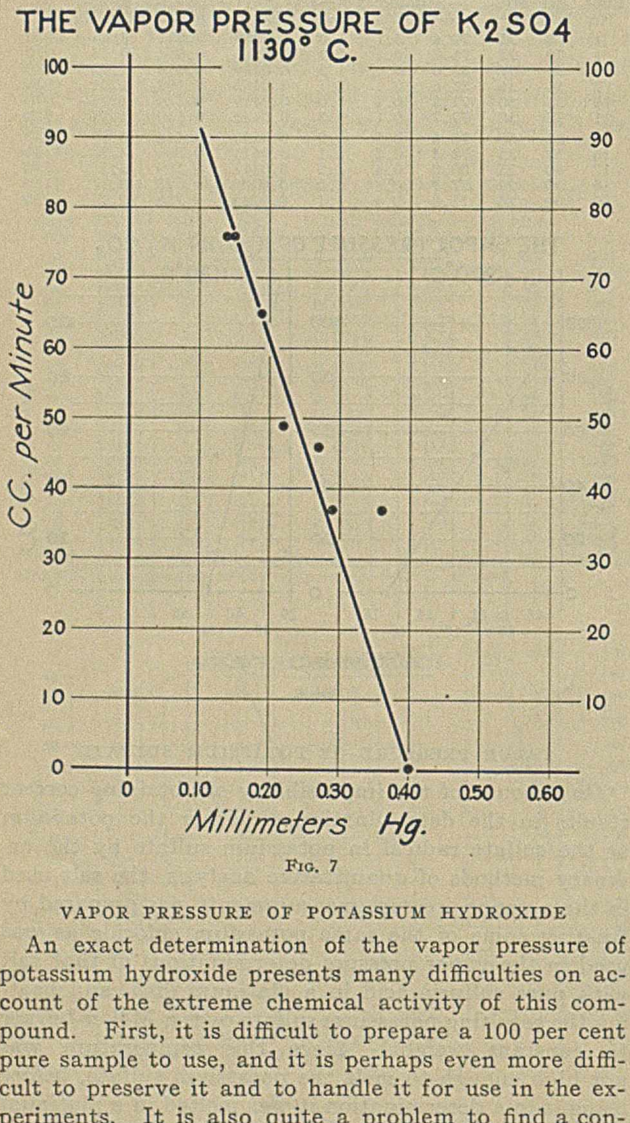

FIG. 7

VAPOR PRESSURE OF POTASSIUM HYDROXIDE

An exact determination of the vapor pressure of potassium hydroxide presents many difficulties on account of the extreme chemical activity of this compound. First, it is difficult to prepare a 100 per cent pure sample to use, and it is perhaps even more difficult to preserve it and to handle it for use in the experiments. It is also quite a problem to find a container made of material which is not attacked by the hot liquid, and of such shape that it will allow free evaporation and at the same time prevent loss of the liquid, which shows an unusual tendency to creep out of the container. Again there is undoubtedly some action between the vapors and the walls of the tube and ends of the plugs in the apparatus, and finally the composition and molecular weight of the vapor is not known. In view of the other uncertainties it did not seem to be worth while to spend a large amount of time preparing a special grade of pure hydroxide for the determinations, and it was thought that results which would give much light on the question of the commercial volatilization of potash could be obtained by use of a sample of chemically pure potassium hydroxide from a reliable dealer in chemicals. The material used, therefore, was from a newly opened bottle of chemically pure potassium hydroxide, purified by alcohol and cast into sticks. A stick of this material was rapidly crushed in a mortar into pieces weighing from 0.3 to 0.6 g., and these pieces were quickly placed in separate glass-stoppered weighing bottles and weighed as soon as possible. Some of the weighed pieces were used in the vapor pressure determinations and others were analyzed. The analyses by the perchloric acid method gave for the total potassium calculated as hydroxide: 84.67, 84.35, 84.80, 84.45, and 83.98, an average of 84.45 per cent for all of the determinations made. The main impurities, water and carbonic acid, should not materially interfere with the volatilization.

In solving the question of containers, both platinum and nickel were tried before silver was finally selected. In the final experiments a weighed piece of potassium hydroxide was contained in a boat of pure silver foil. This inner silver boat was placed in an outer boat also of silver foil, and slightly longer, wider, and shallower. The outer boat in turn was set into a larger nickel boat which served as a support in placing the charge in and removing it from the vapor pressure tube. The object of the outer silver boat was to catch the liquid potassium hydroxide which creeps over the sides of the inner silver boat and thus prevent its loss or its action on the nickel boat. This it did successfully, for in no case was there evidence that the liquid had reached the outside of the second silver boat. The upper edges of the nickel boat after an experiment were found slightly attacked, evidently by the vapors, which formed a little dark, greenish gray powder. The residue in the silver boats was almost colorless to light gray, effervesced only very slightly with water, and gave no odor of free chlorine when the water solution was made acid with hydrochloric acid. The silver of the two boats after removal of the residue with water and hydrochloric acid was bright and showed no evidence of having been attacked. The hydrochloric acid solution was perfectly clear, proving that no silver had gone into solution. This hydrochloric acid solution was evaporated with an excess of perchloric acid, and the total potassium weighed as potassium perchlorate and calculated to potassium hydroxide. The loss of potassium hydroxide by volatilization was then obtained by difference.

Since the formula and molecular weight of the vapors at the temperature of the experiments were not known, it was necessary to assume a molecular weight for the vapors in order to calculate the results as partial pressures. The statement of Roscoe and Schorlemmer,[10] evidently based upon the work of Deville, that the vapors of potassium hydroxide decompose at a white heat into potassium, hydrogen, and oxygen, needs qualifying, for this decomposition, according to Deville's own report,[11] takes place in the presence of incandescent iron. Moreover, according to Deville in the same report, the decomposition ceases if the temperature is lowered below a white heat. Further, according to Watts,[12] who does not give the authority for the statement, potassium hydroxide when heated alone does not decompose at any temperature. Since the temperature of the experiments here reported, 795° C., is far below a white heat, it is not probable that dissociation takes place to an appreciable extent. Hence it was most simple and seemed entirely justifiable to assume that the vapors given off were KOH with a molecular weight of 56.1.

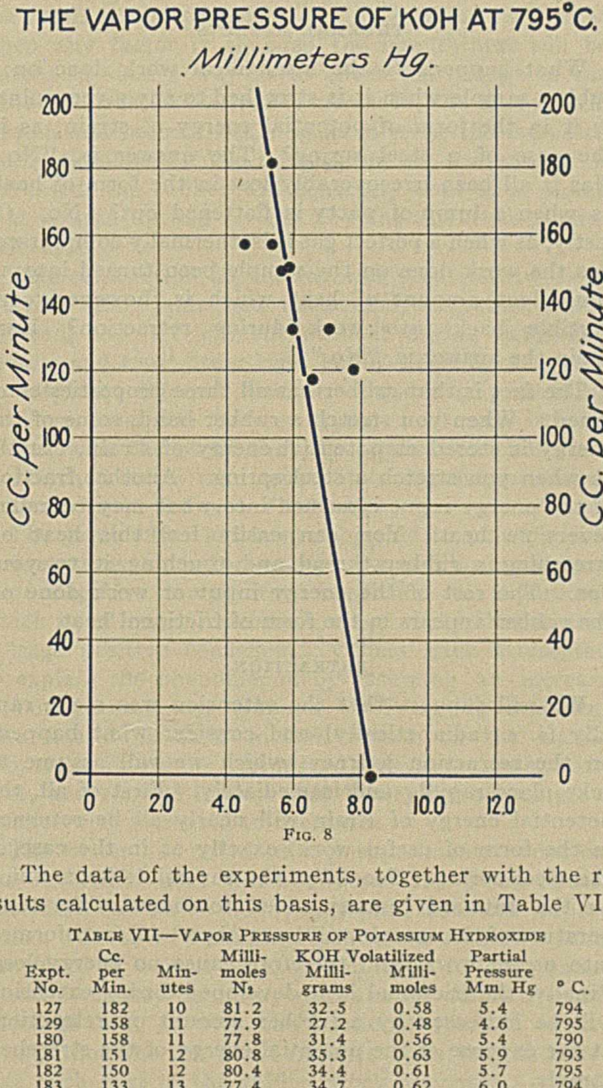

Fig. 8

The data of the experiments, together with the results calculated on this basis, are given in Table VII,

Table VII—Vapor Pressure of Potassium Hydroxide

Expt. No.	Cc. per Min.	Minutes	Millimoles N_2	KOH Volatilized Milligrams	KOH Volatilized Millimoles	Partial Pressure Mm. Hg	° C.
127	182	10	81.2	32.5	0.58	5.4	794
129	158	11	77.9	27.2	0.48	4.6	795
180	158	11	77.8	31.4	0.56	5.4	790
181	151	12	80.8	35.3	0.63	5.9	793
182	150	12	80.4	34.4	0.61	5.7	795
183	133	13	77.4	34.7	0.62	6.0	794
184	133	13	77.2	41.3	0.73	7.1	795
185	121	15	81.2	44.0	0.78	7.2	794
186	118	15	78.7	38.5	0.69	6.6	795

and these results are plotted and extrapolated in Fig. 8. On account of the possibility of variation in the composition of the pieces of the sample used in the different experiments, which variation probably explains the fact that three of the nine points are at slight variance with the mean straight line, a high degree of accuracy is not claimed for the vapor pressure found, namely, 8 mm. at 795° C. It is believed, however, that this result is not in error more than 25 per cent, and that the result plainly shows that the vapor pressure of potassium hydroxide at 800° C. is almost as large as that of potassium chloride at 950° C., and considerably larger than the vapor pressure of potassium oxide in potassium carbonate at 1130° C.

VAPOR PRESSURE OF POTASSIUM OXIDE IN NATURAL SILICATES

In the attempt to determine the vapor pressure of potassium oxide in natural silicates, three samples were used, each of which was ground in agate to pass a 200-mesh sieve.

(1) *Leucite*—This consisted of portions of two large tetragonal trisoctahedron crystals. The original crystals were about 0.75 in. in diameter, colored gray on the outside, and glassy, almost transparent, inside. The sample after grinding was pure white, and analyzed 19.05, 19.10, 18.97, and 19.04; mean, 19.04 per cent K_2O.

(2) *Feldspar*—This sample was part of a crystal of orthoclase, with angles of 90°, very light gray in color, with a slight tinge of red and a glassy luster. The powder was almost pure white with a slight gray tint. Duplicate analyses gave 13.90 and 13.97 per cent of K_2O.

(3) *Glauconite*—The sample was furnished by the Coplay Cement Company. According to their analysis it contained:

	Per cent
Silica	40.56
Alumina and ferric oxide	30.40
Calcium oxide	9.58
Magnesium oxide	2.09
Potassium oxide	6.06
Loss on ignition	10.52
	99.21

It was found to contain iron equivalent to 20.85 per cent of ferric oxide, and analysis gave 6.10, 6.04, 6.07, 6.03, and 6.00; mean, 6.05 per cent of K_2O.

In the experiments a weighed portion of about 0.5 g. was heated for 48 min. in a platinum boat in the vapor pressure tube, while dry nitrogen was passed through at a speed of 35 to 37 cc. per minute. Within the limit of accuracy of the analyses (about 0.0005 g. of K_2O in a 0.5 g. sample) there was no loss of potassium in any of the silicates at 1335° C. or lower. Hence the vapor pressure of potassium oxide in these three natural silicates when heated alone at temperatures under 1350° C. is entirely negligible.

The results of experiments with the three silicates, showing loss of weight and change of state at three temperatures, are given in Table VIII.

Table VIII—Results of Heating Potassium-Bearing Silicates for 48 to 50 Min.

Expt. No.	Temp. ° C.	Silicate Used	Loss of Weight Per cent	Loss of K_2O	Residue, Appearance, etc.
25	1130	Leucite	0.60	None	White, no sintering
28	1245	Leucite	0.73	None	White, trace of sintering
32	1335	Leucite	0.74	None	White, slightly sintered
24	1130	Feldspar	0.00	None	Pale gray, no sintering
27	1245	Feldspar	0.04	None	Pale gray, slightly sintered
31	1335	Feldspar	0.08	None	Nearly all fused to a colorless glass
23	1130	Glauconite	11.59	None	Reddish brown, sintered
29	1245	Glauconite	12.13	None	Dark red, fused
30	1335	Glauconite	12.47	None	Dark greenish glass

SUMMARY

I—The vapor pressure method of von Wartenberg has been adapted to the study of the vapor pressures of potassium compounds and the vapor pressures shown in the following table have been determined.

VAPOR PRESSURES OF POTASSIUM COMPOUNDS EXPRESSED IN MILLIMETERS OF MERCURY

Temp. ° C.	Hydroxide	Chloride	Oxide in Carbonate	Sulfate	Natural Silicates
795	8	...	..	...	..
801	..	1.54	..	...	..
948	..	8.33	..	...	..
970	..	...	1.68	...	..
1044	..	24.1	..	...	..
1130	..	...	5.0	0.4	0
1335	..	...	..	...	0

II—From the results of the vapor pressure measurements with potassium chloride at 801° and 1044° C., together with the boiling point of this compound as given by Borgstrom, the Nernst vapor pressure formula for potassium chloride has been calculated to be:

$$\text{Log } P = \frac{-5326}{T} + 1.75 \log T + 0.000511\,T - 0.7064$$

By means of this formula the vapor pressure curve for potassium chloride from 800° to 1500° C. has been constructed.

III—It has been established by these vapor pressure measurements that the order of volatility of those potassium compounds which are most important in the recovery of potash from cement or other silicate mixtures is as follows: Hydroxide, chloride, oxide from carbonate, sulfate, and natural silicates.

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RUBBER ENERGY[1]

By Wm. B. Wiegand

RUBBER SECTION, AMES HOLDEN McCREADY, LTD., MONTREAL, CANADA

It is proposed to discuss very briefly and nonmathematically some of the many interesting energy relationships of vulcanized rubber.

ENERGY STORAGE CAPACITY

In the accompanying table is shown what is known as the "proof resilience" of the chief structural materials. This is defined as the number of foot pounds of energy stored in each pound of the material when it is stretched to its elastic limit. You will observe that tempered spring steel has less than one one-hundredth the resilience of vulcanized rubber, and that even hickory wood, its nearest rival, also shows less than one per cent of the resilience of rubber.

This property of course is directly made use of in aëroplane shock absorbers, etc., but our present reference to it is made with a view to discussion, first, of the character of this stored energy and its transformation into thermal energy of two kinds; and, second, the modification and in fact remarkable increases in energy storage capacity made possible through the admixture of suitable compounding ingredients.

TABLE I—PROOF RESILIENCE

MATERIAL	FT. LBS. PER CU. IN.
Gray cast iron	0.373
Extra soft steel	3.07
Rail steel	14.1
Tempered spring steel	95.3
Structural nickel steel	14.7
Rolled aluminium	7.56
Phosphor bronze	4.08
Hickory wood	122.5
Rubber	14,600.00

THERMAL EFFECTS

What happens to the mechanical work done on a rubber sample when it is stretched to any given point? Is it in the form of potential energy of strain, as in the case of a steel spring? The answer is, "No." Has it all been irrecoverably lost in the form of heat, as when a lump of putty is flattened out? No. Or lastly, as when a perfect gas is isothermally compressed, has the work done on the sample been turned into an equivalent amount of heat which is, however, convertible back into work during retraction? Here again the answer is, "No."

The fact is that rubber has all three properties combined. When you stretch a rubber band, some of the energy is stored as potential energy of strain, exactly as when you stretch a steel spring. Another fraction of the energy input is turned into what may be called reversible heat. You can easily feel this heat on stretching a rubber thread and touching it to your lips. The rest of the energy input or work done on the rubber appears in the form of frictional heat.

RETRACTION

We will suppose that the extension was made rapidly (*i. e.*, adiabatically) and consider what happens on the retraction journey, which we will assume to take place rapidly and immediately. First of all, the potential energy of strain will nearly all be returned in the form of useful work, exactly as in the case of the steel spring. Secondly, the reversible heat which on the outward journey acted to increase the temperature of the sample will be re-absorbed, transformed into useful work, and therefore cause no energy loss. Finally, the frictional heat developed during extension will be increased by a further amount on retraction, at the expense of the potential energy of the stretched sample.

Thus, when the rubber has been stretched and allowed to return to substantially its original length, it will differ from its original state only by the total amount of frictional heat developed. By the law of conservation of energy, we can at once say that this frictional heat is exactly represented by the difference between the mechanical energy input and output of our system. This phenomenon is, of course, known as hysteresis, and is exhibited by all structural materials. The fact that in the case of rubber the energy storage capacity is several hundred times greater than in the case, say, of steel, explains why hysteresis phenomena become relatively of such cardinal importance to rubber technologists.

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[1] Presented before the Rubber Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

REVERSIBLE HEAT AND THE JOULE EFFECT

Suppose we extend a rubber sample and allow the reversible heat thus generated to disappear. In other words, we stretch it isothermally. We are then dealing with a system substantially in equilibrium. The two factors governing this equilibrium are, first, the load on the rubber, and, second, the thermal condition. Any change in the equilibrium requires a change in these two factors. Conversely, a change in either of these factors will shift the equilibrium. Now one of the fundamental properties of any equilibrium is that when any factor is changed the equilibrium will be shifted in such a way as to offset the change in the factor. Thus, if the load is increased, the sample will stretch and become stiffer so as to resist the increased load. Similarly, if the temperature of the sample is increased, the rubber will contract, since in so doing heat is used up and in this way the disturbance minimized.

This contraction on heating was predicted by Lord Kelvin, after Joule had discovered, or rather rediscovered, the development of heat during extension. Metals and most other rigid bodies behave, of course, in a totally different fashion. Instead of generating heat on extension they consume heat and become cooler, with the result that the application of heat to a stretched metal wire causes it to expand instead of contract, as in the case of rubber.

The Joule effect has been subjected to many misinterpretations, such, for example, as attributing it to a huge negative temperature coefficient of expansion, which is, of course, incorrect, since rubber has in fact a large positive coefficient. Others have attempted to explain the phenomenon by assuming an increase in Young's modulus. Bouasse, the French investigator, who has done such masterly work on the elastic properties of rubber, disproved this hypothesis, however, and showed in fact that Young's modulus grew smaller with increased temperature.

The writer has not done any experimental work on the reversible heat which governs the Joule effect, but there can be no doubt as to its technical importance. Thus, for example, the internal state of a solid tire tread as well as breaker conditions in large pneumatics is clearly bound up with the reversible thermal effect as well as with the frictional thermal effect. Every time the tire tread impacts upon the road surface each part of the rubber stock traverses a stress-strain cycle. Even if we admit that the reversible heat generated during extension is reabsorbed during contraction, we have to consider the gradual building up of internal temperatures due to accumulation of frictional heat. This increase in temperature, acting through the Joule effect, will lessen the extensibility of the heated rubber as compared with adjacent regions at lower temperatures, thus setting up strains which doubtless play a role in breaker separation, the bane of large-size pneumatics. It is therefore highly desirable to work out rubber compounds which will develop not only minimum frictional heat, but also minimum reversible heat. Quantitative measurements of the Joule effect with different compounds and different cures would serve as an index to this quantity.

MECHANICAL PICTURE OF RUBBER

The diagram in Fig. 1, which was first suggested by a former colleague, Dr. F. M. G. Johnson, of McGill, helps clarify one's mental picture of the thermodynamical phenomena associated with rubber strains.

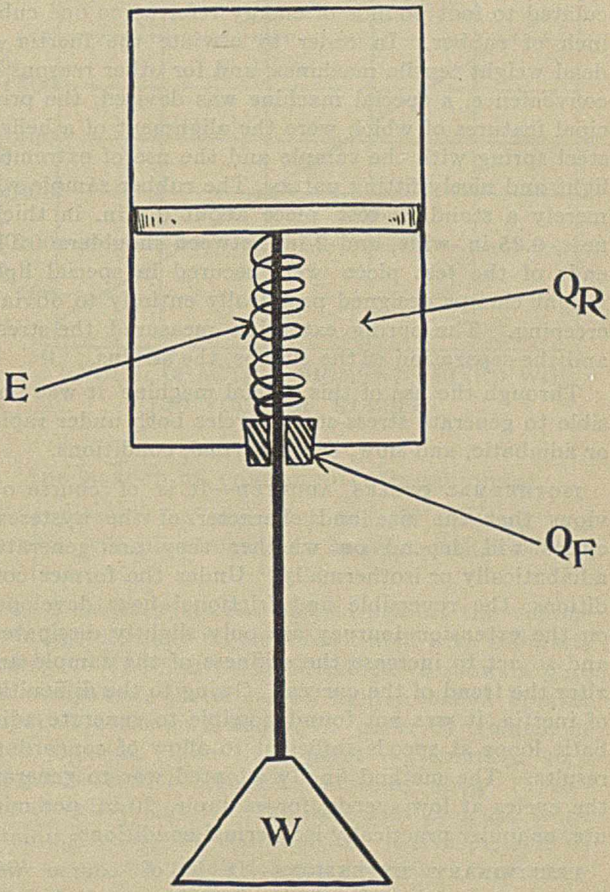

FIG. 1—MECHANICAL PICTURE OF RUBBER

Rubber may be viewed as a combination of a cylinder of gas, a steel spring, and a friction member. Following this picture, extension of the rubber is accompanied in the first instance by compression of the gas, thus generating the reversible heat, Q_R. In the second place, the steel spring is compressed, thus generating the increase in potential energy of strain, E. Lastly, the friction element operates through the extension, generating nonreversible heat, Q_F. When the rubber retracts, the gas expands, the spring retracts, and the friction element contributes another increment to the nonreversible heat.

Suppose now the sample is extended and we apply heat to the system. The gas in the chamber will expand so as to use up heat, raising the weight W, thus shortening the rubber and so constituting the Joule effect.

FRICTIONAL HEAT OR HYSTERESIS

Although the reversible heat has doubtless a decided technical significance, by far the most important energy transformation is that of useful work into heat through hysteresis, and a short account will now be given of some experiments carried out under the writer's direction by Mr. H. F. Schippel.

Briefly, the method consisted in generating hysteresis loops by graphically recording stress-strain curves of extension and retraction up to varying elongations. By means of the planimeter the area of the hysteresis loop was determined and the readings calculated to foot pounds of energy referred to one cubic inch of rubber. In order to obviate the inertia of dead weight tensile machines, and for other reasons of convenience, a special machine was devised, the principal features of which were the alignment of a helical steel spring with the sample and the use of extremely light and nicely fitting parts. The rubber sample was merely a standard test piece about 0.1 in. in thickness, 0.25 in. wide, and 2 in. between shoulders. The ends of the test piece were secured in special light weight clamps designed practically entirely to obviate creeping. The spring extension measured the stress, and the separation of the clamps, the strains.

Through the use of this special machine it was possible to generate stress-strain cycles both under rapid, or adiabatic, and slow, or isothermal, conditions.

ISOTHERMAL CYCLES ADOPTED—It is of course obvious that the size and character of the hysteresis cycles will depend on whether they are generated adiabatically or isothermally. Under the former conditions, the reversible and frictional heat developed on the extension journey are only slightly dissipated, and so act to increase the stiffness of the sample and alter the trend of the curves. Owing to the difficulties of inertia, it was not found possible to generate adiabatic loops at speeds sufficient to allow of concordant results. The method finally adopted was to generate the cycles at low speeds, for example, 20 in. per minute, or under practically isothermal conditions.

PRELIMINARY EXTENSIONS—It is of course well known that the area of the first hysteresis loop is greater than that of the second, and so on. In most cases, however, the third loop differs only very slightly from the succeeding loops, and so in our work when it was the intention to generate the hysteresis loop up to an elongation of 300 per cent, the test piece which had not been otherwise handled after cutting from the molded slab was put through two preliminary cycles up to 300 per cent, and then clamped into the machine, and its hysteresis loop graphically recorded. In taking a succession of loops at increasing elongations the same test piece was used and two preliminary loops made at each elongation. The initial length upon which the cycles were based was the length measured after the two preliminary extensions had been made.

RANGE OF COMPOUNDS USED—The experimental results included tests on a standard series of factory compounds used in tire construction. They thus included practically pure gum friction compounds, lightly loaded breaker compounds, and more heavily loaded tread stock. These various stocks were mixed in the factory under standard conditions, and given laboratory cures ranging from 50 per cent of the optimum cure in each case up to cures 275 per cent over the optimum in some cases.

Hysteresis loops were generated at elongations ranging from 100 to 500 per cent. There is considerable difference in opinion as to whether in measuring hysteresis one should work toward reaching a fixed percentage of the breaking load, irrespective of the elongation, or work to a definite elongation, irrespective of the load required. The latter method seems to the writer the only correct one from the technical standpoint, in view of the fact that the strains incurred, for example, by the skim coat, breaker, and tread of a pneumatic tire are arbitrarily fixed by the inflation pressure and the load.

RELATION BETWEEN HYSTERESIS LOSS AND CYCLIC ELONGATION—Fig. 2 illustrates the results obtained with a typical pure gum, high-grade tire friction with a breaking elongation of upwards of 900 per cent. This particular compound contained 5 lbs. of sulfur to 100 lbs. of rubber, of which 60 were first latex rubber and the other 40 a soft-cured wild rubber. The only other ingredients were a small percentage of thiocarbanilide and 5 lbs. of zinc as activator. The energy units are expressed as one-hundredths of a foot pound calculated to a cubic inch of rubber. The relationship is of the character of a rectangular hyperbola, and the hysteresis increases very sharply for elongations exceeding 300 per cent. Viewing hysteresis as frictional loss, it is natural to expect sharply increased friction to accompany the rapidly increasing lateral compressions in the test piece. Following our mechanical picture, it is analogous to contraction of the friction element upon the moving arm.

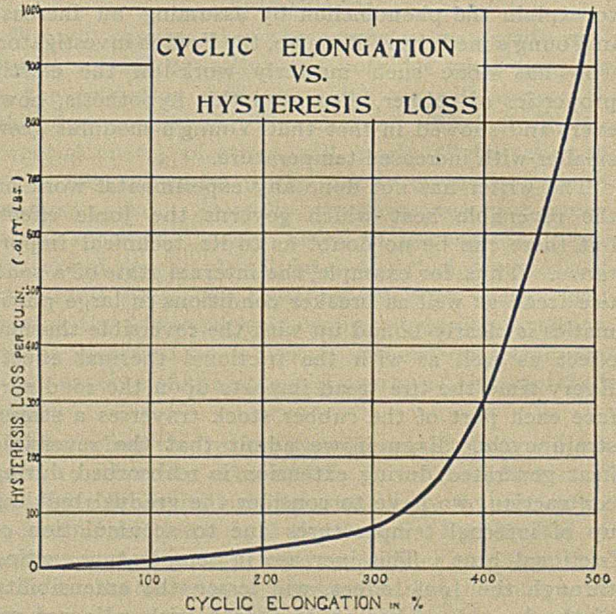

FIG. 2

ADOPTION OF STANDARD LOOP—For comparison of different compounds and for different cures it was decided to adopt a standard cyclic elongation, and in order to reduce experimental error it was of course desirable to select an elongation lower than 300 per cent, or lying on the flat portion of the curve. For

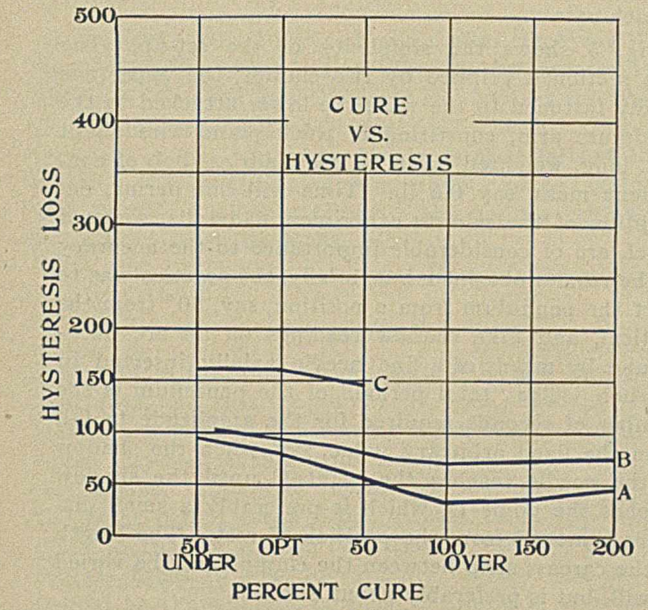

Fig. 3

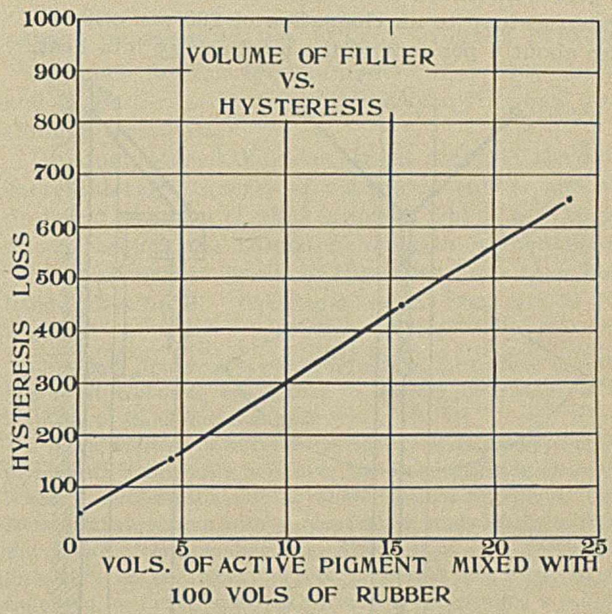

Fig. 4

higher elongations the energy loss changes so rapidly with slight changes in the elongation as to make concordant results difficult. Moreover, a brief calculation of the strains set up, for example, in the skim coat of a pneumatic casing run under service conditions shows that under conditions of standard factory practice the rubber is strained to an elongation of not much more than 200 per cent each time the tire flattens against the road. For comparative purposes we therefore adopted a standard cycle of 200 per cent elongation.

RELATION BETWEEN STATE OF CURE AND HYSTERESIS LOSS

It is commonly held by tire technologists that the state of cure of the friction and skim coat of the carcass has a lot to do with the early or late occurrence of ply separation.

Fig. 3 does in fact show that the state of cure has an influence on hysteresis. What is shown as the normal cure on this chart is the optimum cure as determined by the tensile product. An under-cure of 50 per cent, for example, means that if the optimum curing time is 90 min. at 40 lbs. of steam pressure, the sample was cured for 45 min. Similarly with over-cures. Curves A and B are typical skim coat compounds. Curve C is a breaker compound. It will be observed that minimum hysteresis occurs in the over-cured region. It must, of course, be kept in mind that these data apply only to cycles of 200 per cent elongation, whereas the rubber stock in question has an ultimate elongation of over 900 per cent. Attention must also be called to the danger of assuming that a slight over-cure is therefore desirable. Aging conditions must be taken into consideration, and the writer is of the personal opinion that the optimum cure or, in many cases, an even shorter cure is the correct condition. It is also noteworthy that the actual magnitude of the hysteresis values characteristic of high-grade, pure gum frictions is very low, and that we must look elsewhere for the true cause of ply separation.

THE EFFECT OF COMPOUNDING INGREDIENTS

This presents an enormous field of research, and reference will be confined to a brief outline of the basic facts.

Fig. 4 shows hysteresis plotted against the volume percentage of active pigment associated with 100 parts of rubber. The first point on the curve shows a pure gum compound, the second, a lightly loaded breaker compound containing about 4.5 parts by volume of active pigment. The third point represents a very high-grade tread compound containing about 15 volumes of active pigment: the last, another tread stock containing nearly 24 volumes. By active pigment is meant a pigment which definitely increases the energy storage capacity of the compound and includes pigments such as carbon black, lampblack, zinc oxide, the finer clays, etc. It will be noted that for the particular stocks used there is a linear relationship between the amount of hysteresis and the amount of such pigment present. It is also important to note that the effect of the addition of a highly dispersed phase upon hysteresis is much greater than moderate changes in the state of cure of a compound. It is unnecessary to emphasize the importance of this result from the standpoint of practical compounding.

Here again, however, one must use caution not to overlook the importance of heat conductivity, and it is entirely within the realm of possibility that a pigment, although markedly increasing the hysteresis and so also the frictional heat, may at the same time compensate for this by a greatly enhanced heat conductivity. Thus, for example, carbon black not only causes high frictional heats, but is also a bad conductor, whereas zinc oxide, although producing similarly high hysteresis values, has a very much better heat conductance.

It may be of some interest to indicate roughly the actual percentages of energy which are degraded into heat in these various types of rubber compounds. A pure gum friction or skim coat stock when led through a hysteresis loop to an elongation of 200 per cent degrades about 4 per cent of the total energy into heat.

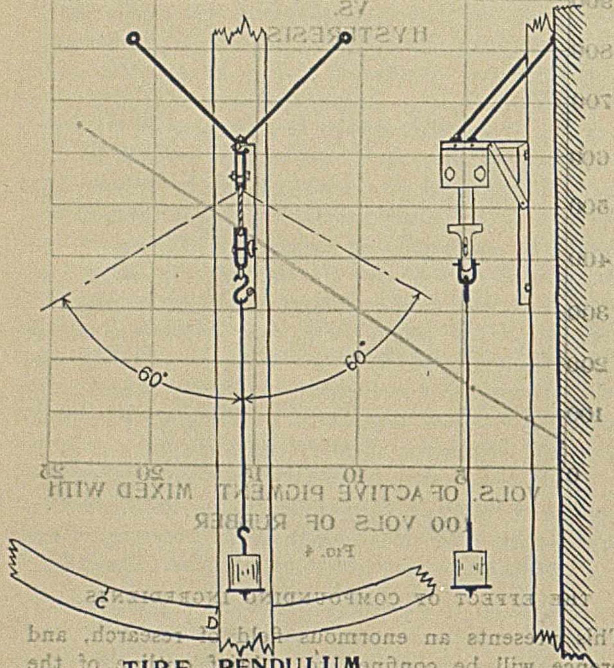

Fig. 5

A stock containing about 5 volumes of zinc oxide degrades about 8 per cent, whereas a tread stock containing, say, 20 volumes of zinc oxide degrades in the neighborhood of 14 per cent of the total energy input in each cycle.

FABRIC ENERGY LOSSES

We have dealt thus far with the degradation of energy into frictional losses in and by the rubber substance itself. These are of paramount importance in the case of solid tires, for example. However, in the case of pneumatic tires, which consist primarily of layers of fabric held together and waterproofed by rubber, we have to consider the extent to which frictional heat is developed by the carcass fabric itself. It is true that the hysteresis loss of an inflated casing taken as a whole can be accurately determined by the electric dynamometer. This, however, is an expensive machine, and has the further disadvantage of not being able to determine in what proportion the various constituent parts of the casing contribute to the integral result. The writer has therefore applied the principle of the damped pendulum to the study of casing energy losses. Briefly, the method consists in inserting a 1-in. carcass section in the arm of a pendulum which is allowed to swing from a fixed position until it comes to rest. The more perfectly resilient the carcass wall, the longer will such a pendulum swing. In order to analyze the elastic properties of the various structural components of the carcass, it is necessary merely to strip off the tread and breaker and repeat the series of vibrations with the carcass alone. In order to ascertain the effect of the number of plies of fabric the carcass is stripped down ply by ply and the total period of the pendulum redetermined in each case.

Fig. 5 shows the simplicity of the set-up. The inch section is gripped by two clamps, the upper one rigidly fastened to the wall, the lower attached to the pendulum arm, consisting of thick piano wire about 2 ft. long, weighted down by a cylindrical bob of convenient mass, say 0.5 lb. Time will not permit description of the minute experimental details, some of which are of considerable importance to the accuracy of the results obtained, but, briefly, the practice was to start the pendulum from a position, say, 60° from the vertical, and take shadow readings on an arc background by means of a fine needle axially inserted in the bob. The "total period" of the pendulum is the number of seconds required for the amplitude to fall from the fixed arbitrary value, say, when the shadow of the needle reaches the point C until the shadow reaches the point D, which is preferably a small distance removed from the position of rest. The length of the carcass strip between the clamps may be varied at will, but is preferably about 2 in.

SIGNIFICANCE OF TOTAL PERIOD—The total period, *viz.*, the time required for the pendulum to damp down from the position C to the position D is clearly a measure of the time required for the potential energy of the pendulum system to fall from that corresponding to the height of its center of gravity when the pointer is at C to that corresponding to D. It is therefore inversely proportional to the rate of generation of frictional heat through the various internal energy losses in the casing section. If the tire were of theoretically perfect resilience the pendulum would keep on swinging forever, except, of course, for external losses due to air resistance, etc.

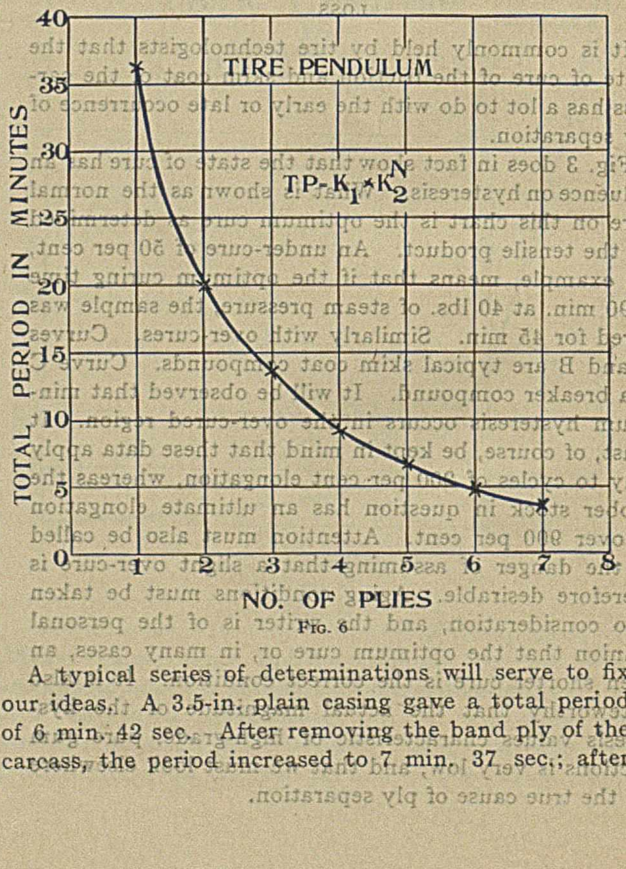

Fig. 6

A typical series of determinations will serve to fix our ideas. A 3.5-in. plain casing gave a total period of 6 min. 42 sec. After removing the band ply of the carcass, the period increased to 7 min. 37 sec.; after removing the second ply, to 8 min.; after removing the third ply, to 10 min. 55 sec. When all the carcass plies had been removed and the tread and breaker inserted, the pendulum swung for 21 min. 4 sec. As a matter of fact, it was found in many hundreds of tests that the total period of the pendulum when plotted against the number of plies of fabric in the carcass lay on a smooth curve, shown in Fig. 6.

This curve is of the exponential type, the equation of which is

$$TP = K_1 \times K_2^N,$$

where TP is the total period, K_1 and K_2 are empirical constants, and N is the number of plies of fabric. An interesting deduction from this curve is that the frictional losses in a casing are not a linear function of the number of plies of fabric. As a matter of fact, the total period for a 5-ply carcass bears the same ratio to that of a 4-ply carcass, as that of a 4-ply carcass bears to that for a 3-ply carcass. In other words, as the number of plies of fabric is increased the frictional heat increases not in arithmetic but in geometric progression. This constant ratio we have called the "ply factor," and its value in a typical square fabric casing lies very close to 0.7 for ranges of from 2 to 7 plies. If the total period for a 6-ply section is 100 min., that for a 7-ply section will be 70 min. If there were no fabric friction, this factor would of course become unity, except for the small losses due to the skim coat between the plies.

INFLUENCE OF GUM STOCKS ON CASING ENERGY LOSSES—It was at first thought that the condition of the skim coat and friction between the plies of fabric might profoundly influence the casing energy losses, and a series of tire sections was therefore prepared of various degrees of under- and over-cure. To our great surprise the effect of these exaggerated under- and over-cures upon the total period of swing was entirely negligible in every case.

EFFECT OF TREAD AND BREAKER—Our results, furthermore, showed that, for example, in the case of a 3.5-in. 4-ply casing, the total period of swing for the complete section was almost exactly the same as that for a 4-in. 5-ply casing, stripped of its tread and breaker. We thus see that the entire tread and breaker of a casing contribute no more to the energy losses than does a single ply of carcass fabric.

CORD CONSTRUCTION—These remarkable results made it at once desirable to ascertain the effect of cord construction, the advantages of which, from the standpoint of internal chafing, seemed obvious. Our experiments fully bore out this idea, and in fact we found that a 5-in. cord carcass swings almost exactly three times as long as a square fabric carcass of the same size. Cord fabric is therefore three times as efficient as a transmitter of energy as square fabric. Our purpose in thus briefly describing the pendulum method of investigation is not to expound the behavior of the various structural elements of a casing, but rather to illustrate the usefulness of a simple, convenient, cheap, and yet accurate physical apparatus in helping to solve the pressing problems of our industry.

EFFECT OF PIGMENTS ON ENERGY STORAGE CAPACITY

So much for the transformations of rubber energy and in particular its degradation into frictional heat through hysteresis.

Of equal interest, however, is the study of the total energy storage capacity of vulcanized rubber and the profound changes in this quantity which can be induced through the admixture of suitable ingredients. The experimental details of this work have been published elsewhere.[1] The fundamental facts are as follows:

1—A pure gum stock is totally unsuitable for some of the most important technical applications of rubber by reason of its inability to stand abrasive wear.

2—The addition in suitable amounts of certain compounding ingredients enormously improves the wear-resisting power of rubber. Our investigation as to the reasons underlying these facts naturally began with a quantitative study of the effect of the various compounding ingredients upon the mechanical properties of the stock. These properties are very largely expressed by the stress-strain curve, and on selecting a suitable basic mix and adding to it regularly spaced increments by volume of the most important inorganic compounding ingredients, it was at once discovered that profound changes in the character of the stress-strain curve were thereby induced. These changes may be divided into two classes.

One class comprises merely a *foreshortening of the curve.* Thus, for example, the addition to the basic mixing of increasing percentages by volume of barytes produces a stock which, when gradually stressed to the failure point, preserves the same values of elongation and load as in the case of the pure mixing. The only difference is that failure occurs earlier. In other words, this pigment simply dilutes or attenuates the mechanical properties of the mixing. It plays a passive rôle.

In the other class the stress-strain relationships are profoundly altered. Thus, for example, if glue or zinc oxide or one of the blacks be added to the basic mix in increasing amount, the mechanical properties of the resultant vulcanisate show the following changes:

First, the curvature of the stress-strain curve is diminished and at suitable pigment concentrations actually disappears. That is to say, rubber can be so compounded as to display the same kind of stress-strain relationship as in the case of steel and the other rigid structural materials, *i. e.*, Hooke's law obtains. Again, certain of these same pigments, if not added in excessive amounts, produce compounds, the tensile strength of which at rupture remains undiminished or even increased over large compounding ranges. In these cases the final elongation is, however, markedly reduced. In the other cases, although linear stress-strain relationships are induced, both tensile strength and elongation fall off more or less equally.

It has been thought justifiable in view of these striking differences in behavior to call pigments of the second class active pigments and those of the former class inert pigments.

In Table II are brought together, along with the energy storage capacities which are here designated the total energy of resilience, the dispersoid characteristics of the pigments in question, and also the increase in total volume of the compounded rubber when stressed to 200 per cent elongation. These volume increases, for the details of which you are referred to a recent paper[2] by my colleague, Mr. Schippel, prove

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[1] *Can. Chem. J.*, **4** (1920), 160; see also abstract in *India Rubber World*, **63** (1920), 18. Both references give curves illustrating the effect of various pigments on the energy storage capacity of the rubber.

[2] THIS JOURNAL, **12** (1920), 33.

TABLE II

PIGMENT	Apparent Surface	Displacement of S. S. Curve	Total Energy of Resilience	Volume Increase at 200% El.
Carbon black...	1,905,000	42	640	1.46
Lampblack	1,524,000	41	480	1.76
China clay.....	304,800	38	405	...
Red oxide......	152,400	29	355	1.9
Zinc oxide......	152,400	25	530	0.8
Glue...........	152,400	23	344	..
Lithopone......	101,600	..	...	...
Whiting........	60,390	17	410	4.6
Fossil flour.....	50,800	14	365	3.5
Barytes........	30,480	8	360	13.3
			Base 450	

beyond any doubt that particularly in the case of the inert pigments the application of stress causes a partial separation of the pigment from the rubber with resultant development of vacua at the poles. In the active pigments, those which show a positive effect upon the energy storage capacity, this separation from the rubber matrix is very slight. Column 2, which gives the sq. in. of surface per cu. in. of pigment, indicates that the extraordinary differences in behavior are without doubt attributable to differences in surface energy. When a stock containing one of the active pigments is stressed to rupture, the energy required to do so goes partly towards distorting the rubber phase and partly towards tearing apart the rubber from the pigment particle.

Again, the fact that in the case of the active pigments the rubber remains more nearly adhesive to each particle means more uniform stress on the rubber phase, and so enhanced tensile properties and energy capacity.

Surface energy has, of course, two factors. The capacity factor is represented by the specific surface, and it is the variations in this factor which appear to predominate in the behavior of the various pigments. The other factor, the intensity factor, which is represented by the interfacial surface tension, is also doubtless of importance, as is shown by the fact that zinc oxide occupies a somewhat anomalous position in the energy column. It is, namely, a more active pigment than would be indicated by its developed surface. Briefly, any pigment of a degree of subdivision corresponding to a surface development of over 150,000 sq. in. per cu. in. may be expected to belong to the active class. It must of course be remembered that the activity of a pigment depends entirely upon the percentage present in the mixing. Maximum activity is developed for volume percentages lying between 5 and 25. Inert pigments of course develop no activity no matter how much or how little is added.

THE STRUCTURE OF COMPOUNDED RUBBER

In view of the important role played by surface energy in the properties of compounded rubber, and also in view of the recently demonstrated fact of the physical separation of the constituent particles from their rubber matrix under conditions of strain, it is clearly of importance that we should know something about the spacial distribution of the component particles of a mixing. Thus, for example, how much barytes may one add to a compound before the particles actually touch each other? How far apart are the particles of zinc oxide in a tread compound containing, say, 20 volumes of this pigment?

These interparticle distances are of theoretical importance, not only for the proper calculation of the forces acting upon the rubber phase occupying the interstices, but also in connection with the influence, if any, of electrostatic charges upon the pigment particles during mixing.

Let us first assume that sufficient pigment has been added to cause actual contact between the particles. Now it is not at all a simple matter to calculate what percentage must be added to bring about this condition. The question involves a study of the theory of piling. Thus, for example, if we fill a quart measure with marbles, the number we can get into the measure depends upon the character of the piling which they assume. If, after laying in the first layer we place succeeding layers in such a way that each marble lies vertically over and touching the one beneath, we obtain what is known as cubical or loose piling. If, however, we shake the marbles down until they lie together as closely as possible, the piling assumes a totally different character, known as normal, close, or tetrahedral piling.

This question of cubical or tetrahedral piling is important in all studies of granular bodies. Thus, for example, the rigidity of mortar under the trowel, or the firmness under the foot of the wet sand on the seashore are both due to the fact that the granules are in a condition of close or normal piling, the disturbance of which by an external force requires an increase in the over-all volume, which in turn is resisted by the vacua which tend to be formed.

If a test tube be loosely filled with sand and subsequently gently tapped, the sand will settle down a considerable distance in the tube. The sand was originally more or less loosely piled. It was certainly not piled in the most loose manner possible, namely, cubically, but occupied some intermediate position. On gently tapping the tube the particles are freed, and, attracted downward by the force of gravity, assume a spacial arrangement more nearly normal or tetrahedral.

THE PILING OF COMPOUNDING INGREDIENTS—We have now to consider what happens when a pigment is worked into the rubber in a plastic state on our mix mills. Owing to the high viscosity of the gum the force of gravity is not free to act as it did in the case of the sand in the test tube or the marbles in the quart measure. Taking first a case where so much pigment is added that the particles are compelled to touch each other, it is possible to calculate the amount of pigment required on the assumption, first, that the particles are arranged cubically or loosely, and, second, tetrahedrally or closely.

On the former assumption, irrespective of the size of the particles (which are, however, assumed to be uniformly spherical), the amount required would be 52.4 per cent of the total by volume. On the second assumption, the figure comes out at 74.1 per cent.

Now it is a well-known fact in mill practice that a compound containing 50 per cent by volume of pigment is almost unmanageable on the mill. We therefore deduce that with the customary amount of milling the pigment particles probably exist in a condition more closely approximating the loose or cubical piling than the close or tetrahedral piling. The writer has, however, observed that in working with extremely heavily loaded stocks it is possible, by continued milling, to bring about a more or less sharply defined increase in plasticity with the possibility of working in an additional amount of pigment. With due regard to the breaking down of the rubber owing to this excessive milling, it still remains highly probable that the additional mastication has caused a more even distribution of the rubber phase throughout the mass, which is equivalent to saying that the particles have been rearranged to more nearly normal piling. The writer has in fact succeeded in milling in over 60 per cent by volume of pigment in this way (*i. e.*, 60 volumes pigment to 40 volumes rubber).

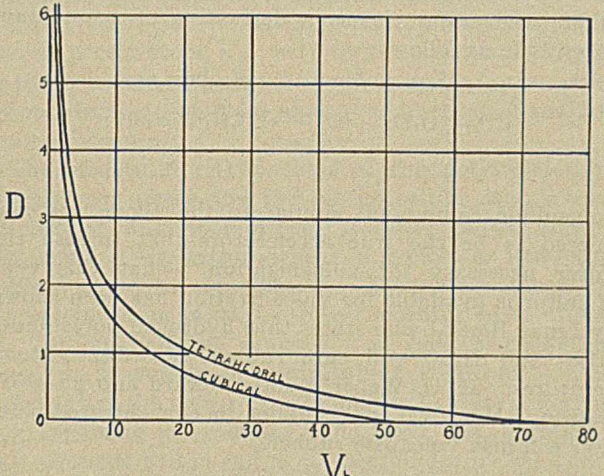

FIG. 7—INTERPARTICLE DISTANCE *vs.* VOLUME PER CENT PIGMENT

SPACIAL ARRANGEMENT WHEN NOT IN CONTACT—Fig. 7 shows interparticle distances for percentages of pigment ranging all the way from 0 to 80 per cent. The ordinate D shows the distance between the particles referred to their radius as unity. The upper curve shows conditions when the particles are tetrahedrally disposed. Under working conditions in the factory very few compounds contain more than 35 per cent by volume of pigment. Taking, for example, a typical tire tread compound containing, say, 20 per cent of pigment by volume and assuming tetrahedral arrangements, the particles will be distant from each other by a little over their own radius. Assuming cubical arrangement they would be closer together, namely, distant by about three-quarters of their radius. This of course presupposes spherical shape. In actual practice, the pigment particles are by no means spherical, but on the average they are more nearly spherical than of any other definite geometrical shape, and the error due to assuming sphericity will not be large.

The question as to whether in such cases where the particles are not in actual contact one ought to assume a tetrahedral or a cubical space arrangement is (at least to the writer) very difficult to answer by mathematical analysis. It should be quite possible, however, to reach an approximate solution by numerous direct microscopic measurements on thin sections by transmitted light, and we hope to secure results of this kind in the near future. In any case, the values shown on this chart represent the extremes between which the true values must lie, and we are of the opinion, as intimated above, that the action during milling is that the rubber phase will tend to become as evenly distributed as possible, and that therefore the tetrahedral arrangement is the more nearly in accordance with actual conditions.

The writer fully realizes that the foregoing analysis hardly even scratches the surface of the problem of the structure of compounded rubber. Of cardinal importance are, for example, the direct measurement of the surface tension between zinc oxide and rubber, carbon blacks made under different conditions and rubber, and so on. When these values are once determined the capacity factor of the surface energy as measured by the average degree of dispersion of any given pigment can in our opinion be most accurately measured by its admixture under standard conditions in a rubber compound, and the determination of the decrease or increase in energy storage capacity as compared with other samples of the same pigment. This would seem to be of particular value in the case of the finer pigments, such as the blacks, the individual particles of which are beyond the resolving power of our microscopes.

Reverting to the title, "Rubber Energy," we see that along with its already distracting array of properties chemical, rubber provides the thermodynamician with plenty of nuts to crack. The interrelationships of its thermal, mechanical, and surface energies make up a field of research which has lain fallow long enough and which should be zealously cultivated.

REACTIONS OF ACCELERATORS DURING VULCANIZATION. II—A THEORY OF ACCELERATORS BASED ON THE FORMATION OF POLYSULFIDES DURING VULCANIZATION[1]

By Winfield Scott and C. W. Bedford

GOODYEAR TIRE AND RUBBER CO., AKRON, OHIO, AND QUAKER CITY RUBBER CO., PHILADELPHIA, PA.

The investigation of organic accelerators, as shown by the literature of the past five or six years, appears to be confined largely to a search for new compounds or a combination of compounds to catalyze the addition of sulfur to rubber. It has been shown that these accelerators are almost entirely organic nitrogen compounds, and as a result nearly all classes of nitrogen-containing substances have been tried. Furthermore, it has been shown that the nitrogen of such compounds is basic or becomes basic during vulcanization by the action of heat, sulfur, or hydrogen sulfide.

It has been previously proposed that a sulfur reaction of the accelerator is necessary, and certain reaction products in some way make sulfur available for vulcanization. In some cases a sulfur reaction is doubtless necessary to form the true accelerator, which is a polysulfide.

Ostromuislenski[2] attributes the activation of sulfur by aliphatic amines to the formation of thiozonides of the type R-NH-S-S-S-NHR, which readily

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[1] Presented before the Rubber Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Chem. Abs.*, **10** (1916), 1944.

give up their sulfur to the rubber. The formation of thiozonides is illustrated by the following equation:

$$2R\text{-}NH_2 + 4S \longrightarrow R\text{-}NH\text{-}S\text{-}S\text{-}S\text{-}NH\text{-}R + H_2S$$

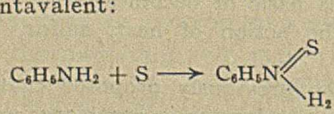
By this scheme, the true accelerator is produced together with hydrogen sulfide by the reaction of the amine and sulfur. Such an explanation necessarily excludes the tertiary amines, since they have no hydrogen attached to the nitrogen, and it is also limited to those amines that react with sulfur at curing temperatures. In the formation of thiozonides, hydrogen sulfide is a by-product and does not function directly in producing a true accelerator.

André Dubosc[1] states that a part of the curing action of accelerators is due to the polymerizing effect of thiocyanic acid produced by a sulfur reaction on the accelerator. He illustrates these reactions by means of equations, but makes no statement that such reaction products were determined experimentally. As an example of these reactions, it is stated that aniline reacts with sulfur at 140°, in this manner:

$$C_6H_5NH_2 + 4S \longrightarrow HCNS + 2HC{\equiv}CH + CS_2 + H_2S$$

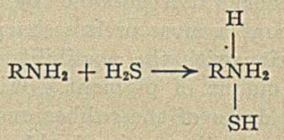
The writers have been unable to duplicate these results, and no reference to any such reaction could be found in the literature on the subject. Dubosc attributes the activation of sulfur entirely to the reaction between hydrogen sulfide and sulfur dioxide. It is known that vulcanization takes place if these two gases are allowed to react in the presence of rubber. Since the publication of the above-mentioned article by Dubosc, a patent[2] has been granted to S. J. Peachey, covering the process. While there are accelerators, such as *p*-nitrosodimethylaniline, which generate both hydrogen sulfide and sulfur dioxide during the cure, certainly the great majority of accelerators do not activate sulfur in this way, since they function in rubber stocks that are practically oxygen-free.

The latest theory for the action of accelerators during vulcanization is that of Kratz, Flower and Coolidge.[3] These writers attribute the accelerating action of amines, such as aniline, to the formation of an unstable addition product of aniline and sulfur, in which the sulfur is temporarily attached to the nitrogen, making it pentavalent:

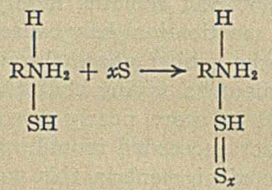


The compound thus formed gives up its sulfur to the rubber and is then regenerated by a further reaction with sulfur.

The writers believe that the mechanism of the action of amines is represented differently from that given by the above investigators, and that hydrogen sulfide is one of the important factors in acceleration. It is believed that, in general, amines catalyze the addition of sulfur to rubber in the following manner:



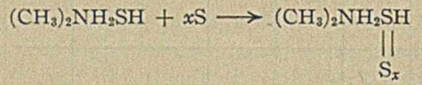
$$RNH_2 + H_2S \longrightarrow \overset{H}{\underset{SH}{RNH_2}}$$



$$\overset{H}{\underset{SH}{RNH_2}} + xS \longrightarrow \overset{H}{\underset{\underset{S_x}{SH}}{RNH_2}}$$

As a specific example, dimethylamine, with hydrogen sulfide and sulfur, forms a derivative of ammonium polysulfide as follows:

$$(CH_3)_2NH + H_2S \longrightarrow (CH_3)_2NH_2SH$$



$$(CH_3)_2NH_2SH + xS \longrightarrow (CH_3)_2NH_2\underset{S_x}{SH}$$

Polysulfide compounds similar to the above are considered to be the true accelerators that furnish the sulfur necessary for vulcanization. That this type of sulfur is available for vulcanization has been shown by Ignaz Block,[1] who states that hydrogen polysulfides (H_2S_2 and H_2S_3) will cure rubber at ordinary temperatures. C. O. Weber[2] quotes Gerard and his work showing that alkali polysulfides in concentrated solution will also vulcanize rubber.

ORGANIC ACCELERATORS

All organic accelerators do not function in the same manner as the bases, and for this reason the writers choose to divide accelerators into two classes.

I. *Hydrogen Sulfide Polysulfide Accelerators*—In this class belong those bases which form polysulfides similar to yellow ammonium sulfide.

II. *Carbo-sulfhydryl Polysulfide Accelerators*—This includes all accelerators that contain the grouping $\equiv$C-SH, such as the thioureas, dithiocarbamates, thiurams, mercaptans or the disulfides which may be formed from them by oxidation or by reaction with sulfur.[3]

To the first class belong all basic organic accelerators or such compounds as produce basic accelerators under curing conditions. Certain inorganic accelerators may also be included. These will be discussed later in the paper.

The second class also includes certain of the Schiff bases[4] which form thiourea derivatives by a sulfur reaction during the cure. Further discussion of this class will be reserved for a later paper.[5]

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[1] *India Rubber World*, **39** (1919), 5.

[2] Brit. Patent 129,826.

[3] THIS JOURNAL, **12** (1920), 317.

[1] D. R. P. 219,525.

[2] "Chemistry of India Rubber," p. 47.

[3] Although the term polysulfide is applied to each class of accelerators, it should be noted that they are distinct types. In Class I, the polysulfide sulfur is related to a sulfhydryl group attached to *nitrogen*, while in Class II the polysulfide sulfur is held by a sulfhydryl group attached to *carbon*. In the so-called disulfides and their higher sulfides, the hydrogen of the sulfhydryl group is considered as having been eliminated in hydrogen sulfide.

[4] Bedford and Scott, THIS JOURNAL, **12** (1920), 31.

[5] The reaction of carbon disulfide on amines to form thioureas and hydrogen sulfide is reversible, and it is entirely possible that by the action of hydrogen sulfide during vulcanization the thioureas are changed to the more powerful dithiocarbamates which are intermediate to the complete transformation to amine and carbon disulfide. It is also possible that the thioureas may form polythio compounds direct, through the carbo-sulfhydryl group.

The phenylated guanidines belong to both classes, since at curing temperatures they easily react with hydrogen sulfide to form thioureas and free amines. Diphenylguanidine, for example, gives thiocarbanilide and ammonia.

The difference in behavior of the two above-mentioned classes of accelerators was well illustrated by the following experiment: A rubber cement containing rubber, sulfur, and zinc oxide was divided into two portions. To the first portion was added piperidyl ammonium polysulfide; there was no apparent change after standing for 2 mo. To the second portion was added an amount of piperidine equivalent to that which was used in the first sample, and a small amount of carbon disulfide was stirred into the mixture. This cement jelled in less than 24 hrs., showing the well-known higher curing power of the dithiocarbamates as compared with basic amines and imines.

The present paper will deal with the first-mentioned class of accelerators, *i. e.*, with those accelerators which, in the presence of hydrogen sulfide under curing conditions, form polysulfides analogous to those of sodium and ammonium.

The structural relationships of the polysulfides of the nitrogen bases and the more positive metals are not clearly understood at present, although it is known that some of the sulfur is held in a more or less loose form of chemical combination. This is evidenced by the precipitation of sulfur from concentrated solutions on dilution, and the generation of heat when sulfur dissolves in sulfide or hydrosulfide solutions. It is certain that the sulfur of polysulfides is quite different from rhombic or α-sulfur, and that the aggregate S_8 is changed to the sulfur of polysulfides by the combined action of hydrogen sulfide and basic accelerators.

It is a well-known fact that sulfur will react with rubber resins and proteins at temperatures near 140° with the formation of hydrogen sulfide. This hydrogen sulfide in the presence of basic accelerators forms hydrosulfides which in turn take up sulfur to form polysulfides. These polysulfides pass on part of their sulfur to the rubber and constitute the true curing agents. Such a mechanism applies also to the curing action of alkali and alkaline-earth hydroxides. The fact that basic magnesium carbonate will react with hydrogen sulfide and sulfur in water suspension to form polysulfide solutions no doubt accounts for its mild accelerating power. Lime and magnesia do not function well in deresinated rubbers where much of the hydrogen sulfide producing materials have been removed. The sulfides and polysulfides of the alkali and alkaline-earth metals should function in deresinated or synthetic rubbers.

The Bayer Company patent[1] on basic organic accelerators contains a broad claim covering all bases with a dissociation constant greater than 1×10^{-8}. This claim covers those bases which readily react with hydrogen sulfide and sulfur to form polysulfides at ordinary or at curing temperatures. Weak bases such as aniline cannot be expected to form polysulfides to the same extent as strong bases like dimethylamine, since the formation of polysulfides is in some way dependent upon basicity. It has been found that weak bases such as aniline, *p*-toluidine, and quinoline, dissolve more sulfur at 100° in the presence of hydrogen sulfide than when it is absent. Aniline will dissolve about 1 per cent more sulfur at 100° and about 4 per cent more at 130°.

The relative accelerating power of the organic bases is dependent upon the facility with which they form polysulfides and the extent to which they are able to activate sulfur and make it available for the rubber. This will, in some measure, be dependent upon the basicity. In a previous paper by the writers[1] it was stated that at least a part of the accelerating action of hexamethylenetetramine is due to the fact that during the cure there are produced, among other products, ammonia and carbon disulfide which, alone or with basic products present in the rubber, form dithiocarbamates. It may be added that "Hexa" also forms hydrogen sulfide by sulfur reaction, which with the ammonia undoubtedly forms ammonium polysulfides. This accelerator may, therefore, be classed under both types since it is both a hydrogen sulfide and a carbo-sulfhydryl polysulfide accelerator.

Aldehyde ammonia, by the action of heat alone, forms ammonia, while with sulfur it also gives hydrogen sulfide. Heat also produces other bases such as the alkyl pyridines or collidines. This material appears to be solely a hydrogen sulfide polysulfide accelerator. The ammonia condensation products of other aliphatic aldehydes behave in a similar manner.

p-Phenylenediamine is an accelerator that is much more active than would be assumed from its basicity. At curing temperatures, this accelerator reacts with sulfur to form large amounts of ammonia and hydrogen sulfide together with certain weaker bases. If the reaction be carried out under a cold reflux, the condenser will frequently become clogged with the white solid compounds of ammonia and hydrogen sulfide which are described by Roscoe and Schorlemmer. The action of *p*-phenylenediamine in the cure is entirely that of a hydrogen sulfide polysulfide accelerator.

The three above-mentioned accelerators are not dependent on the rubber resins or proteins for their supply of hydrogen sulfide, since this is one of their sulfur reaction products. It is to be expected that these accelerators will function in a deresinated or a synthetic rubber, and the Bayer patents state that this is true. It is also known that piperidine will cure in a nitrogen-free rubber. Here we have a strong base acting apparently without the aid of hydrogen sulfide. Piperidine, however, reacts with sulfur at temperatures lower than those used in vulcanization, with the formation of hydrogen sulfide. Both the sulfur reaction product and the unchanged piperidine may then use this hydrogen sulfide to form polysulfides with sulfur.

INORGANIC ACCELERATORS

Inorganic accelerators that function in the cure by the removal of hydrogen sulfide the writers choose to term "secondary accelerators," while those that

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[1] U. S. Patent 1,149,580.

[1] *Loc. cit.*

function in the same manner as the organic polysulfide accelerators may be classed with them as "primary accelerators." A third class consists of those compounds that are both primary and secondary accelerators.

I. *Secondary Accelerators*—Litharge, zinc oxide, etc., seem to act no further than to form the corresponding sulfides, in connection with hydrogen sulfide polysulfides.

II. *Primary Accelerators*—To this class belong the sulfides and hydrosulfides of the alkali and alkaline-earth metals.

III. *Accelerators That Are Both Primary and Secondary*—Inorganic oxides and hydroxides function first as secondary accelerators forming sulfides or hydrosulfides which then take up sulfur and act as primary accelerators. Such accelerators are sodium and calcium hydroxides, magnesium oxide and basic carbonate, etc.

Secondary accelerators are believed to function as aids to organic polysulfides by breaking them up into colloidal sulfur and the original nitrogen base. This may be illustrated by the decolorization of polysulfide solutions by litharge or zinc oxide. Ferric oxide does not act as a secondary accelerator, and neither does it readily decompose the polysulfide solutions. The solubility of organic accelerators in sulfur and rubber gives them much more intimate contact with hydrogen sulfide at the time of its formation than is the case with the comparatively large particles of litharge or zinc oxide. Hydrogen sulfide is therefore available for the formation of organic polysulfides before being taken up by the secondary accelerators. The decomposition of a polysulfide by a secondary accelerator regenerates the free base, which with more hydrogen sulfide and sulfur re-forms the polysulfide. Secondary accelerators do not act as true catalysts; once formed into sulfides they do not react again with hydrogen sulfide.

SUMMARY

1—All organic accelerators are believed to function through the formation of some type of polysulfide.

2—Organic bases and compounds that form bases during vulcanization are believed to form polysulfides through the aid of hydrogen sulfide. These are termed "hydrogen sulfide polysulfide accelerators."

3—Thioureas, dithiocarbamates, thiurams, and mercaptan compounds are believed to form polysulfides directly, or by first forming disulfides, and are termed "carbo-sulfhydryl polysulfide accelerators."

4—It is proposed that the function of such compounds as litharge and zinc oxide may lie in the decomposition of polysulfides into colloidal sulfur and amines.

5—Such inorganic compounds as sodium hydroxide, calcium hydroxide and magnesium oxide are believed to function as "primary accelerators" through the formation of inorganic polysulfides.

THE ACTION OF CERTAIN ORGANIC ACCELERATORS IN THE VULCANIZATION OF RUBBER—III[1]

By G. D. Kratz, A. H. Flower and B. J. Shapiro

Falls Rubber Co., Cuyahoga Falls, Ohio

It has for some time been generally recognized that although aniline is effective as an accelerator in the absence of zinc oxide, diphenylthiourea functions but mildly in the absence of, and strongly in the presence of this substance. Reference to this effect has already been made indirectly in the literature several times, and recently Twiss[1] has given curves for physical test results which demonstrate quite clearly the effectiveness of diphenylthiourea as an accelerator in the presence of zinc oxide. His statement that diphenylthiourea is practically inert in the absence of zinc oxide is, however, not in accord with our findings.

In a previous paper of this series[2] we have shown that in the acceleration of the vulcanization of a rubber-sulfur mixture, the activity of one molecular part of diphenylthiourea is less than that of an equimolecular quantity of aniline, but equal to that of one molecular part of aniline and one molecular part of phenyl mustard oil.

Our former experiments, however, were confined to the determination of sulfur coefficients at one cure only. In the present instance, we desired to compare the relative effects of aniline and diphenylthiourea over a series of cures, and to effect this comparison both by means of the sulfur coefficients and the physical properties of the various mixtures and cures. Further, it was desired to compare mixtures which contained zinc oxide, as well as the rubber-sulfur mixtures previously employed.

In the experimental part of this paper we have given results obtained with six different mixtures, as follows a rubber-sulfur control, a control which contained zinc oxide, and similar mixtures which contained either one molecular part of aniline or diphenylthiourea. All of the mixtures were vulcanized for various intervals over a wide range of time. After vulcanization, comparisons of sulfur coefficients and physical properties were made.

Summarizing these results briefly, we found that, in a rubber-sulfur mixture, the accelerating effect of aniline is considerably greater than that of diphenylthiourea, when judged either by sulfur coefficients or on the basis of the physical properties of the vulcanized mixtures. In mixtures which contained zinc oxide, however, the reverse was found to be true, and diphenylthiourea was more active than aniline when judged by either of the above criteria. It was also evident that in the case of the mixtures which contained zinc oxide, although the tensile strength of the mixture which was accelerated by diphenylthiourea increased more rapidly than in the case of the mixture accelerated by aniline, the same maximum tensile strength was attained by each. The sulfur coefficients at their respective maxima were practically identical. While the maximum tensile strength of the rubber-sulfur mixture which was accelerated by aniline was the same as that obtained when zinc oxide was present in the mixture, it was attained only at a much higher sulfur coefficient. Lastly, it was also found that the tensile strengths of the mixtures that contained zinc oxide and which were accelerated by either aniline or diphenylthiourea, particularly the latter, were in-

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[1] Presented before the Rubber Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[1] *J. Soc. Chem. Ind.*, **39** (1920), 125*t*.

[2] This Journal, **12** (1920), 317.

creased tremendously during the first part of the vulcanization, and at very low sulfur coefficients. This would indicate the possibility of certain substances (accelerators) increasing the physical properties of a vulcanized mixture without greatly affecting the sulfur coefficient.

This point is of interest as it already has been noted by ourselves,[1] Cranor,[2] and others, that with mixtures which contain zinc oxide and a strong organic accelerator, the correct (or optimum) cure is obtained at abnormally low sulfur coefficients when compared with those obtained for unaccelerated mixtures. No explanation has been offered for this phenomenon. Bedford and Scott,[3] however, regard diphenylthiourea as the aniline salt of phenyldithiocarbamic acid after H_2S has been liberated. This salt is extremely unstable, owing to the weakly basic properties of aniline, and in this respect, according to Krulla,[4] is unlike the metallic salts of the same acid. In this connection, it is particularly pertinent to note that Bruni[5] has recently found the zinc salts of the mono- and disubstituted dithiocarbamic acids to be violent accelerators. It is quite possible, then, that such a salt may be formed during the vulcanization process in mixtures which contain both diphenylthiourea and zinc oxide;[6] and that, irrespective of its action as an accelerator, the zinc portion of such a salt may be responsible for the physical improvement imparted to the mixture.

Our present results, moreover, particularly when interpreted with the assistance of the excess sulfur coefficients obtained for the various mixtures at different times of cure, show that when aniline is employed as the accelerator in the presence of zinc oxide, the effect of the latter substance is manifested almost entirely in the physical properties of the mixture. When aniline is replaced by diphenylthiourea the reverse is true, and the activity of the original substance as an accelerator is greatly increased when measured by either the sulfur coefficients or physical properties. In the latter instance, then, the zinc oxide most probably either assists in the decomposition of the diphenylthiourea to a more active substance, or combines with the decomposition or alteration products of the original substance with the formation of a zinc salt, which is responsible for the increase both in the sulfur coefficients and tensile strength of the mixture. Our results with aniline as the accelerator, however, do not indicate the formation of such a salt.

Thus, in the presence of zinc oxide, the activity of aniline and diphenylthiourea as accelerators appears to be of a different nature. Evidently, an acid substance, probably a thiocarbamic acid, capable of reacting with zinc oxide, is formed as one of the decomposition products of diphenylthiourea. The excess accelerating activity is attributed to this zinc salt. When aniline is employed as the accelerator, there is no evidence of such salt formation.

EXPERIMENTAL PART

The present experiments were designed to effect a comparison of the sulfur coefficients and physical properties of representative mixtures when accelerated by 0.01 gram-molecular quantities of either aniline or diphenylthiourea. The six following mixtures were employed for this purpose, and each was vulcanized for a series of cures:

A—Rubber-sulfur control
B—Rubber, sulfur, and aniline
B-I—Rubber, sulfur, and diphenylthiourea
C—Rubber, sulfur, and zinc oxide control
D—Rubber, sulfur, zinc oxide, and aniline
D-I—Rubber, sulfur, zinc oxide, and diphenylthiourea

The quantities of each substance employed in these mixtures are shown in Table I. The amounts of aniline or diphenylthiourea added to these respective mixtures represent 0.01 gram-molecule of the accelerator for each 100 g. of rubber in the mixture. Otherwise, the same general method of procedure was adopted in the course of this work as in that previously reported in Part I.[1]

TABLE I

INGREDIENT	Mixture A	Mixture B	Mixture C	Mixture D	Mixture B-I	Mixture D-I
Rubber..........	100.00	100.00	100.00	100.00	100.00	100.00
Zinc oxide........	...	...	100.00	100.00	...	100.00
Sulfur	8.1	8.1	8.1	8.1	8.1	8.1
Aniline...........	...	0.93	...	0.93	...	...
Diphenylthiourea..	...	...	...	...	2.28	2.28

The rubber used was of good quality, first latex, pale crepe, a different sample of the lot used in our former experiments. The various mixtures were mixed on the mill, vulcanized, and tested in the same manner as before. The physical properties of the vulcanized samples were determined on a Scott testing machine of the vertical type, with the jaws opening at the rate of 20 in. per min. A recovery period of 48 hrs. was allowed before physical tests were made. Combined sulfur was estimated by our method previously reported in detail.[2]

The various mixtures were vulcanized at 141.5° C. for different intervals of time up to 240 min.[3] The sulfur coefficients and physical properties of the different cures for each mixture were determined. These results are given in detail in Table II and shown graphically in Fig. 1. Generally speaking, the results obtained were in good agreement, and fairly smooth curves for physical properties were obtained.[4]

For brevity and clearness, the results obtained for each mixture have been considered separately.

MIXTURE A—This mixture of rubber and sulfur served as a control only.

MIXTURE B—Comparing Curves A and B, aniline not only acts as an accelerator, but also slightly increases the physical properties of a rubber-sulfur mixture after vulcanization.

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[1] THIS JOURNAL, 11 (1919), 30; *Chem. & Met. Eng.*, 20 (1919), 418.

[2] *India Rubber World*, 61 (1919), 137.

[3] THIS JOURNAL, 12 (1920), 31.

[4] *Ber.*, 46, 2669.

[5] Brit. Patents 140,387 and 140,388.

[6] The action of diphenylthiourea with zinc oxide is apparently similar to the action of the natural accelerator with magnesium oxide, as pointed out in a previous paper [THIS JOURNAL, 12 (1920), 971]. In both cases the oxide serves in a contributory capacity rather than as a primary accelerator. It is obvious that no one oxide will activate all accelerators equally well

[1] THIS JOURNAL, 12 (1920), 317.

[2] *India Rubber World*, 61 (1920), 356.

[3] In the experiments described in Parts I and II vulcanization was carried on at a temperature of 148° C.

[4] Satisfactory physical test results for representation graphically are obtainable with considerable difficulty. We have found it necessary, particularly when seeking results for stress-strain diagrams, to employ three men, one to operate the machine and two to take readings.

TABLE II

(All Mixtures Vulcanized at 141.5° C.)

	Mixture A			Mixture B			Mixture C			Mixture D			Mixture B-I			Mixture D-I		
Cure in Minutes	Sulfur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulfur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulfur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulfur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulfur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent	Sulfur Coefficient	Tensile Strength, Lbs. per Sq. In. at Break	Final Length at Break Per cent
30	0.794	..	...	1.126	545	1180	1.005	..	...	1.434	540	710	0.913	(1)	1210	1.603	2210	820
45	0.856	279	1250	1.317	1019	1170	1.055	306	680	1.490	1366	770	1.063	(1)	1360	1.912	2381	780
60	1.038	..	..	1.583	1228	1120	1.207	592	750	1.838	1819	770	1.335	(1)	1260	2.297	2442	790
75	1.090	494	1220	1.898	..	...	..	..	...	..	1968	750	1.609	533	1230	2.623	..	..
90	1.531	709	1150	2.482	1621	1060	1.558	1041	760	2.382	2350	720	1.953	789	1230	2.962	2730	830
120	2.089	871	1180	3.351	2046	1100	1.765	1815	780	2.801	2808	780	2.496	1053	1210	3.755	2699	770
150	2.236	1159	1130	4.033	2410	1100	2.237	1950	760	3.266	2721	770	3.109	1303	1150	4.521	2619	750
180	2.470	1521	1130	4.939	2670	1030	2.620	2032	750	4.226	2663	740	4.027	1779	1110	5.357	2020	690
210	3.179	1842	1100	5.264	2566	970	3.340	2184	760	4.806	2245	700	4.730	2021	1080	6.379	1118	530
240	3.751	2124	1060	6.268	2131	910	3.615	1978	730	5.564	1837	660	5.624	2362	1050	7.079	754	440

[1] Test pieces did not break.

MIXTURE C—The inclusion of zinc oxide in Mixture C was found to have little or no effect upon the sulfur coefficients when compared with the results obtained for A.

MIXTURE D—The sulfur coefficients obtained for this mixture were found to be uniformly lower than the corresponding cures of B. Moreover, the maximum tensile strength of D was attained at a much lower sulfur coefficient than in the case of B, although this maximum tensile strength was almost the same in both instances.

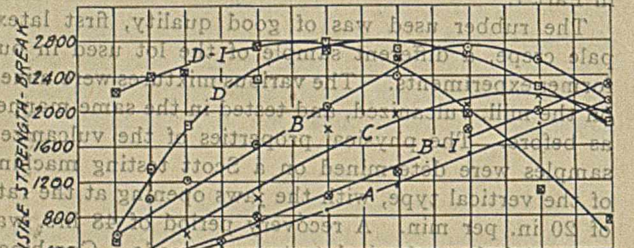

FIG. 1

MIXTURE B-I—From the curves it is seen that in a mixture of rubber and sulfur the activity of diphenylthiourea is much less than that of aniline, when judged by either sulfur coefficients or physical properties. In fact, both the tensile strengths and final lengths of B-I are practically the same as those of its control mixture, A. The sulfur coefficients of B-I, however, were decidedly higher than those of A, and, contrary to the statement of Twiss,[1] we cannot regard diphenylthiourea as practically inert as an accelerator in a mixture of rubber and sulfur only.

MIXTURE D-I—The sulfur coefficients for D-I were considerably higher than those of any of the other mixtures; although the maximum tensile strength was of the same magnitude, it was reached in shorter time.

The curves showing the comparison of the final lengths are given in Fig. 1. It is obvious that the physical manifestations, especially in Mixtures D and D-I, are found in the tensile strength, rather than in the final lengths, of the vulcanized mixtures. Consequently, the tensile strengths of such mixtures, particularly until maximum tensile strength was reached, are better indications of the point known as the "optimum cure" than are the loads required to effect a given extension.[2]

The effect of the two accelerators, aniline and diphenylthiourea, have been summarized in Fig. 2, wherein with Mixtures A and C as controls, the excess sulfur coefficients were plotted against their times of vulcanization. A comparison of the curves for B and D show that, when judged by sulfur coefficients only, the activity of aniline as an accelerator is increased in the absence of zinc oxide.[3] On the other hand, a comparison of B-I and D-I shows that diphenylthiourea is approximately twice as active in the presence of zinc oxide than when this substance is absent from the mixture. In fact, the difference between the curves for B-I and D-I is so great that our results indicate the formation of a new and more active accelerator than the original diphenylthiourea, or its decomposition products. It is not impossible that the decomposition products of diphenylthiourea react with the zinc oxide in the presence of sulfur to form varying amounts of a zinc salt of a dithiocarbamic acid. Salts of the latter type have already been mentioned as violent accelerators. On the other hand,

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[1] *Loc. cit.*

[2] As Whitby has stated ("Plantation Rubber and the Testing of Rubber," 1920, p. 395, Longmans, New York), complete stress-strain diagrams are probably required for an accurate determination of this point.

[3] The sulfur coefficients and physical properties of Mixture D were less concordant than those of any of the other mixtures.

the fact that the curve for Mixture D, which contains aniline and zinc oxide, falls below that of B, which contains aniline but no zinc oxide, argues against the formation of diphenylthiourea (and the subsequent formation of the zinc salt of its decomposition or conversion products) from the aniline originally present in the mixture.

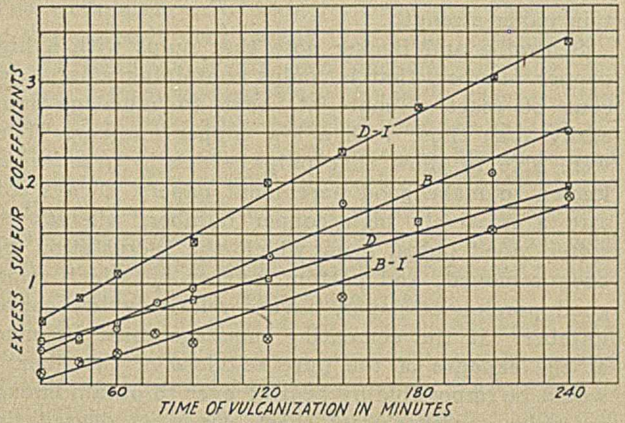

FIG. 2

The preceding observations are probably applicable to mixtures of the same general type and composition as employed in the course of this work only.

CONCLUSIONS

(1) In a rubber-sulfur mixture, the activity of aniline in the acceleration of vulcanization is much greater than that of a molecularly equivalent quantity of diphenylthiourea.

(2) In mixtures which contain zinc oxide, diphenylthiourea is more active than aniline.

(3) In mixtures accelerated by aniline, either with or without zinc oxide, the same maximum tensile strength is obtained, accompanied by a higher sulfur coefficient in the absence of zinc oxide than when this substance is present.

(4) Mixtures which contain zinc oxide, and which are accelerated by either aniline or diphenylthiourea, show large increases in tensile strength in the early stages of the vulcanization.

(5) Mixtures which contain zinc oxide and which are accelerated by either aniline or diphenylthiourea, attain the same maximum tensile strength at approximately the same sulfur coefficients.

(6) There is apparently no general relation between the physical properties and sulfur coefficients of accelerated mixtures.

CELLULOSE MUCILAGE[1]

By Jessie E. Minor

Emerson Laboratory, Springfield, Massachusetts

During the past year, Schwalbe and Becker[2] have published some very interesting conclusions as to the exact chemical changes which occur in the making of paper from wood and cotton, based on laboratory experiments, and some practical applications of these facts. These conclusions seemed to be in such complete accord with conclusions reached earlier by the author that it was deemed worth while to present this summary of both lines of work.

Schwalbe and Becker have assumed that the first step of the decomposition of cellulose consists in the formation of an insoluble hydrocellulose or oxycellulose which has properties very similar to the hemicelluloses of wood incrustation, in that it reduces Fehling's solution and is in general unstable and reactive. Decomposition of this hydrocellulose or oxycellulose or of the hemicellulose produces a mucilaginous substance which has a higher copper number than the hydro-, oxy-, or hemicellulose from which it was made, and which constitutes the cementing material of the parchment paper. If the decomposition is carried too far, the mucilage is decomposed and we get sugars or acids.

In our previous publications we have assumed that pure cellulose exercises a marked positive residual valence by means of which it strongly adsorbs hydroxyl ions from the solution, the adsorption being greatly aided by mechanical treatment. These hydroxyl ions, by means of their close proximity to the cellulose, are able to hydrolyze the cellulose molecule with increasing velocity into a series of products of which the earlier ones are insoluble and mucilaginous, the latter ones soluble dextrins or acids. Hauser and Herzfeld have shown that the first product, which Schwalbe and Becker call hydrocellulose, is a mixture of cellulose with more or less easily soluble dextrins, for if the pulp is thoroughly washed with hot water the dextrin is washed away, the copper number is reduced, and the development of mucilage is retarded.

If these reactive dextrins were adsorbed by pure cellulose, they would without doubt catalyze the decomposition of the cellulose, giving an adequate explanation for the increase in reaction velocity as decomposition proceeds. The first evidence of the presence of these dextrins would be merely the increased reactivity of the cellulose but, since they are mucilaginous by nature, we should gradually get the increased slowness of the pulp and the turbidity of the solution due to aggregates of cellulose and dextrin. When the insoluble cellulose became completely changed to soluble dextrin or sugar, the solution would lose its turbidity, but this would not occur until after all the fiber structure had been destroyed. Schwalbe and Becker say that when a mucilage is formed by beating, a reducible substance must be present in the original material. In other words, the earlier decomposition reaction must be so catalyzed by the adsorbed dextrins disseminated throughout the pulp mass as to occasion a rapid formation and an accumulation of mucilage at the time when, by drying, reaction ceases.

Another evidence for this adsorption theory is in the colloidal properties of the mucilaginous product. If this mucilage is allowed to dry slowly in the air, one obtains a horny, rather viscous mass which swells quite decidedly in water-saturated air, much more

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[1] Presented at the Cellulose Symposium of the Division of Industrial and Engineering Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Z. angew. Chem.*, **33** (1920), 14, 57, 58.

than ordinary cellulose. This is probably related to the larger surface exposed to adsorption when in the colloidal state. If the mucilage is excessively dried, then the power to take up water goes back to the normal value for cellulose, and if it is then pressed, as hard ironed or pleated cloth or calendered paper, then the adsorption is still further decreased.

Further interesting evidence of the variation in the nature of these decomposition reactions is shown by the effects of cold and hot water upon cellulose. When a wood pulp lies in *cold* water, the slowly formed dextrins are firmly adsorbed by the cellulose, thus forming the insoluble, reactive aggregate which gives slowness to the stock. Mechanical beating increases the velocity of the reaction to such an extent that the increase in copper number is quite apparent, but washing decreases the copper number by slowly removing the more rapidly formed and, therefore, less firmly adsorbed soluble products. *Hot* water treatment so hastens hydrolysis and weakens adsorption that mucilaginous products are destroyed more rapidly than made. An interesting experiment which bears on this point was recently made in our laboratory. A part of a sample of good parchment pulp, which had been merely disintegrated in a beater, was triturated in a mortar for 1.5 hrs., then the triturated and the nontriturated portions were washed with water which was neutral to methyl red in filter papers which had also been washed neutral to methyl red. The triturated pulp was decidedly more alkaline than the original sample and, when washed with hot, neutral water, the alkalinity increased. On washing later with cold, neutral water, both pulps became acid to the indicator, but on again washing with hot water, more alkalinity was developed. This alternating of acidity and alkalinity could be continued for some time. Apparently, hot water developed hydration enough more rapidly than it could be washed out through a filter paper to have its alkalinity apparent to this sensitive indicator, whereas the more slowly formed hydrate of the cold water is washed out as quickly as formed. Incidentally, since, after triturating for 1.5 hrs., the pulp tested more alkaline than before, and this in the presence of an indicator which can easily detect the excess alkalinity of hydration in hot water, it would seem reasonably certain that acids are not developed by beating except in the presence of an oxidizing agent like bleach.

Schwalbe and Becker showed that, if pulp is allowed to remain in hot water, 100° C., for 24 hrs., pulp degradation will proceed so far that, after subsequent beating, the copper number is decreased and the strength of the paper made from the pulp very much lessened. The making of paper from wood or cotton would then consist in so controlling the decomposition reactions as to get the minimum of soluble sugars and acids, which constitute a complete loss of material, and such a ratio between mucilage and undecomposed fiber as will give the maximum strength and all other desired physical properties to the finished paper. For a plain paper, the maximum fiber length and strength and just enough mucilage to hold the fibers together are desired, whereas for a parchment it is essential that the mucilage be sufficient in quantity to give grease-proof qualities to the paper, and, with this amount of mucilage, it is possible to sacrifice considerable fiber strength and still maintain paper strength.

Schwalbe and Becker note that pulps with a high copper number, that is, pulps containing a large per cent of reactive material, beat to mucilage more easily than those with a low copper number. They were able to show that pulps, which in practice are known to make good parchment papers, always contain a relatively high copper number, whereas the softer wood pulps, from which the incrustation has been removed, and cotton, neither of which make good parchment paper, have a relatively low copper number. If the cementing mucilage must be made at the expense of the pure cellulose of the fiber, it would be impossible by beating ever to obtain enough to make a grease-proof sheet, since its degradation occurs probably as rapidly as its formation. Therefore, for parchment making, the papermaker chooses a pulp which is rich in the reactive hemicelluloses, that is, one in which the wood fiber incrustation has been attacked just sufficiently to cause it to yield easily to the beating process, but not sufficiently to make it soluble, then beats it until he has obtained the maximum mucilage formation consistent with the maximum fiber disintegration allowable. In experiments performed in the laboratory by Schwalbe and Becker and in our laboratory, it has been shown that parchment quality can be developed in a pulp of low copper number by treating it with acid or an acid-forming salt previous to beating, so that the hydrocellulose formation is accelerated and the subsequent mucilage formation increased. In an experiment with a sulfite pulp of low copper number, the time required to reach a standard slowness was reduced by acid softening from 3.75 hrs. to 20 min. Under the same treatment a parchment pulp with a high copper number required 2 hrs. 10 min. to reach the same slowness. Mullen pop tests upon hand sheets made from this acid-treated pulp show a decided increase in strength over those made from the same pulp, not acid treated, and the blistering quality of the paper is decidedly developed by this treatment. So far as known, this treatment has not been tried on a commercial scale and the engineering details have not been worked out, but it would seem that it would make it quite possible to make good, blistering, grease-proof, parchment paper from such pulps as that recovered from old paper. The practical difficulties are in the standardization of the exact conditions for the acid treatment, since excessive acid hydrolysis would also accelerate mucilage destruction.

A German patent has been issued for a process of treating waste papers with chlorine and water, enough partially to decompose the cellulose, then grinding under water and incorporating this mass with paper pulp to make a close, strong sheet of paper. It would seem as if a similar mixture would also be satisfactory to use as a waterproof coating for papers.

According to Schwalbe and Becker, another evidence for the colloidal nature of cellulose mucilage is in its ready splitting of metal salts and adsorption of the base. This is to be expected from the more strongly negative residual valence of the hydrolyzed product. The accumulation of residual valence over the surface of the molecule very largely favors the colloïdal state by its repulsion of its own particles carrying like charges. Particles carrying opposite charges, like metal ions, are readily adsorbed, and the rate of adsorption would increase with increased hydration and hydrolysis. A practical application of this is found in the partial conversion of the cloth of gas mantles into a hydrolyzed product before impregnation with metals, a treatment which, because of increased adsorption, causes a better retention of metal.

When a pulp is treated with alum, the liquid very quickly becomes acid, but the acidity is very readily washed out, leaving an alkaline pulp. This is due to a splitting of the salt and an adsorption of the free base by the fiber, leaving the free acid in the solution. The power of splitting salts and adsorbing their bases increases as the amount of mucilage in the pulp is increased, and this is further evidenced by the increase in the colloidal properties of the cellulose on hydrolysis.

This theory would also explain why, when mordanting with the salt of a weak acid like an acetate, the presence of some strong acid, like sulfuric, which aids the hydrolysis of the fibers, gives a better coloring.

The adsorption of metal very markedly weakens the strength of the paper made from it, no doubt by diverting some of the intermolecular affinities to the holding of the metal. By means of this loss of strength, Schwalbe and Becker were able to determine that papers impregnated with as little as 0.25 per cent of magnesium chloride and hung in an air which was partially saturated with moisture, were able to split the salt and adsorb the metal, and that the amount of metal adsorbed depends on the amount of moisture present. The greatest effect was with an air which contained decidedly less moisture than enough to saturate it. The function of the air is, no doubt, to aid hydrolysis of both salt and fiber.

Through this theory of the easy hydrolysis of salt and fiber in moist air, one can explain the fact that loose piles of freshly colored, unwashed fibers take on a deeper color than do fibers not so spread out. The loss of weight experienced in dyeing cotton goods may be attributed to the further fiber hydrolysis forming some soluble products. In steaming under pressure with basic dyes, we find not only the possible formation of a dye-fixing hydrocellulose arising from the hydrochloric acid of the dye, but also oxidation through atmospheric oxygen in the steam, which would give reactive oxycellulose.

Although acid presence aids mucilage formation and dyeing, it must always be used with care, inasmuch as excess causes loss of strength of the finished product. Looking at the matter from a purely theoretic standpoint, it would seem as if it would be much safer not to attempt acid treatment on the fiber, the strength of which it is desired to preserve, but to impregnate such a product with a mucilage which has been separately prepared, possibly using it as a part of the size.

SUMMARY

In the foregoing the author has attempted to develop the following propositions:

(1) The first step in the decomposition of cellulose forms a mucilaginous soluble dextrin which easily reduces Fehling's solution. These dextrins, as soon as formed, are adsorbed by pure cellulose, thus forming a reactive insoluble aggregate, called hydrocellulose.

(2) Mucilage differs from hydrocellulose in the larger per cent of soluble adsorbed dextrins present.

(3) These adsorbed dextrins serve to catalyze the hydrolysis of cellulose.

(4) Complete hydrolysis leaves only soluble dextrins.

(5) Mucilage, possibly through its colloidal nature, has a greater power of adsorbing water than has pure cellulose.

(6) Cold water immersion causes a slow hydrolysis. Hot water hastens hydrolysis and weakens adsorption, so that mucilaginous products are destroyed as rapidly as formed.

(7) With methyl red as an indicator, it is possible to detect the increase in the alkalinity of the hydration of pulp.

(8) Pulps with an original high copper number beat to mucilage more easily than those with a low copper number, owing to the larger amount of catalyst present.

(9) The copper number of bleached pulp can be increased by a careful acid treatment prior to beating.

(10) Cellulose mucilage will split a salt and adsorb the metal ion more easily than pure cellulose, owing to the more colloidal state.

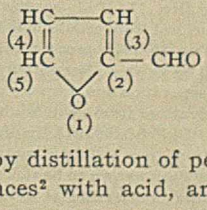
(11) Moisture or acid treatment aids dyeing by forming mucilage.

THE PREPARATION AND TECHNICAL USES OF FURFURAL[1]

By K. P. Monroe

Color Investigation Laboratory, U. S. Bureau of Chemistry, Washington, D. C.

Although it has long been known that furfural (2-furaldehyde)



may be prepared by distillation of pentose or pentosan containing substances[2] with acid, and this has indeed

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[1] Presented before the Dye Section at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 14, 1920.

[2] Döbereiner, *Ann.*, **3** (1832), 141; Stenhouse, *Ibid.*, **35** (1840), 301; Fownes, *Ibid.*, **54** (1845), 52; v. Babo, *Ibid.*, **85** (1853), 100, Völckel, *Ibid.*, **85** (1853), 65; Schwanert, *Ibid.*, **116** (1860), 258; Stenhouse, *Ibid.*, **156** (1870), 199; Gudkow, *Z. Chem.*, **1870**, 360; Williams, *Jahresb.*, **1872**, 770; Heill, *Ber.*, **10** (1877), 936; v. Meyer, *Ibid.*, **11** (1878), 1870; Hill, *Am. Chem. J.*, **3** (1881), 36; Stone and Tollens, *Ann.*, **249** (1888), 227; Günther, de Chalmot and Tollens, *Ber.*, **25** (1892), 2569; Gross, Bevan and Smith, *Ibid.*, **28** (1895), 1940; Tollens, *Ann.*, **286** (1895), 301; Krüger and Tollens, *Z. angew. Chem.*, **9** (1896), 44; Semmler, *Ber.*, **39** (1906), 731; Erdmann and Schäfer, *Ibid.*, **43** (1910), 2401; Gildemeister and Hoffmann, "Die äterischen Ole," Leipzig, **1910**, p. 448.

been the basis for quantitative estimation of pentosans,[1] the published methods[2] seem highly unsatisfactory on account of the low yields obtained, and on account of the tedious processes involved in extraction of the aldehyde from its dilute aqueous solution by immiscible solvents.[3] The potential value of furfural in chemical industry, which will be discussed later, led to the present investigation of corncob pentosan[4,5] as a promising source and to the following method, which yields as pure furaldehyde approximately 26 per cent of the weight of the solids contained in corncob adhesive, and involves very simple and economical operations for the production and subsequent separation of the aldehyde from dilute aqueous solution:

Five hundred grams of corncob adhesive, prepared according to the method of La Forge and Hudson,[6,7] and consisting of a concentrated aqueous suspension of gums rich in pentosan, were thoroughly mixed in a 3-liter round bottom flask with a solution of sulfuric acid prepared by mixing 150 cc. of concentrated sulfuric acid (sp. gr. 1.84) and 500 cc. of water. To prevent foaming during the subsequent heating operation, a lump of paraffin was added and the liquid heated to boiling. Since preliminary experiments had indicated the desirability of removing furfural from the reaction mixture as rapidly as it is formed, a vigorous current of steam was passed through the mixture; the rate of steaming and the flame under the flask were so adjusted that the volume of liquid in the flask remained approximately constant while the distillate was collected at the rate of 15 to 20 cc. per minute. After five 800-cc. portions of distillate had been obtained the operation was suspended. In the meanwhile the portions of distillate were filtered to remove traces of paraffin and fractionally distilled from a flask provided with an efficient fractionating column.[1] It is a somewhat anomalous fact in view of the high boiling point of furfural (162°) that, by careful fractionation of the very dilute solution which constitutes the original distillate, nearly all the aldehyde is obtained in the first 100 cc. of distillate, boiling between 97.5° and 100°. After fractionation, the furfural phase (20 cc.) in the combined distillates was separated from the supernatant saturated aqueous solution,[2] which was returned to the flask for refractionation. The combined portions of the furfural phase were then fractionated from a small distilling flask. After rejection of the first 2 or 3 cc. of distillate, which contained water, the thermometer rose rapidly to 161.5°, and the remainder boiled between 161.5° and 162°,[3] which indicated a very satisfactory degree of purity. An average yield of 53 g. (or 26 per cent of the solid material contained in the adhesive) of pure furaldehyde was so obtained.

While furfural has hitherto chiefly been known as a rare organic chemical, on account of difficulties of preparation and the consequent high price, numbers of uses are already known, and the future field for development seems very promising if it becomes available in quantity and at less cost. An interesting portion of this field is the one concerning the dye industry, since at least two useful and promising direct dyes may be obtained by simple interaction of furaldehyde with alkali sulfides and hydroxides.[4,5,6] Hard resins similar to the well-known Bakelite and Condensite may be obtained by the condensation of furfural

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[1] Brown, "Handbook of Sugar Analysis," Wiley and Sons, **1912**, p. 372.

[2] For example, the directions given in Beilstein, "Organische Chemie," **3**, 3rd Ed., and by Emil Fischer, "Anleitung zur Darstellung organischer Präparate," Braunschweig, **1908**. Bran is the source of pentosan; the yields reported are 3 and 2.5 per cent, respectively.

[3] European patents have been issued on the technical preparation of furfural by treatment of cellulosic material with steam and acid at temperatures below 150°. This process has been operated in France and Germany (Meunier, and Beckmann and Dehn, *Loc. cit.*). The price quoted on French technical furfural is 20 francs per kilo, and two French firms have stated in private communications to the author that furaldehyde is available in any quantity desired.

Fr. Patent 446,871, Dec. 17, 1912, process for simultaneous preparation of methylene and furfural from cellulosic material, issued to V. Raisin; Swedish Patent 40,482, Dec. 16, 1913, process for production of furfural from cellulosic material, issued to H. O. V. Bergström; Fr. Patent 464,608, March 26, 1914, process for the separation and recovery of volatile acids, methylated products and furane derivatives from cellulosic material, issued to A. and E. Lederer; Fr. Patent 485,967, Feb. 26, 1918, improvements on the method of manufacturing pure furfural from cellulosic material, issued to E. Ricard.

[4] Corncobs have long been known to be rich in xylan, and consequently have been utilized for the preparation of xylose. Stone and Lotz, *Am. Chem. J.*, **13** (1891), 348; Hudson and Harding, *J. Am. Chem. Soc.*, **40** (1918), 1601; La Forge and Hudson, THIS JOURNAL, **10** (1918), 925; Monroe, *J. Am. Chem. Soc.*, **41** (1919), 1002.

[5] Another agricultural waste product which suggests itself as a promising source is cottonseed hulls, which are known to be rich in xylan. Hudson and Harding, *J. Am. Chem. Soc.*, **39** (1917), 1038.

[6] *Loc. cit.*; La Forge, U. S. Patent 1,285,247. This method involves the separation and partial hydrolysis of pentosans contained in the cobs by extraction with water at 150°. The aqueous solution of gums so obtained is then evaporated to the desired concentration.

[7] The author wishes to express his gratitude to Dr. La Forge for kindly furnishing the corncob adhesive.

[1] The ready separation of furfural from dilute aqueous solution by column distillation is mentioned in the European patents (*Loc. cit.*). This method is not given in any of the hitherto published directions for laboratory preparation although it has evidently been recognized that simple distillation from aqueous or saturated salt solution concentrates the aldehyde in the first portions of distillate. On the laboratory scale the efficiency of a bare column in fractionation of relatively low boiling mixtures is known to be low on account of the comparatively small heat loss to the surrounding air; this was partially compensated by substitution of an inverted Allihn condenser with bulbs loosely packed by broken glass. A rapid current of air was drawn through the jacket in a direction counter to that of the stream of vapor.

[2] The mutual solubility of water and furfural has been investigated by Rothmund, *Z. physik. Chem.*, **26** (1898), 454. By interpolation of these data, the saturated aqueous phase at room temperature (25°) is seen to contain approximately 8 per cent furfural, while the saturated furfural phase contains approximately 5 per cent water.

[3] Compare Schiff, *Ann.*, **220** (1883), 103; Brühl, *Ibid.*, **235** (1886), 7. The freezing point of pure furfural is given by Walden, *Z. physik. Chem.*, **73** (1910), 261, as —36.5°.

[4] Austrian Patent 72,235, August 15, 1915, process for manufacture of a dyestuff from furfural, issued to A. and E. Lederer. One dye obtained according to the specifications of this patent by interaction of furfural and sodium sulfide is a direct dye, fast to wool and silk, and very readily gives shades ranging from light terra cotta to deep seal-brown. The dye obtained by interaction of furfural with ammonium hydrosulfide is claimed by the produced patentees to be fast to wool, silk, and cotton.

[5] D. R. P. 264,915, March 15, 1913, process for the preparation of baths which dye animal and vegetable fabrics direct orange or reddish brown, issued to A. and E. Lederer. These dyes are obtained by interaction of furfural and alkalies. Cotton absorbs the dye very slowly; yellow shades may be obtained by after-treatment in an acid bath.

[6] Unfortunately the analog of malachite green which is obtained by condensation of furfural and dimethylaniline has little promise as a dye stuff, since it is not fast to light. Other interesting color bases have been prepared by condensation of furfural with aromatic amines: Stenhouse *Ann.*, **156** (1870), 199; Schiff, "Ueber Farbstoffbasen aus Furfurol," *Ibid.*, **201** (1880), 355; **239** (1887), 349; de Chalmot, *Ibid.*, **271** (1892), 11; Ehrhardt, *Ber*, **30** (1897), 2012; Knövenagel, *Ibid.*, **31** (1898), 2613; Zincke and Mühlhausen, *Ibid.*, **38** (1905), 3824; Dieckmann and Beck, *Ibid.*, **38** (1905), 4122; *J. prakt. Chem.*, [2] **72** (1905), 555; Carletti, *Zentr.*, II, **1906**, 825, König, *J. prakt. Chem.*, [2] **88** (1913), 193.

with phenols.[1] By interaction of furfural with aniline alone or with acetone in the presence of alkalies, soluble resins are obtained which may prove useful in the varnish industry.[2] Furfural has also found use as a solvent and insecticide.

FURTHER STUDIES ON PHENOLIC HEXAMETHYLENETETRAMINE COMPOUNDS[3]

By Mortimer Harvey and L. H. Baekeland

Laboratory of the Department of Chemical Engineering,
Columbia University, New York, N. Y.

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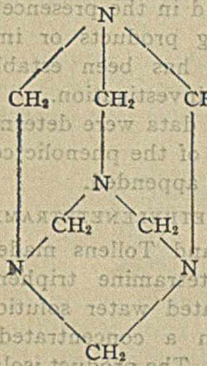
The production of resins or resinoid substances of the Bakelite type[4] by the interaction of phenols with compounds containing an active methylene group has, of late, acquired considerable importance in the industry of coal-tar derivatives. The increasing number of applications of these products in the most diversified fields is stimulating research in many directions. That this industry was born and developed in the United States, which to-day is still the leader in this branch of chemical industry, adds interest to any subject of research which directly or indirectly may throw light on the unusually complicated chemistry of this subject.

The theoretical interpretation of the different phases of the Bakelite reaction is not by any means an easy one, and considerable additional research work will be required before permitting ourselves to do much beyond guessing at what really happens. In the meantime, the careful study of the formation of intermediate products can render us considerable help in this subject. Among these intermediate products, the further advances are amorphous mixtures which are not amenable to the usual methods of chemical purification or isolation. Therefore, it is more natural to start first with the intermediates which are well-defined crystalline bodies of which the chemical composition can be determined by well-established methods. The present research work was, therefore, confined to some of the first phases of the reaction, and more particularly to such bodies as are liable to form when ammonia is used in the process, either as such or in the shape of hexamethylenetetramine.

In the formation of these products of the Bakelite type the methylene-containing body may be commercial formaldehyde solution—known as formalin, formol, etc. This commercial product is practically a mixture of several bodies containing active methylene groups, as, for instance, methylal, formaldehyde, the polymers of formaldehyde, their hydrates, etc. The reaction is favored by the addition of so-called condensing agents, or catalysts—whatever that may mean. Acids, salts, and alkalies have been used for this purpose. In some cases where particular effects have to be obtained, ammonia is preferable. If ammonia is added to formaldehyde or to mixtures of phenol and formaldehyde, the ammonia disappears immediately and becomes hexamethylenetetramine:



so that all these reactions wherein formaldehyde and ammonia are used conjointly can be repeated by the direct use of hexamethylenetetramine. But in presence of phenol, the hexamethylenetetramine does not remain as such. It combines with the phenol in the proportion of three molecules of phenol to one molecule of hexamethylenetetramine and produces a well-defined crystalline product, hexamethylenetetramine triphenol, which has been described by Moschatos and Tollens.[1]

In 1909, Lebach[2] pointed out that whenever ammonia is used in the Bakelite reaction, hexamethylenetetramine triphenol is formed in the first stages of the process. Under the action of heat, this product undergoes a further decomposition and resinifies, emitting ammonia.[3]

Contrary to the results of Moschatos and Tollens, who were unable to prepare addition products of hexamethylenetetramine with any of the three cresols or with carvacrol or thymol, Baekeland had succeeded in his laboratory in preparing a corresponding crystalline cresol derivative, but inasmuch as this work had not been carried out with each one of the completely purified cresols and studied by itself, it seemed desirable that each one of the three homologs should be studied separately as to its individual behavior. This research was also extended to carvacrol and the results obtained thus far are set forth. Similar compounds obtained from other phenolic bodies are now under study. In the meantime, the observations concerning the new cresol derivatives are submitted in the present paper.

The reason of the non-success of Moschatos and Tollens in making the cresol derivatives of hexamethylenetetramine is, mainly, that the isolation of these substances is incomparably more difficult than in the case of phenol. The hexamethylenetetramine triphenol forms rapidly and visibly under almost all circumstances, and crystallizes very well from aqueous solutions or even from solutions when a considerable excess of one of the constituents is used. This is not the case with some of the cresol derivatives.

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[1] Beckmann and Dehn, *Sitzb. Akad. Wiss., Berlin*, **1918**, 1201; *Chem. Abs.*, **14** (1920), 642.

[2] Meunier, "Application du Furfurol à la fabrication de résines à vernis," *Mat. grasses*, **9** (1916), 4516.

[3] Submitted by one of authors in partial fulfilment of the requirement for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York, N. Y.

[4] These substances are also known under other trade names, as for instance, Condensite, Resinit, Sipilite, Redmanol, etc.

[1] *Ann.*, **272** (1892), 271.

[2] *Z. angew. Chem.*, **22** (1909), 1600; *J. Soc. Chem. Ind.*, **32** (1913), 559.

[3] A resumé of the literature on this subject is given by L. H. Baekeland, in "The Chemical Constitution of Resinous Phenolic Condensation Products," This Journal, **5** (1913), 506.

The temperature at which they form lies in some cases so close to the temperature at which they decompose that their formation is almost sure to be overlooked if proper precautions are not taken. Furthermore, some of those products have a tendency to remain liquid in the presence of an excess of some of the reacting products or impurities. That such products exist has been established beyond doubt by the present investigation.

In this work data were determined for the relationship of certain of the phenolic condensation products. The results are appended.

HEXAMETHYLENETETRAMINE TRIPHENOL

Moschatos and Tollens made the easily prepared hexamethylenetetramine triphenol by mixing 6 g. of a concentrated water solution of hexamethylenetetramine with a concentrated solution containing 6 g. of phenol. The product isolated had the following composition:

	Calculated for $C_6H_{12}N_4.3C_6H_5OH$ Per cent	Found by M. and T. 1	 2 Per cent	 3	 4
C_{24}	68.25	68.49	68.09	...	...
H_{30}	7.11	7.34	7.44	...	...
N_4	13.27	...	...	13.65	13.77

All the phenols do not react with hexamethylenetetramine to form an addition product in which there are one mole of hexamethylenetetramine and three moles of the phenol. The various groupings about the benzene ring seem to determine the extent to which the addition takes place. The three cresols whose structural formulas are nearly identical with that of ordinary phenol and whose properties are somewhat similar to the latter should form addition compounds the same as does phenol.

HEXAMETHYLENETETRAMINE DI-*m*-CRESOL

The *m*-cresol addition product is the most easily obtainable. At first ordinary *m*-cresol was used in both dilute and concentrated alcoholic solutions; but the expected crystalline intermediate addition products did not appear. The alcoholic solutions were refluxed several hours and the concentrated solutions allowed to stand several weeks to see if the compound would crystallize out. No crystalline product was obtained in this case. There must have been some impurity in the cresol that hindered the formation, for with cresol purified according to Fox and Barker[1] the product crystallized out in 40 min.

A mixture of 315 g. of *m*-cresol and 136 g. of hexamethylenetetramine was heated for an hour in 80 cc. of a 60 per cent (60 parts by volume of alcohol and 40 parts by volume of water) alcoholic solution. Too much heating caused the addition product to decompose and pass over into the noncrystallizing resinous material. By withdrawing portions of the mixture from time to time, and cooling slightly, it could be observed, by the formation of crystals, when the most favorable point was reached before resinification set in. On stopping the heating, crystals appeared even in the hot solution. The crystals were filtered off and pressed on a porous tile to get rid of the adhering sirupy material. The product was then dissolved in hot 95 per cent alcohol. On cooling, long, fine, needle-like crystals separated out.

Analysis showed that the substance was not formed on a 1: 3 basis as is the case with the ordinary hexamethylenetetramine triphenol, but was an addition product of 1 mole of hexamethylenetetramine and 2 moles of *m*-cresol.

	Calculated for $C_6H_{12}N_4.2C_6H_4OH.CH_3$ Per cent	Found 1	 2	 3 Per cent	 4	 Av.
C_{20}	67.40	67.45	67.23	...	...	67.34
H_{28}	7.87	8.03	7.80	...	...	7.96
N_4	15.73	...	...	15.59	15.80	15.69

Hexamethylenetetramine di-*m*-cresol has not a true melting point, since when the substance is held at a temperature around its point of liquefaction, 90° C., it undergoes decomposition, passing over into the irreversible resinous stage. The compound is very soluble in hot 95 per cent alcohol, the solubility increasing with the temperature. A characteristic feature is that when it is placed in a sufficient amount of water or ether there is a very decided tendency towards a splitting of the product. In water the solubility of the hexamethylenetetramine shows up predominantly, as it is dissolved by the water leaving insoluble cresol as an oil. In ether the solubility of the *m*-cresol predominates, and the compound breaks up leaving the insoluble hexamethylenetetramine as a precipitate. The solubility in benzene is moderate, but increases with the temperature. Acetone has the same effect on the substance as has ether, that is, breaking up the structure by dissolving out the soluble cresol and leaving the insoluble hexamethylenetetramine.

HEXAMETHYLENETETRAMINE DI-*p*-CRESOL

Pure *p*-cresol was first made from *p*-toluidine. When it was found that an addition product was formed with hexamethylenetetramine, a larger quantity of the material was made by the method given by Fox and Barker.[1]

A mixture of 385 g. of *p*-cresol and 167 g. of hexamethylenetetramine in 150 cc. of 95 per cent alcohol was heated on a steam bath for 1.5 hrs. The same precaution must be observed here as in the case of the formation of the *m*-cresol compound. On allowing the liquid to stand at room temperature, crystals separate out. The compound was recrystallized from 50 per cent alcohol.

The addition product has no melting point, but begins to resinify at the temperature of liquefaction, 87.0° C. The decomposition is shown when the substance turns brown and partially resinifies upon heating in a sealed glass tube for 3 hrs. at a temperature of 90° to 100°.

Analysis shows that it has the same proportion of the two constituents as the *m*-compound, namely, 1 mole of hexamethylenetetramine and 2 moles of *p*-cresol.

	Calculated for $C_6H_{12}N_4.2C_6H_4OH.CH_2$ Per cent	Found 1	 2	 3 Per cent	 4	 Av.
C_{20}	67.40	67.18	67.35	...	...	67.27
H_{28}	7.87	8.20	8.01	...	...	8.10
N_4	15.73	...	...	15.82	15.71	15.76

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[1] *J. Soc. Chem. Ind.*, 37 (1918), 260.

[1] *Loc. cit.*, p. 268.

The same qualitative solubilities as applied to the *m*-cresol product apply to the *p*-cresol compound.

HEXAMETHYLENETETRAMINE MONO-*o*-CRESOL

Pure *o*-cresol was made according to the method of Fox and Barker.[1]

A mixture of 475 g. of *o*-cresol and 205 g. of hexamethylenetetramine in 100 cc. of 95 per cent alcohol was heated on a water bath for 2.5 hrs. On allowing to cool at room temperature, crystals separated out. These were recrystallized from 95 per cent alcohol.

The compound behaves somewhat differently from the *p*- and *m*-cresol addition products, since on heating there was no sharp melting point to the liquid stage, followed by a final passing over to the resinous material. A small portion seemed to soften on heating and show signs of melting, but most of the substance either sublimed or charred.

Analysis showed that the proportion of hexamethylenetetramine to *o*-cresol was 1: 1.

	Calculated for $C_6H_{12}N_4.C_6H_4OH.CH_3$	Found			
		1	2	3	4
	Per cent		Per cent		
C_{13}	62.90	63.12	63.20	...	...
H_{20}	8.07	8.07	7.94	...	...
N_4	22.55	...	...	22.74	22.69

It was thought that it might be possible to isolate a compound of *o*-cresol which would have the same proportions of the two constituents as have the *p*- and the *m*-cresol intermediates. The crystals of hexamethylenetetramine were dissolved directly in the *o*-cresol, and with portions of this solution various runs were made in which the time factor of heating was the variable. Heating was accomplished on a water bath, the time varying from 2 to 10 hrs. For the runs with a small amount of heating the solution was clear, while with the runs extending over 10 hrs. the solution was dark brown, showing that a reaction had set in with the formation of the resinous material. After allowing the solutions to stand several days the crystals were filtered off, pressed on porous tile, and recrystallized from alcohol. In all cases analysis of the crystals showed that the product was a compound with a 1: 1 proportion of hexamethylenetetramine and *o*-cresol.

Crystals obtained after 8 hrs.' heating showed the following composition:

	Calculated for $C_6H_{12}N_4.C_6H_4OH.CH_3$ Per cent	Found Per cent
C_{13}	62.90	63.04
H_{20}	8.07	8.22
N_4	22 55	22.70

From this it appears that there is but one addition product of *o*-cresol and hexamethylenetetramine, and that is with one mole of each of the two constituents present.

HEXAMETHYLENETETRAMINE HYDROQUINOL

Moschatos and Tollens[2] give for the preparation of this compound 4 g. of hexamethylenetetramine in 5 g. of water mixed with 33 g. of hydroquinol in 4 g. of water. The product, purified by washing with water and with ether, and drying over sulfuric acid, analyzed as follows:

	Calculated for $C_6H_{12}N_4.C_6H_4(OH)_2$	Found by M. and T.		
	Per cent	1	2	3
C_{12}	57.60	57.20	...	...
H_{18}	7.20	7.77	...	...
N_4	22.40	...	22.57	22.47

This was checked up as follows: 5 g. $C_6H_4(OH)_2$ in 9 cc. of water were mixed with a solution of 6 g. of hexamethylenetetramine in 10 cc. of water. The solution was heated on a water bath for 30 min., then allowed to stand over night. Crystals washed with water, then ether, and dried over sulfuric acid. Analysis showed:

	Calculated for $C_6H_{12}N_4.C_6H_4(OH)_2$ Per cent	Found Per cent
C_{12}	57.60	57.35
H_{18}	7.20	7.11
N_4	22.40	22.46

On heating, part of the compound sublimed and part charred with very little melting. This behavior is similar to that of the hexamethylenetetramine *o*-cresol compound.

HEXAMETHYLENETETRAMINE RESORCINOL

Moschatos and Tollens formed the compound by heating a mixture of 2 g. of hexamethylenetetramine dissolved in 3 g. of water and 3 g. of resorcinol dissolved in 3 g. of water. The composition of the compound was found by Moschatos and Tollens to be as follows:

	Calculated for $C_6H_{12}N_4.C_6H_4(OH)_2$	Found by M. and T.			
		1	2	3	4
	Per cent		Per cent		
C_{12}	57.60	57.14	57.35	...	...
H_{18}	7.20	7.43	7.42	...	...
N_4	22.40	...	...	22.09	22.32

By following the same order of procedure as outlined above, a precipitate was easily obtained. On analysis the composition was found to be the same as that represented by Moschatos and Tollens:

	Calculated Per cent	Found Per cent
C_{12}	57.60	57.39
H_{18}	7.20	7.10
N_4	22.40	22.34

This compound also shows no melting point, which is similar to the hydroquinol and the *o*-cresol intermediates. It seems to be a characteristic feature of the hitherto observed phenol hexamethylenetetramine compounds that it is necessary that there be at least 2 moles of the phenol to 1 of the hexamethylenetetramine in order that there be a well-defined point of liquefaction.

HEXAMETHYLENETETRAMINE CARVACROL

The carvacrol obtained for use in this work was made from cymene.[1] It ran 93 per cent pure, the other constituents being approximately 6 per cent thymol and 1 per cent thiophenols. The product was purified according to the method developed by Mr. Allan Leerburger:

> A very stiff paste of the carvacrol and lead acetate was allowed to stand at room temperature for 30 hrs. The mass was broken up and the phenols extracted with petroleum ether. The carvacrol-lead acetate compound is soluble in the petroleum ether, whereas the thymol-lead acetate is insoluble in the ether, giving a means of separating the two phenols. After allowing the petroleum ether to evaporate, the liquid was washed with

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[1] *Loc. cit.*

[2] *Ann.*, **272** (1892–3), 282

[1] Hixson and McKee, THIS JOURNAL, **10** (1918), 982

a normal solution of mercuric chloride (using as the solvent 50 parts by volume of water and 50 parts by volume of alcohol). This removes the thiophenols, leaving the carvacrol as the oil. The carvacrol then distilled in a 4-bulb fractionating column, the portion boiling between 237° and 239° C. being taken.

One mole of hexamethylenetetramine in just sufficient 95 per cent alcohol to dissolve the crystals was mixed with 3 moles of the purified carvacrol. The mixture was heated on a water bath for 40 hrs., then allowed to stand at room temperature for 1 wk. The uncrystallized mass was dissolved out by mixing with kerosene. The fine precipitate was filtered, and the crystals dissolved in hot 95 per cent alcohol. On cooling the alcoholic solution the compound crystallized out readily. Further purification was made by repeating the crystallization from hot 95 per cent alcohol.

The compound shows a point of liquefaction at 148° C., at which point it resinifies quickly. It is very soluble in hot 95 per cent alcohol, but insoluble in the cold alcohol. An important point is that it is very soluble in ether and acetone. Some of the cresol compounds, as has been stated, may be broken up in water, ether, and acetone, the two latter solvents dissolving out the easily soluble cresols and leaving the insoluble hexamethylenetetramine as a precipitate. This difference in solubility between the carvacrol and cresol compounds may be due to the difference in linkings of different phenols with the hexamethylenetetramine.

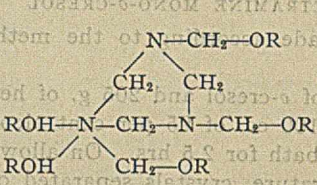
Analysis showed that the compound was not of the same order of addition as were cresol and phenol products, which were in the proportion of 1 mole of hexamethylenetetramine to 2 moles of the *m*- or *p*-cresol, and 3 moles of phenol to 1 mole of hexamethylenetetramine. The composition was found to be as follows:

	Run 1 Per cent	Run 2 Per cent	Average Per cent
Carbon	76.95	77.10	77.02
Hydrogen	9.20	9.27	9.23
Nitrogen	4.92	4.99	4.96

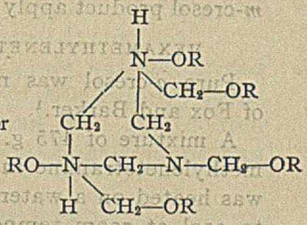
From the table below it is clearly seen that the hexamethylenetetramine is not directly added to the carvacrol as it is in the case of the cresols and phenols.

	$C_6H_{12}N_4.C_{10}H_{14}O$	$C_6H_{12}N_4.2C_{10}H_{14}O$	$C_6H_{12}N_4.3C_{10}H_{14}O$	Found
Carbon	66.25	71.00	73.25	77.02
Nitrogen	19.35	12.75	9.50	4.96
Hydrogen	8.96	9.10	9.16	9.23

The percentages found do not correspond to any simple proportion of addition, as was shown in the case of the other phenols mentioned. However, if we assume that a nitrogen is broken out of the structure of the hexamethylenetetramine to form ammonia with hydrogens of the hydroxyls of 3 moles of carvacrol, and further that 2 moles are taken up additively by one or two of the other nitrogens, the percentages of carbon, hydrogen, and nitrogen correspond exactly with the percentages as found. The smell of ammonia toward the end of the heating in the formation of this compound seems to bear out this point that ammonia is split out, but no quantitative determination has thus far been undertaken. The diagrams, in which R represents the radical part of the carvacrol structure, illustrate possible arrangements.



or



It is to be pointed out that although the interpretation of the structure of hexamethylenetetramine is thus far rather arbitrary, and although the correct one may be found to be quite different from the above, the percentages of elements will in all cases be the same for the theoretical carvacrol compound.

	Calculated from Above Structure Per cent	Found Per cent	Deviation Per cent
Carbon	76.95	77.02	0.07
Nitrogen	4.84	4.96	0.12
Hydrogen	9.10	9.23	0.13

All this becomes rather easy of interpretation if in the formation of the hexamethylenetetramine carvacrol compound there has been 1 mole of ammonia split out and there have been 2 moles of carvacrol added to one of the nitrogen.

ENERGY RELATIONSHIP OF PHENOLIC HEXAMETHYLENE COMPOUNDS

APPARATUS—For the heat of combustion of the phenol, hexamethylenetetramine, and hexamethylenetetramine triphenol, an Emerson adiabatic bomb calorimeter provided with a proper stirrer and a Beckmann thermometer graduated to give an estimated reading of 0.001° were used. For the heat of solution the bomb was eliminated and the metal can for the water replaced by a glass container. The substance whose heat was to be determined was held in a glass-stoppered weighing bottle, the cover of which was removed by small wires passing through the third hole in the top of the calorimeter jacket.

DATA—The water equivalent of the calorimeter was determined in the ordinary way by burning a material whose heat of combustion was known. Naphthalene from the U. S. Bureau of Standards laboratory was used. By weighing the separate parts of the bomb and accessories, the water equivalent of the bomb was found to be 453 g.; without the bomb it was found to be 70 g. The error in the first number was ±2 g., and that in the second number was ±5 g. Checking these values against other standard substances, 6320 was obtained for benzoic acid, whereas the Bureau of Standards gives 6329 cal. per g. as the correct result. The second value was used in finding the heat of solution of as pure sodium hydroxide as could be made without wasting too much time. The following shows a comparison of the heat of solution of sodium hydroxide as determined by Thomsen, and by Berthelot, and as obtained in this study:

	Kg. Cal.
Thomsen	9.94
Berthelot	9.78
Present work	9.85

The errors here would seem to be due to the varied purity of the NaOH used, rather than to the manipulation of the apparatus.

(*a*) *Heat of solution of hexamethylenetetramine.*

	Kg. Cal.
Run 1	4.902
Run 2	4.896
AVERAGE	4.899[1] (where 1 Cal. = 1000 small calories)

[1] Delepine (*Bull.*, [3] **15**, 1200) gives the heat of solution of hexamethylenetetramine at 15° C. as 4.8 Cal.

(*b*) *Heat of solution of phenol.*

	Kg. Cal.
Run 1	—2.92
Run 2	—2.87
AVERAGE	—2.89[1]

[1] Landolt and Bornstein, 3rd Ed., p. 419, give for the heat of solution of phenol —2.6 Cal.

(*c*) *Heat of reaction of phenol and hexamethylenetetramine in an aqueous solution*—In this observation the phenol was first added to the water, then solid hexamethylenetetramine added in the manner stated above. The excess of rise of temperature above that given by the hexamethylenetetramine would be due to the reaction of the amine and the phenol. This is the weak point of this method of determining the heat of formation of hexamethylenetetramine triphenol, since it is difficult to obtain accurately the amounts of amine and phenol that have combined in solution. After the reaction the hexamethylenetetramine solution was distilled to obtain the phenol, the amount of which was determined by the tribromophenol method.[1] The error in this way would be in the dissociation of the triphenol compound on distillation of the phenol. It was found that the energy reaction was

$$(CH_2)_6N_4Aq. + 3C_6H_6OAq. = (CH_2)_6N_4.3C_6H_6O.Aq. + 3.739 \text{ Cal.}$$

(*d*) *Heat of formation of hexamethylenetetramine.*

Heat of combustion of commercial hexamethylenetetramine:

Run 1—7.380 Cal. per g. at constant volume

Heat of combustion of hexamethylenetetramine resublimed in laboratory:

Run 2	7.397 Cal. per g. at constant volume
Run 3	7.399
AVERAGE	7.398

By means of the Hempel gas apparatus and freshly prepared solutions of sodium hydroxide and pyrogallol, the following results on the products of combustion were obtained:

PRODUCTS	Actual Result Grams	Theoretical Result Grams
N_2	0.40	0.38
HNO_3	0.119	0.112
CO_2	1.80	1.88

To represent the above results we can write the equation

$$(CH_2)_6N_4 + 18.55(O) = 6CO_2 = \\ 5.89H_2O + 1.89N_2 + 0.22\,HNO_3 + 0.1036.9 \text{ Cal.}$$

We know that

$$6(C) + 12(O) = 6CO_2 + 6 \times 96.98 \text{ Cal.} \qquad (1)$$

(Land. and Born., 4th Ed., p. 855)

$$11.78(H) + 5.89(O) = 5.89H_2O + 68.357 \times 5.89 \text{ Cal.} \qquad (2)$$

(Land. and Born., 4th Ed., p. 850)

$$0.22(H) + 0.22(N) + 0.66(O) = 0.22HNO_3 + 41.60 \text{ Cal.} \qquad (3)$$

(Land. and Born., 4th Ed., p. 854)

Substituting these three equations in the found equation above, we have:

$$6(C) + 12(H) + 4(N) = (CH_2)_6N_4 — 43.18 \text{ Cal.}$$

Therefore the heat of formation of hexamethylenetetramine = —43.18 Cal.

(*e*) *Heat of formation of phenol*—Berthelot[1] gives the heat of combustion of phenol at constant pressure and 18° C. as 736.00 Cal. per mole.

Required: $6(C) + 6(H) + (O) = C_6H_6O + x \text{ Cal.}$

Found: $C_6H_6O + 14(O) = 60\,O_2 + 3H_2O + 736.00 \text{ Cal.}$

We know that:

$$6(C) + 12(O) = 60\,O_2 + 96.98 \text{ Cal.} \qquad (1)$$

$$3H_2 + 30 = 3H_2O + 68.36 \times 3 \text{ Cal.} \qquad (2)$$

Substituting Equations 1 and 2 in the found equation we obtain

$$6(C) + 6(H) + O = C_6H_6O + 50.96 \text{ Cal.}$$

Accordingly the heat of formation of phenol is 50.96 Cal. per mole. This value is different from the one Berthelot gives[2] because he uses the heat of formation of CO_2 as 94.30 Cal. and the heat of formation of water as 69.00 Cal. These values are not considered correct and better values are used in the calculations above.[3] The value 736.00 Cal. per mole for the heat of combustion of phenol is used here because it represents the value obtained in this research.

(*f*) *Heat of solution of hexamethylenetetramine triphenol.*

Average value obtained was —10.671 kg. Cal.

(*g*) *Heat of formation of hexamethylenetetramine triphenol.*

The heat of combustion of hexamethylenetetramine triphenol at constant pressure was found to be 3228.30 Cal. per mole.

Required: $24(C) + 30(H) + 3(O) + 4(N) = (CH_2)_6N_4.3C_6H_6O + x \text{ Cal.}$

Found: $(CH_2)_6N_4.3C_6H_6O + 30.73(O) = 24CO_2 + 14.71H_2O + 1.71N_2 + 0.58HNO_3 + 3228.30 \text{ Cal.}$

We know:

$$24(C) + 48(O) = 24(CO_2) + 96.98 \times 24 \text{ Cal.} \qquad (1)$$

$$29.42(H) + 14.71(O) = 14.71H_2O + 68.357 \times 14.71 \text{ Cal.} \qquad (2)$$

$$0.58(H) + 0.58(N) + 1.74(O) = \\ 58\,HNO_3 + 41.60 \times 0.58 \text{ Cal.} \qquad (3)$$

Substituting these three equations in the above found equation and solving, we obtain the required equation:

$$24(C) + 30(H) + 3(O) + 4(N) = \\ (CH_2)_6N_4.3C_6H_6O + 128.76 \text{ Cal. per mole}$$

The heat of formation of hexamethylenetetramine triphenol, starting with crystals of phenol and amine, is as follows:

Required: Hexamethylenetetramine + 3 phenol = H.T.P. + x Cal.

or $(CH_2)_6N_4(\text{crys.}) + 3C_6H_6O(\text{crys.}) = (CH_2)_6N_4.3C_6H_6O(\text{crys.}) \times \text{ Cal.}$

We know:

$$6(C) + 12(H) + 4(N) = (CH_2)_6N_4 — 43.18 \text{ Cal.} \qquad (1)$$

$$18(C) + 18(H) + 3(O) = 3C_6H_6O + 3 \times 50.96 \text{ Cal.} \qquad (2)$$

$$24(C) + 30(H) + 3(O) + 4(N) = \\ (CH_2)_6N_4.3C_6H_6O + 128.76 \text{ Cal.} \qquad (3)$$

Subtracting (1) and (2) from (3) we obtain:

$$(CH_2)_6N_43C_6H_6O = (CH_2)_6N_4.3C_6H_6O + 19.06 \text{ Cal.}$$

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[1] Allen's "Commercial Organic Analysis," 8th Ed., Vol. 3, p. 307.

[1] *Ann. chim. phys.*, [6] **3** (1888), 326.

[2] Vol. 2, p. 818.

[3] Landolt and Bornstein, 4th Ed., p. 855.

(*h*) *Heat of combustion of hexamethylenetetramine di-p-cresol.*

	At Constant Volume, 20° C. Cal. per G.
Run 1	8.024
Run 2	7.992
Average	8.008

(*i*) *Heat of combustion of hexamethylenetetramine di-m-cresol.*

At constant volume and 20° C. = 8.010 Cal. per gram

(*j*) *Heat of combustion of hexamethylenetetramine mono-resorcinol.*

	At Constant Volume and 20° C. Cal. per G.
Run 1	6.730
Run 2	6.700
Average	6.715

In the addition reactions of hexamethylenetetramine with a phenol thus far investigated there does not seem to be any definite rule by which one is enabled to determine the number of moles of phenol that will combine with the hexamethylenetetramine.

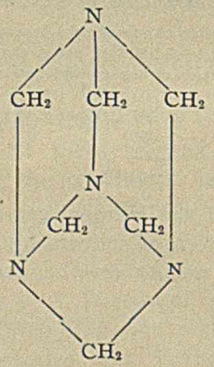
Falk and Nelson[1] have assumed that in catalytic reactions there are binary and ternary compounds formed. Kendall[2] has called attention to the important general rule that stable addition compounds are formed when there is a marked chemical contrast (acidic and basic) between the two reacting components. Thus in the additive compound formed between organic acids and phenols, the stability is very much greater when the organic acid is strong and the phenol weak, or *vice versa*, than in the case in which both substances exhibit the same degree of acidity. A similar generalization holds for the addition compounds between two acids, or between an acid and a ketone, or an acid and an aldehyde.

In the case of the addition compounds formed in this work we have the phenol acting as the acid and the hexamethylenetetramine as the base. It might be assumed from this and from Kendall's generalization that the greater the chemical contrast the greater the stability of the compounds formed, and the greater the number of moles of phenol combining with the basic hexamethylenetetramine. This is not the case, however, in this instance. The degree of acidity seems to have very little to do with the extent of the reaction. Ordinary phenol, which is a weaker acid than *o*-cresol, combines in the proportion of three moles of phenol to one of hexamethylenetetramine, whereas the cresol combines in the proportion of 1: 1. Nitric acid, a very strong acid in comparison with the phenol, combines only in the proportion of 1 mole of hexamethylenetetramine to 2 moles of acid. Hence we cannot apply the generalization stated above to the case of phenol addition products. Again, the three cresols have practically the same order of hydrogen-ion concentration,[3] but with the *p*- and *m*-compounds there are 2 moles adding, whereas with the *o*-cresol there is only 1 mole adding to the hexamethylenetetramine.

Since the activity of phenol is greatly diminished in the case of the cresols, by the presence of a methyl group, it might be said that the more negative the benzene ring is made with negative groups (nitro and hydroxy) the greater the activity and the greater the number of moles uniting. With hydroquinol and resorcinol, where there are two hydroxy groups, the opposite is true. They react slowly with hexamethylenetetramine, and then only in the proportion of one mole of the phenol to one of the amine. Picric acid, which contains three nitro groups and one hydroxy group, should represent a substance in which the benzene ring has practically the maximum of negative groups, and hence should have high combining properties. Moschatos and Tollens found that the proportion was only 1: 1. As yet no rule can be laid down connecting the acidity, or the degree to which the benzene ring is made negative by negative groupings, with the additive properties of phenols and hexamethylenetetramine.

Why should two moles of *p*- and *m*-cresol unite with one mole of hexamethylenetetramine, while only one mole of *o*-cresol unites with one mole of amine? One difference lies in the structure assumed for the three cresols. The hydroxy group of the *p*- and *m*-cresols has on each side of it a hydrogen, while the hydroxy group of *o*-cresol has a hydrogen on but one side. From this it would seem that the extent of addition depends upon the number and activity of the hydrogens adjacent to the reacting hydroxy group.

The structure of hexamethylenetetramine as given by



does not seem to represent all the facts as presented by the addition products with phenols. Here the four nitrogens are all tertiary in character and we should expect that hexamethylenetetramine would add four moles of an alkyl halide. A. Wohl[1] found that but one mole of methyl iodide was taken up additively. In all the phenol addition compounds that have been isolated there is not one case where the number of moles of phenol combining with one mole of hexamethylenetetramine is greater than three. In the carvacrol compound found in this investigation there is strong evidence that one nitrogen is more reactive than the others. This is shown by the fact that ammonia has been split out with one of the nitrogens before one of the other three has added any phenol.

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[1] *J. Am. Chem. Soc.*, **37** (1915), 1732.

[2] *Ibid.*, **36** (1914), 2498.

[3] Scudder, "Conductivity and Ionization Constants."

[1] *Ber.*, **19** (1886), 1840

Hexamethylenetetramine is formed from ammonia and formaldehyde. Tertiary amines are formed from ammonia and an alcohol. Alcohol is a lower oxidation product than is the aldehyde. Again, amides are formed from ammonia and an acid, the latter being of a higher oxidation than the aldehyde. From this we might expect that hexamethylenetetramine should not be represented wholly as a tertiary amine, but should exhibit a character midway between the tertiary amine and an amide.

It does not seem from these considerations that the structure of hexamethylenetetramine is properly represented when written in the above manner.

STUDIES ON BAST FIBERS. II—CELLULOSE IN BAST FIBERS

By Yoshisuke Uyeda

Laboratory of Agricultural Chemistry, University of California Agricultural Experiment Station, Berkeley, Cal.

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In a previous paper,[1] the proximate analysis of Korean bast fibers, according to the modified methods proposed by Dore,[2] for the analysis of wood, was discussed from the standpoint of textile chemistry. The scheme of analysis proposed by Dore was found to be well applicable to cellulose material other than wood.

Generally speaking, our knowledge of the nature of the substances which make up the structure of the materials belonging to so-called compound cellulose, and of the forms in which these substances are present, as well as their special functions in the plant, is still very limited. One of the chief reasons for this is that no accurate method for the analysis of cellulose-containing material has been established, and consequently the results obtained by the various investigators have not been directly comparable. From this point of view, the analytical studies recently made by Dore may be regarded as a forward step in cellulose chemistry.

Cellulose is the chief constituent of the bast fibers, and the amount of it in the fiber is, to a great extent, a measure of its industrial importance. For instance, the full bleached textile goods of the bast fibers may be considered chiefly composed of cellulose itself. In determining the cellulose content of the bast fibers by the chlorination method, the alkali treatments before chlorination were found to have an important effect on the yields of cellulose as reported in the previous paper.

In the present paper, the effects of various preliminary treatments before chlorination on the yields of cellulose are presented, and the properties of the cellulose thus obtained are studied and discussed from the standpoints of cellulose and textile chemistry.

SCOPE OF THE WORK

The original method of Cross and Bevan[3] for the determination of cellulose is taken as a starting point of the work. Renker[4] published a critical study of the determination of cellulose in various cellulose materials; and in his method the material was directly subjected to chlorination by the Cross and Bevan method without the preliminary alkali treatment. Schorger[1] also confirmed the method of Renker by his experiments with woods. Johnsen and Hovey[2] proposed a new method of hydrolysis, using a mixture of glacial acetic acid and glycerol before chlorination in the cellulose determination. Recently Dore[3] compared these three methods of treatment in the case of wood and decided in favor of the Renker procedure.

Now, it is of much interest to determine whether the relation which was found by Dore is applicable to bast fibers. The bast fibers, which belong to the so-called pectocelluloses, differ much in composition from woods, which are classified as lignocelluloses, and contain substances which are easily converted into soluble forms by the action of alkali.

In the present work, the same three methods are used. After preparation by (1) no preliminary hydrolysis, (2) alkali hydrolysis, and (3) acid hydrolysis, the materials are subjected to chlorination, according to the improved method of Johnsen and Hovey, which was also recommended by Dore. But it is very obvious that the yields of cellulose obtained by these three methods are not directly comparable. Whether a smaller yield may indicate a purer cellulose or may signify a partial destruction of the cellulose itself is very questionable. It is, therefore, very necessary to standardize the purity of the cellulose thus obtained. In this work two methods are available for this requirement. One is to determine the quantity of α- or normal cellulose in the residue of the various cellulose processes by using the mercerization test of Cross and Bevan,[4] as recommended by Dore,[5] of this laboratory, and the other is to estimate the furfural yield by Tollens and Kroeber's method.[6]

EXPERIMENTAL

The Korean hemp fiber whose proximate composition was given in the previous paper[7] is taken as the sample material for this investigation. The fiber is cut into small pieces, having an average length of 1 cm., and preserved in a Mason fruit jar throughout the experiment. Portions of one gram each are weighed and dried for 16 hrs. in a constant temperature electric oven kept at 100° C., extracted for 6 hrs. with benzene, then for 6 hrs. with 95 per cent alcohol, as described in the previous paper. After this treatment, the cellulose estimations are made in three ways, as described in the paper published by Dore.[8] Results are given in Table I.

From Table I it will be seen that the results for yield of cellulose by Method 1 are in good agreement, but those from Methods 2 and 3 vary considerably be-

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[1] This Journal, **12** (1920), 573.

[2] *Ibid.*, **11** (1919), 556.

[3] "Cellulose," 2nd Ed., p. 95.

[4] "Bestimmungsmethoden der Cellulose," Berlin, **1910.**

[1] This Journal, **9** (1917), 561.

[2] *Paper*, **21** (1918), No 23, 36.

[3] This Journal, **12** (1920), 264.

[4] "Paper Making," **1918**, p. 97.

[5] This Journal, **11** (1919), 556.

[6] *J. Landw.*, **48** (1900), 357.

[7] Uyeda, *Loc. cit.*

[8] This Journal, **12** (1920), 266.

tween individuals. In other words, absence of hydrolysis before chlorination gives a better result than any hydrolytic treatment preceding chlorination, from the standpoint of analytical chemistry.

TABLE I—WEIGHTS OF RESIDUE BY VARIOUS HYDROLYTIC PROCESSES, AND COMPARISON OF CELLULOSE OBTAINED BY THE THREE METHODS
(Percentage on Air-dry Basis—8.83 Per cent Moisture)

	Residue after Hydrolysis		Cellulose	
TREATMENT	Individual	Average	Individual	Average
1—Renker's modification of Cross and Bevan's method, no hydrolysis			71.08	
			71.14	
			70.80	
		88.05[1]	70.44	70.81
2—Original Cross and Bevan method, treated for 30 min. with 1 per cent NaOH	67.92		63.28	
	68.97		64.66	
	70.90		65.82	
	69.80	69.39	65.99	64.93
3—Johnsen and Hovey's method, treated for 4 hrs. with acetic acid and glycerol	76.42		67.60	
	75.34		67.16	
	77.80		70.02	
	77.02	76.64	69.54	68.58

[1] Loss on drying	8.83
Loss on extraction with benzene	1.92
Loss on extraction with alcohol	1.20
Total	11.95
Average residue by difference	88.05

Next, the α- or normal cellulose in the total cellulose residues thus obtained by various methods is determined by means of the Cross and Bevan mercerization test. The dry material in the Gooch crucible is transferred as completely as possible to a small beaker, 50 cc. of cold 17.5 per cent NaOH solution are added, and allowed to stand just half an hour. At the end of that period it is diluted with 50 cc. of cold water, filtered off on the original Gooch crucible, and washed with about one liter of cold water, then with acetic acid several times, and finally with sufficient cold water. It is dried for 16 hrs. at 100° C., and weighed. The results are tabulated in Table II.

TABLE II—α-CELLULOSE FROM TOTAL CELLULOSE OBTAINED BY THREE METHODS
(Percentage on Air-dry Basis—8.83 Per cent Moisture)

	Total Cellulose		α-Cellulose		Ratio α-Cellulose: Total Cellulose
TREATMENT	Individual	Av.	Individual	Av.	
1—Renker's method	71.08		63.98		
	70.44	70.76	62.44	63.21	0.89
2—Original Cross and Bevan method	64.66		59.79		
	65.99	65.32	61.22	60.50	0.92
3—Johnsen and Hovey's method	70.02		61.30		
	69.54	69.78	62.68	61.99	0.88

If the yield of α-cellulose from the total cellulose be considered as a basis of standardization of the cellulose obtained, it will be seen that the cellulose obtained by the original Cross and Bevan method shows the highest purity of the three, and the other two indicate about the same degree.

TABLE III—FURFURAL YIELDS OF THE CELLULOSE
(Percentage on Air-dry Basis—8.83 Per cent Moisture)

	Furfural from Total Cellulose		Furfural from α-Cellulose		Ratio of Furfural from α-Cellulose to Furfural from Total Cellulose
TREATMENT	Individual	Av.	Individual	Av.	
1—Renker's method	1.35		1.12		
	1.98	1.66	1.14	1.13	0.68
2—Original Cross and Bevan method	1.40		0.78		
	2.09	1.74	0.78	0.78	0.44
3—Johnsen and Hovey's method	1.06		0.56		
	0.83	0.94	0.57	0.56	0.59

Determinations of the furfural yields of the total and α-cellulose obtained by the three processes are made by subjecting the material to distillation with 12 per cent hydrochloric acid and precipitating the furfural in the distillate with phloroglucinol solution as furfural phloroglucide. A Gooch crucible with an asbestos filter is conveniently used, and the results are expressed in terms of furfural calculated from the phloroglucide obtained (Table III).

The total cellulose, as well as α-cellulose, by the Johnsen and Hovey method yields the least quantity of furfural of the three methods used. In determining the furfural yield, the coloration taking place when the phloroglucinol solution is added to the distillate is to be noted.

In the case of total cellulose obtained by Renker's method and by Cross and Bevan's method, the solution first becomes deep brown, but changes into greenish, and on standing, to a deep dark green, and the black precipitate of phloroglucide is obtained. In the case of the total cellulose obtained by Johnsen and Hovey's method, both the solution and the precipitate remain brown, as does the α-cellulose by all three methods. The solution is bright brown and the precipitate has the same color.

DISCUSSION OF RESULTS

It is desirable to discuss the results obtained by the three methods from the standpoint of cellulose chemistry, especially as applied to the textile industry. The physical properties of the cellulose obtained by Renker's method are very different from those of the product by the original Cross and Bevan method. While the latter is entirely separated into individual fibers like cotton fiber, that by Renker's modification retains the form of the original vascular bundle, and is somewhat viscous, apparently due to gummy substance (probably pectin) remaining in it. As Renker, Schorger, and recently Dore, have brought out with the lignified materials, the cellulose free from lignin may be obtained by Sieber and Walter's modification of the Cross and Bevan chlorination method. But, in the course of the chlorination of the bast fibers, the present author observed that the alkali-treated fiber is more easily bleached to pure white by the chlorination than the other two methods. Sometimes it is found scarcely possible to bleach white by the four periods of successive chlorinations in Sieber and Walter's treatment, especially in the case of the Renker method. Now the physical nature of cellulose obtained by Johnsen and Hovey's method is somewhat similar to that by Renker's method. From these facts it may be concluded that the pectin substance is satisfactorily removed only by alkali treatment, and the cellulose free from pectin in some degree can be obtained only by the original Cross and Bevan method. Therefore, this is the nearest to the true cellulose or normal cellulose of the three obtained. But, as Renker pointed out, it is questionable whether or not the cellulose itself is attacked by the alkali treatment.

Let us now consider these yields of cellulose from the standpoint of textile chemistry. The problem is very important in the bleaching process of the hemp fabrics. In the practice of the bleaching process, dilute alkali treatment, bleaching by hypochlorite (termed "chemicking"), and the exposure to direct sunlight (termed "sun-bleaching") are combined and repeated. The object is to bleach as white as possible without weakening the strength of the fiber. Alkali treatment before chemicking is, of course, very effective in bleaching, and this fact is in good agreement with the observation which is made on the original Cross and Bevan method. There is, however, danger of impairing the strength of the fiber if the alkali treatment is overdone. One of the important reasons for the weakening of the fiber is, in the author's opinion, that the alkali dissolves the pectin substance or the binding material between the individual fibers which make up the bast fiber. If the bleaching operation be carried out ideally, we may expect to find the bleached fabrics of the hemp fibers in the condition of pure cellulose, something similar to the cellulose obtained by Renker's method. As far as these three methods are concerned from the standpoint of textile chemistry, it seems to the author that Renker's method has a most important suggestion as to yield of cellulose.

The chemical nature of the cellulose obtained by these three methods should next be discussed. The mercerization test proposed by Cross and Bevan is very important for the cellulose process, especially in the case of the textile fibers. Not only does it serve as a means of determining the purity of the cellulose itself, but also it shows the chemical behavior of the fiber toward the alkaline reagents, and the latter fact should be duly considered in the practices of the textile industry. Pectin substance which is retained in the cellulose obtained by Renker's and by Johnsen's method may be partly removed by the alkali in the mercerization test, so that the α-cellulose obtained is in the condition of separated individual fibers like cotton.

The determination of furfural yields of the celluloses obtained serve, no doubt, as an indication of the degree of the chemical purity of the cellulose. Johnsen and Hovey's[1] claim as to the purity of cellulose obtained by their proposed method holds true, in some points, in the case of the bast fibers as shown in the present work. Now, the question is as to the mother substance of the furfural yield. As to the chemical composition of the pectin substance, it is very obscure, but several contributions are available by Ehrlich,[2] von Fellenberg,[3] Schwalbe and Becker,[4] and Cross and Bevan.[5] Taking the views of these various investigators into consideration, we may regard the pectin in the bast fibers as partly dissolved during the mercerization tests, and the α-cellulose obtained by the three methods as accordingly yielding less furfural than the total cellulose. We now see that the pectin substance present in the bast fiber is one of the mother substances which give furfural. The furfural-yielding mother substances are designated as "furfural yielding complex" by Cross and Bevan[6] or may be shortened to "furfurose" or "furfurosan." According to Tollens and his pupils, pentosan (araban, xylan, etc.) and methyl pentosan are considered as the chief substances which give the furfural. Pentosan is estimated by Tollens and Kroeber's method,[1] while methyl pentosan can be determined by that of Ellet and Tollens.[2] But, recently, it has been ascertained that besides these carbohydrates belonging to the pentosans, hexosans also yield oxymethylfurfural. Cross and Bevan[3] have assigned to wood cellulose an oxycellulose structure which gives considerable amount of furfural. Cross and Bevan[4] classify the bast fibers in the same group from the point of view of chemical constitution, that is, those of maximum resistance to hydrolytic action and containing no directly active carbonyl group. The present author is of the opinion that the bast fibers, especially hemp fiber, have, in some points, a composition related to wood cellulose; and the cellulose of the hemp itself may have an oxycellulose structure in some degree. The fact that the cellulose obtained from hemp has a much larger affinity towards basic dyestuff than that of cotton may be looked upon as suggesting this view. From these considerations it seems to the present author that when the cellulose, as well as the α-cellulose derived from it, is subjected to distillation with hydrochloric acid by Tollens and Kroeber's method, it gives a mixture of furfural, methylfurfural, and oxymethylfurfural, which, however, is simply expressed in terms of furfural in the present work. While the furfural phloroglucide has a greenish black coloration, methylfurfural phloroglucide is brown.[5] This phenomenon was clearly observed in the present work, in that the α-cellulose gave a brown phloroglucide, consisting chiefly of methylfurfural and oxymethylfurfural. Further study is planned from the standpoint of carbohydrate chemistry.

SUMMARY

1—The estimation of cellulose in bast fibers is made by the three methods proposed, *i. e.*, Renker's modification of Cross and Bevan's method, the original Cross and Bevan method, and Johnsen and Hovey's method, according to the scheme of Dore.

2—The chemical behavior of the cellulose obtained is studied from the standpoint of cellulose chemistry.

3—Renker's modification of Cross and Bevan's method is suggested as the most practical method for the estimation of cellulose in bast fibers from the textile chemistry point of view.

4—The function of pectin substance in bast fibers is discussed.

5—It is suggested that the cellulose of the hemp fiber has, in some degree, an oxycellulose structure.

ACKNOWLEDGMENT

I wish to express my thanks to Mr. W. H. Dore, whose valuable suggestions and direction have made the present work possible.

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[1] *Paper*, **21** (1918), No. 23, 36.

[2] Ehrlich, *Chem.-Ztg.*, **41** (1917), 197.

[3] *Biochem. Z.*, **85** (1918), 118; *Chem. Abs.*, **12** (1918), 2196; *Schweiz. Mittlg. Lebensm. Hyg.*, **5** (1914), 256; *Chem. Abs.*, **9** (1915), 448; *Schweiz. Mittlg. Lebensm Hyg.*, **7** (1916), 42; *Chem. Abs.*, **10** (1916), 2772.

[4] *Z. angew. Chem.*, **32** (1919), 126, 229.

[5] "Cellulose," p. 217.

[6] *Ibid.*, p. 99.

[1] *Loc. cit.*

[2] *J. Landw.*, **53** (1905), 20.

[3] "Cellulose," p. 82.

[4] *Ibid.*, p. 78.

[5] Oshima and Tollens, *Ber.*, **34** (1901), 1425.

LABORATORY AND PLANT

GASOLINE FROM NATURAL GAS. V—HYDROMETER FOR SMALL AMOUNTS OF GASOLINE

By R. P. Anderson and C. E. Hinckley

United Natural Gas Co., Oil City, Pennsylvania

Received October 15, 1920

In testing natural gas for gasoline it is important to determine the gravity of the gasoline obtained. When the quantity of gasoline is insufficient to float the extremely small hydrometers that are available for this purpose, it is convenient to possess an instrument which requires but 4 cc. of gasoline for a gravity determination. Such an instrument is shown in Fig. 1. It is a modification of hydrometers Nos. 4060 and 4072 of Eimer and Amend's 1913 catalog, and may be ordered from this firm.

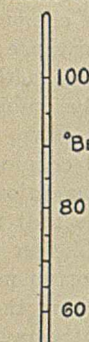

Fig. 1

The instrument is designed for immersion in water at 60° F., and when the bulb B is filled to the mark with gasoline at 60° F. the gravity of the gasoline is obtained directly from the position of the hydrometer in the water, the stem being calibrated from 60° to 100° Bé.

A study of the effect of temperatures other than 60° F. upon the reading of the instrument discloses the fact that the temperature correction is small as compared with that necessary in the case of the ordinary hydrometer. This is because the contraction or expansion of the gasoline with change of temperature is partially compensated for by the corresponding contraction or expansion in the water in which the hydrometer is immersed. The relationship between the contraction (or expansion) of the gasoline and that of the water is shown graphically in Fig. 2. The three, straight, diagonal lines picture the change in weight of 4 cc. of gasoline of three different temperatures.[1] The curved lines show the change in weight of 23 cc. and 47 cc. of water for the same temperature range.[2] Twenty-three cc. represent the proper volume of the hydrometer up to the 80° Bé. mark in order that the most complete temperature compensation may be obtained between 50° and 70° F., and 47 cc. represent a hydrometer volume which gives excellent compensation at the temperature of the maximum density of water.

The actual error in hydrometer reading resulting from incomplete compensation may be computed for any given conditions of temperature, gravity of gasoline, and hydrometer volume as shown in Table I. The effect of the expansion or contraction of the hydrometer with change of temperature upon the degree of compensation is too small to need consideration in this connection.

Table I—Hydrometer Compensation
(Hydrometer Volume 23 Cc., Gravity of Gasoline 80° Bé.)

Temp. ° F.	Change in Weight of Gasoline (4 Cc.)	Change in Weight of Water (23 Cc.)	Uncompensated Change in Weight Total	Uncompensated Change in Weight Per Cc. of Gasoline	Error Degrees Baumé
50	+0.0200	+0.01587	+0.00413	+0.00103	—0.32
55	+0.0100	+0.00890	+0.00110	+0.00027	—0.08
65	—0.0100	—0.01109	+0.00109	+0.00027	—0.08
70	—0.0200	—0.02401	+0.00401	+0.00100	—0.31

Computations of the sort illustrated in Table I have been made for three grades of gasoline (60°, 80°, and 100° Bé.), for temperatures from 32° to 70° F., and for hydrometer volumes of 23 and 47 cc., and the results are shown in graphical form in Fig. 3. An error of +1° Bé. as used in this figure means that 1° Bé. must be subtracted from the observed hydrometer reading to obtain the gravity at 60° F., and with an error of —1° Bé., 1° Bé. must be added. Fig. 3 may thus be used in correcting observed Baumé gravities to a temperature basis of 60° F.

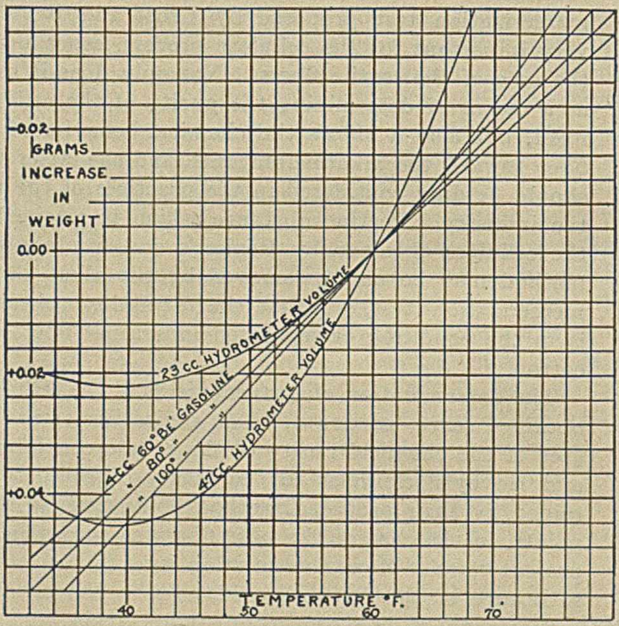

Fig. 2

It will be noted from the figure that the hydrometer with a 23-cc. volume may be used for gravities from 60° to 100° Bé., over a temperature range from 50° to 70° F., with a maximum correction of 0.6° Bé. This portion of the figure is ruled to 1° F. and 0.1° Bé. for convenience in applying corrections.

In the case of the hydrometer with a 47-cc. volume, the most desirable temperature range is from 36° to 40° F. It may be used from 37° to 40° F. with a maximum correction of ±0.6° Bé. At 35.7° F., the correction is zero for 60° Bé. gasoline; for 80° Bé. gasoline the temperature for zero correction is 37.7° F., and for 100° Bé. gasoline, 39.7° F. The 47-cc. hydrometer is the desirable one to employ in obtain-

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[1] The change in weight of 1 cc. of 60° Bé. gasoline for 1° F. is taken as 0.00045 g.; for 1 cc. of 80° Bé. gasoline, 0.0005 g.; and for 1 cc. of 100° Bé. gasoline, 0.00055 g. See This Journal, 12 (1920), 1011.

[2] Data on change of density of water with change of temperature taken from Smithsonian Tables, "Handbook of Chemistry and Physics," 7th Ed., p. 322.

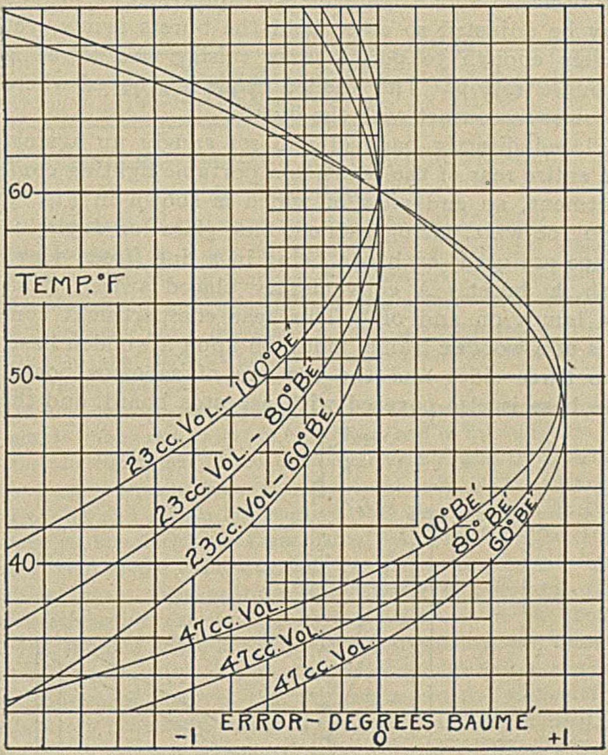


Fig. 3

ing the gravity of gasoline condensed and collected at temperatures not much above 32° F., since, under these conditions, warming to 60° F. would involve a considerable change in gravity as a result of evaporation of the more volatile constituents. It will be noted also that the 47-cc. hydrometer may be employed between 36° and 66° F. with a maximum correction of ± 1.0° Bé.

SUMMARY

1—A hydrometer has been described which makes possible the rapid and fairly accurate determination of the gravity of gasoline when the quantity is insufficient to float the usual type of hydrometer. Only 4 cc. of liquid are necessary.

2—The magnitude of the corrections necessary to change observed gravities to a 60° F. basis depends upon the volume of the hydrometer. A chart has been prepared to be used in making corrections for hydrometer volumes of 23 and 47 cc. The desirable range of temperature for the hydrometer with a volume of 23 cc. is from 50° to 70° F., and for the hydrometer with a volume of 47 cc. from 37° to 40° F. The maximum error for the 47-cc. hydrometer over a range from 36° to 66° F. is ± 1° Bé., and consequently, for approximate work, the correction may be omitted entirely.

A COLD TEST APPARATUS FOR OILS

By G. H. P. Lichthardt

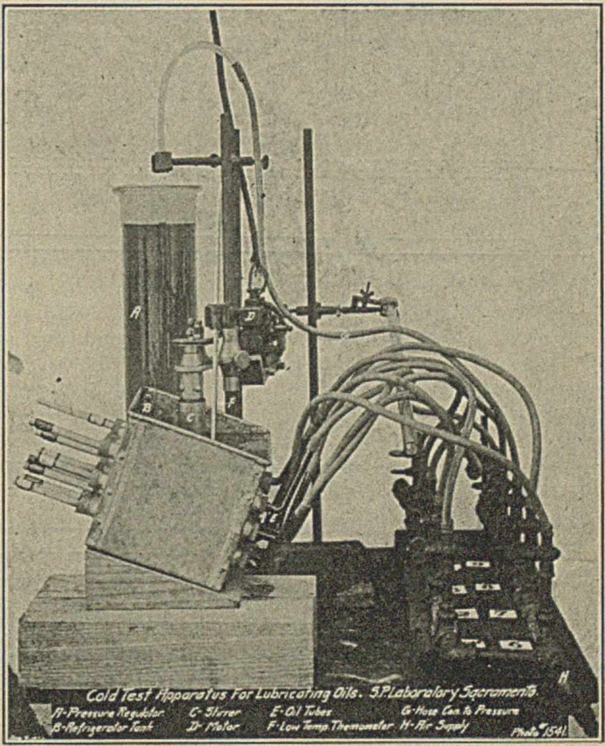
Southern Pacific Railroad Co., Sacramento, California

Received September 27, 1920

The apparatus herein described for making the cold test is the result of an attempt to eliminate, as far as possible, the personal equation in this useful test which has long been used to show, in a comparative manner at least, certain qualities and characteristics of fixed oils. That the test is unsatisfactory has long been recognized by various observers, and to do away with this error, Martens, in a paper which was abstracted in the *Journal of the Society of Chemical Industry* in 1890, recommended that a U-tube be used in a freezing mixture and connected with air pressure, the temperature at which the air begins to flow under these conditions being taken as the cold test of the oil under investigation.

In an attempt to improve the application of methods which would show the lowest temperature at which oils will flow, many of the suggested schemes were tried. Since the one described by Martens seemed to be the most promising, the apparatus which is the subject of this paper was devised.

Results can be obtained within 0.25° F. or less, depending upon the thermometer, and the personal error is to all intents and purposes nil.



The apparatus consists of a refrigerator tank, B, containing nine tubes of glass, 0.3 in. inside diameter, which are bent at one end and are connected with the air supply H. The cooling box is of galvanized iron and square in shape, the dimensions being 6 × 6 × 6 in., and contains the freezing mixture which consists of acetone and carbon dioxide snow. The mechanical stirrer C, operated by the motor D, insures uniform temperatures throughout. The readings are taken from a low-temperature thermometer, F, and the air pressure is regulated by the glass tube inserted in the water contained in the jar A.

The test is applied by placing enough of the oil under investigation in the tube to occupy 6 in. of the tube length, after which the freezing mixture is added, circulation being maintained by the mechanical stirrer. When the oil becomes solid and does not move under an air pressure of 16 in. of water, the temperature is noted and then allowed to rise, which it does very slowly. Readings are taken every quarter or half minute, as the case may be, the appearance of the oil in the straight part of the tube protruding from the box being taken as the "cold test."

TITRATION BENCH

By W. A. VanWinkle
409 East Buttles St., Midland, Michigan

Received November 15, 1920

For making evening titrations[1] under working conditions approximating very good daylight the titration bench herein described and illustrated has proved very satisfactory.

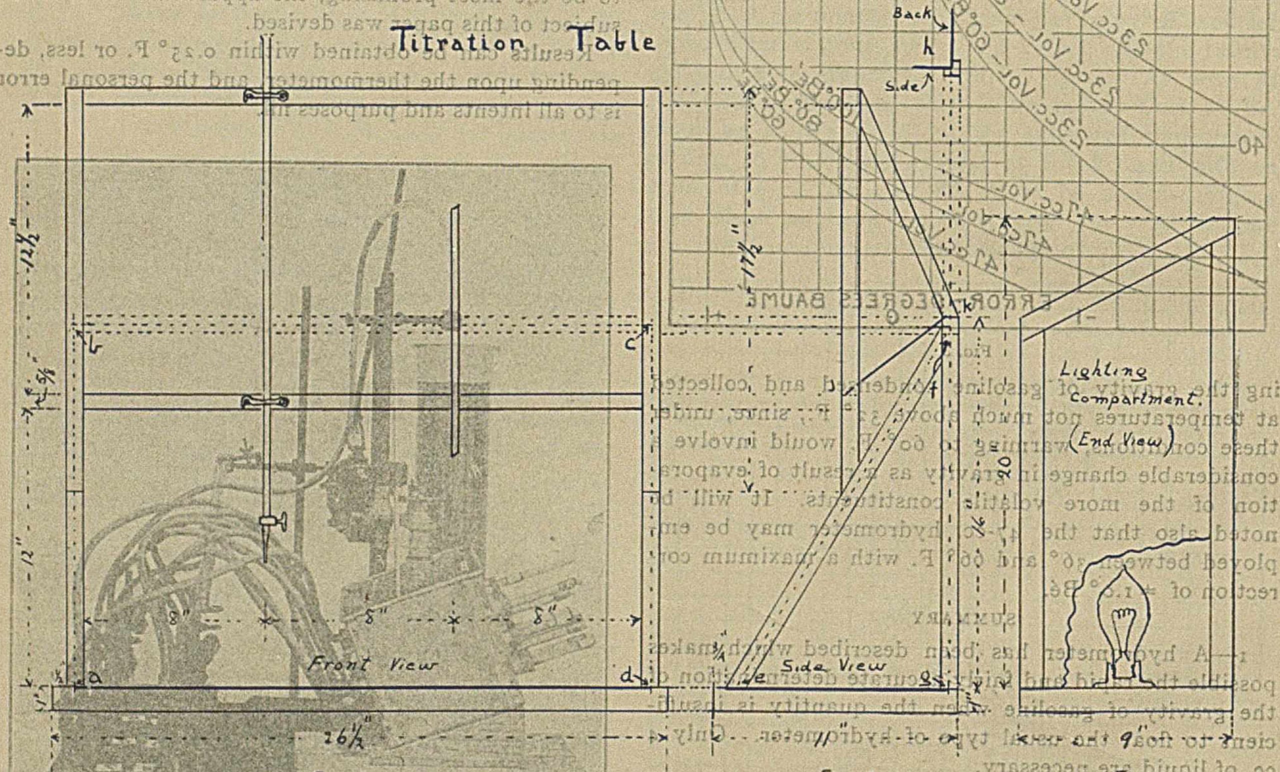


Fig. 1

Fig. 2

Fig. 3

The base is made of one-inch board, 26.5 × 11 in., and has inlaid upon its surface, and placed flush with the border, a glass plate 25 × 10 in., the under side of which has three coats of white (lithopone) paint. (See heavy lines in Figs. 1 and 2.) Mounted upon this base is a hardwood frame, made of $^5/_8 \times {}^5/_8$ in. strips, which holds two triangular ground-glass sides and rectangular ground-glass back in position. One of the triangular plates is indicated by *e*, *f*, and *g*, in Fig. 2; the rectangular plate by *a*, *b*, *c*, and *d* in Fig. 1. These three plates are held securely in position by having the wooden frame slotted or sawed to fit the edges of the plates. The vertical edges of the two sides must be butted snugly up against the back, as shown by *h* in Fig. 2. To protect the eyes of the operator from the light a special rectangular screen of ground glass, 23.25 × 5.5 in., is placed back of the burets, as shown by the end view, *j-k*, in Fig. 2. Each buret is held by two spring-brass hooks, which turn upon screws, which may be adjusted so as to hold the burets firmly, yet loosely enough to permit easy raising and lowering during titration. The wooden frame is grooved where it comes in contact with the burets.

Placed directly back of and set snugly up against the entire rear of the bench is a portable lighting compartment, an end view of which is shown in Fig. 3. Two 100-watt, nitrogen-filled, blue glass (or daylight) lamps are used, each one being in a line (front view) with a buret. A conveniently placed switch turns the lamps on and off. This rear compartment consists of a wooden frame, mounted upon a wooden base. The three sides and the top are of asbestos board. The base is also covered with asbestos board, and the surface of the latter should lie in the same plane as that of the inlaid glass plate lying below the burets; then no interfering shadow will be cast upon this plate. Asbestos board is used to insure against fire and also because its roughened, dull white surface gives a fairly uniform diffusion of the light. For ventilation a hole should be cut in the rear wall up near the top; also one in each side, near the base. Unless this is done the temperature may mount quite high.

All wooden parts are painted a dull white. An electric lamp (not shown) placed on the top of the lighting compartment and on a line midway between the two burets facilitates the reading of the latter. The ground-glass plates are ground upon one side only and the smooth surface should be placed toward the burets, otherwise difficulty will be experienced in cleaning the plates from spatterings.

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[1] *J. Am. Chem. Soc.*, **42** (1920), 337.

ADDRESSES AND CONTRIBUTED ARTICLES

REFINING RAW SUGARS WITHOUT BONE-BLACK[1]

By C. E. Coates

Louisiana State University, Baton Rouge, Louisiana

The following is a general discussion of a condition which has risen somewhat suddenly in the Louisiana sugar industry, and is of necessity both informal and incomplete. In particular, it is specifically not a discussion of the various methods of refining raw sugar used at present in sugar refineries devoted entirely to that purpose.

Off and on for a good many years there have been sporadic attempts to buy raw sugars in the tropics and to take advantage of the idle equipment in the Louisiana sugar houses by refining this sugar between seasons without the use of bone-black. Every now and then a few bags of raws were slipped into the regular routine during the sugar season, but in the main the crop was ground in the usual way and the house cleaned up before melting began. The ventures were largely experimental, the most exhaustive experiments having been carried on about 10 yrs. ago in a sugar house which ran all summer and turned out a large quantity of a good grade of granulated sugar. It was understood, however, that the results were not particularly satisfactory financially, owing to the small margin then existing between 96 test and granulated sugar. In the nature of things, the bone-black refinery is slightly more efficient than the sugar house in melting raws and can exist when the margin between raws and granulated is so small that the sugar house would be losing money. Just what this margin is it is almost impossible to say at the present time, but when 96 test sugar was selling for 4 cents it was estimated that 80 cents per hundred margin was about an even break, and anything above this showed a slight profit. With margins running from $1.80 up, the proposition looked, on the face of it, very attractive to a good many planters, and they went into it without thinking much about equipment or yield, and without knowing much about the process.

Superficially, it looks like a pretty easy thing to melt raw sugars, and turn out granulated. Practically, it is not in the least simple, and differs at every point from the ordinary sugarhouse practice. Here we have a raw material of high cost, which must be manufactured and sold as a perfect finished product. Profits are determined in ordinary times by the quality of the product, but leaving this out of consideration the margin between raws and granulated even when large is rarely large enough to stand much loss in process, as can be seen from the following rough estimate.

One hundred lbs. of 96 test sugar, sold in bags and delivered at 18 cents a lb., will yield with good refinery practice 93 lbs. of granulated sugar and 7 lbs. of molasses with practically 1 per cent of loss in process. The 93 lbs. of granulated selling at 20 cents per lb. give us $18.60. Add 20 cents for the molasses, which is liberal, making $18.80 or 80 cents gross profit. The raw sugar is bought in bags costing about 12 cents per hundred lbs. sugar and sold in barrels costing about 40 cents per hundred. The net loss for cooperage is 25 cents per hundred lbs. Subtracting this from 80 cents we get 55 cents, which must cover both cost of manufacture and profit. If, on the other hand, raw sugar is selling at 4 cents and granulated at 5 cents, 93 lbs. of raws give $4.65. Add 10 cents for molasses and subtract 20 cents per hundred cooperage less rebate on bags. This leaves 55 cents for gross profit, which must include cost of process and profit. Assuming cost of process for 4-cent sugar to have been 35 cents, this gives about 20 cents per hundred margin for net profit for 4-cent sugar. With 18-cent sugar, however, the cost of process is certainly double. Probably it does not miss 70 cents by very much, which would show a loss of 15 cents per hundred instead of a profit, even though the margin in one case is 100 points and in the other case 200 points. But that is not the worst of it. With 4-cent sugar, if the yield is not 93 lbs. but 91 lbs., this reduces its profits by 10 cents. With 18-cent sugar a yield of only 91 lbs. adds 40 cents to the deficit. It would hardly pay to melt 18-cent sugar on a plantation at less than 300 points, as can be seen from the following: A very good yield is 90 lbs. and about 8 lbs. of molasses. 90 × 21 cents is $18.90, plus value of molasses 20 cents, making $19.10, gross profit $1.10. Calling the cost of process 70 cents and cooperage 25 cents, this leaves 15 cents profit, which is little enough. The purpose of these calculations is merely to show that a margin which pays with 4-cent sugar would mean bankruptcy with 18-cent sugar. It is well to impress this point on the planter, because otherwise when he sees the refiner getting 2 cents margin he may overestimate the refiner's profit and try it himself with somewhat disastrous results.

With the above as a foreword let us now cover briefly certain of the points which the sugar planter must meet when he melts raws.

BUYING RAWS

In buying raws there would be considerable choice if the planter could choose. At present he takes what he can get, but ordinarily he might be able to buy a specific lot of raw sugar on quality. Polarization is, of course, the prime factor in valuing raws, but in addition to this, raws with hard, fairly large grains give better yields than soft, small-grained sugars, losing less on washing and giving washed sugar of a higher purity. Light colored raws give better yields than dark raws. Raw sugars also have a tendency to deteriorate in storage, due to the solution of the sucrose grain in the molasses film and its inversion by bacteria. The smaller the grain the greater the surface exposed to this action, and hence the greater the loss in storage. It is quite simple to argue out a good deal for one's self about raw sugars, keeping in mind just what a grain of raw sugar is like. It consists practically of fairly pure sucrose of over 99 purity, which has separated from a mother liquor of molasses, which has a purity of approximately 45. The molasses film of raw sugar is, of course, not the final molasses, but is the run off from a massecuite of perhaps 65 purity. This molasses will have an apparent Brix of about 79, and real total solids of about 76. Molasses of such a density is subject to fermentation. If the Brix of the run-off had been 83, the molasses would have been so dense that it would hardly ferment. Sugar of this type, therefore, would keep better than sugar from a lighter massecuite of the same polarization, which accounts for the fact that if the raw sugar be much washed its keeping qualities may be impaired. The deterioration of raw sugar is much more considerable and more rapid on occasions than one would suspect. It is, therefore, well for the planter to be prepared to work up his raws as soon as possible and to keep them in storage as short a time as possible.

YIELDS

In buying raws refineries have taken 96 test sugar as a standard. Before the war, when sugar sold at about 4 cents, the refineries gave a premium of about one-twelfth of a cent a pound for every degree of polarization above 96 test, and imposed a penalty of about one-eighth of a cent per pound for every degree of polarization below 96 test. These figures differed at different times. It was generally considered that the premium was too low and the penalty too high. Be this as it may, the whole system was clumsy and illogical and became increasingly absurd as the

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[1] Presented before the Section of Sugar Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

price of raw sugars advanced. Some time ago, therefore, the buyers and sellers in New York agreed upon a new sliding scale, which is used at the present time and is presumably fair to both sides, though the latter point is doubtful.

In Louisiana there has been considerable refining on toll. One sugar company some years ago, when sugar sold at 4.5 cents, received 96 test raws in bags and delivered 93 lbs. granulated in barrels, charging 60 cents toll per hundred raws and keeping the molasses, which at that time was worth about 5 cents. The rebate on the bags would not quite cover the cooperage. Possibly the molasses would have about offset this, leaving the net toll 60 cents. This was considered a satisfactory charge by the refiner at that time, but, of course, it would not apply at the present time. There is no bone-black house refining on toll at present in Louisiana. If there were it would probably be necessary to double the previous toll and add about 25 cents for increased cost of cooperage, the total rate depending upon the cost of raws.

When sugar was refined on the toll basis the deliveries in granulated per 100 lbs. raw were based on polarization, according to Table I. These figures represent perfect refinery practice and are the results of a number of years of practical work. The basis of this table is calculated on the following formula which is mathematically correct:

$$\text{Percentage of granulated sugar on total solids in raws} = \frac{\text{Purity of raws} - \text{Purity of molasses}}{\text{Purity of granulated sugar} - \text{Purity of molasses}}$$

Ninety-six test sugar is assumed to carry 1 per cent of moisture (= 99 total solids) and to be of 97 purity. Molasses is supposed to be of 40 purity, and granulated sugar of 100. One pound of sugar is allowed as a reasonable loss in refining. Substituting these figures we get

$$\frac{97-40}{100-40} = 0.95 \text{ lbs. on } 100 \text{ lbs.}$$

$$\text{Total solids in raws } 0.95 \times 99 = 94$$

$$94-1 = 93 \text{ lbs.}$$

of granulated sugar recovered per 100 lbs. of 96 test melted, with 6 lbs. of molasses of 40 purity and 1 lb. of sucrose lost in process. The table has been modified to fit actual results.

TABLE I—YIELDS OF GRANULATED PER 100 LBS. RAWS

Polarization Raw Sugar Degrees	Granulated Lbs.
98.0	95.0
97.5	94.5
97.0	94.0
96.5	93.5
96.0	93.0 (standard)
95.5	92.1
95.0	91.25
94.5	90.4
94.0	89.5
93.5	88.2
93.0	87.7
92.5	86.9
92.0	86.0

The premiums for over-polarization are 1 lb. of granulated for every degree. Penalties for under-polarization are 1.8 lbs. granulated for every degree. One per cent of non-sugars is assumed to prevent 1 per cent of sucrose from crystallizing. That this table, though empirical, is not far wrong may be seen from the following figures obtained recently by an exceedingly well-equipped bone-black refinery: Polarization, 95.7; yield granulated, 92.46 lbs., molasses 7.37 lbs.; loss of sucrose in process 0.804 lb. The above table would also give 92.46. In refining sugar by bone-black 3.5 to 4 gal. of oil were burned per 100 lbs. raws melted.

It must not be forgotten, however, that raws of the same polarization and different qualities give different yields. A soft, small-grain raw of 95 test with gummy molasses and high ash would yield considerably less sugar to the refinery than a hard, large-grain sugar carrying normal molasses of low ash. This fact is well understood by the refiners, but it is practically impossible to allow for it in buying raws. For this reason the planter should have it clearly mentioned in the contract on what basis sugar, polarizing above or below 96 test, shall be adjusted to a 96 test basis. This refinery table is certainly fair to the seller and should be used until something better can be suggested. It must be kept in mind also that these are bone-black refinery figures, which show probably 2 to 4 lbs. more recovery of granulated than can be obtained in any Louisiana sugar house with its present equipment. Whereas this equipment varies so greatly in different sugar houses that it would be impossible to lay down a hard and fast rule for recovery to be expected, the writer is inclined to think that if 2.5 lbs. of sugar were deducted from the above table and 3.5 lbs. of molasses added it would be about the best which could be expected at present, though there is no reason why, as far as yield goes, a sugar house cannot do as well as a refinery.

WEIGHING AND SAMPLING

Raw sugar is always received in bags and when received must, of course, be stored immediately. Many sugar houses are not equipped for handling and storing raw sugar, but this equipment is neither expensive nor difficult to obtain, and has been installed in several places. In making this installation it is particularly necessary to instal scales. For many reasons, which need not be particularized, the sugar house should know exactly the number of pounds of raws entering the house, and should take these weights itself. The usual tare for bags is accurate enough.

In sampling raw sugar at the present time it is exceedingly difficult to get a fair sample. The old 96 test sugar was usually washed a little, but many Cuban raws at present seem not to be washed at all for the most part, and seem purposely made to carry all the molasses they will hold. If this sugar is allowed to stand in the bag the molasses will slowly drain to the bottom. Sugar from the top may polarize 96°, and sugar from the bottom 92° or less. Neither is it possible for an inexperienced man to take a fair sample of the sugar—nor the experienced, for that matter. It might be thought that a trier run from top to bottom would give a fair sample, but if the bag has had its position changed during the shipment and is standing on its end instead of lying on its side, the drainage of the molasses might change the nature of the sample completely. While the usual method of sampling may be fair enough for duty purposes where the bags in the cargo have not been moved for some time, the problem at the sugar house is by no means easy. In fact, I am inclined to believe that errors in polarization due to sampling are responsible for some of the apparent inefficiency in process. These samples should be taken with the greatest of care by the chief chemist or some trained man.

WASHING

The raw sugars after dumping are carried by a conveyor to a mingler. In some places an extemporized mingler has been made out of a wooden trough, and a screw conveyor. This is not a mingler and does not accomplish its purposes. A mingler is a semicircular trough through which runs a shaft provided with arms which churn up the sugar and segments of a screw which gives the mass a slight forward motion. The violent agitation of the mass is necessary to break up the lumps of sugar and is particularly important with the low-grade molasses sugars we are getting at present. In the mingler the sugar is mixed intimately with about 15 per cent by weight of wash. From the mingler it falls into an ordinary mixer which keeps the mass stirred up while it is being fed to the centrifugals. In spinning, the first run-off, called greens or wash sirup or affination liquor, may be separated from the wash proper, but this does not pay unless large quantities are melted. The wash sirup will be about 15 per cent by weight on the raws melted and has a purity of about 85. The washing is continued until the sugar has a purity of about 98.5 to 99. Higher than this it is not desirable to go, for economic reasons. From 1 to 3 gals. of water in a 40-in. machine is all that is required. This wash may go into a separate tank and part of it be used in affinating new raw sugars. If there is an excess the remainder goes in with the washed sugars for melting. It is obvious, therefore, that the wash water used should be but little more than that necessary to make enough wash for affination purposes. In most sugar houses there is no separation of affination liquor and wash, and the raw sugar is mingled with pure water or with the mixed wash sirup, the separation of wash not being thought worth the trouble.

MELTING

In nearly all Louisiana sugar houses the washed sugars are melted with wash water from the presses and from the bags. This is considered bad practice by refineries. The object is to keep the purity of the dissolved washed sugars as high as possible. Press wash and bag wash, while valuable, are usually of lower purity than the melted sugars. While this is true and under ideal conditions would be used as a basis for practice in Louisiana houses, the improvement brought about by substituting pure water for press and bag wash is not great and might not be advisable where the cost of evaporation is high. This cost must always be high where only single-effect evaporation is practiced, as is often the case at the present time. Early in the year the raws were melted to about 20 Brix in order to facilitate filtration. The density was gradually raised until at about 30 Brix it was found possible to cut the effects out completely and do all the evaporation in the pan. This was convenient, but being single-effect evaporation it is, as just said, quite expensive. All water used for washing and for melting should be as pure as possible, and if necessary it should be filtered. This detail is important but is sometimes overlooked.

DEFECATION

The liquor obtained by melting raw sugars is turbid and dark in color. Any sirup suitable for making white sugar must be reasonably light in color and above all things must be bright and free from suspended particles. In raw sugars these particles consist of bagacillio, wax, silica, calcium salts, and ordinary dirt, together with yeasts, molds, pectin, and albumins. If boiled the albumin precipitate is coagulated, but the coagulum is not large. After boiling, most of the turbidity can be removed by filtration through ordinary filter paper, though the particles are so fine that simple filtration has so far not proved successful commercially. The problem, however, indicates purely mechanical filtration, but as this was formerly not thought practicable it was customary to add certain chemicals to the sirup to produce a gelatinous precipitate which would carry down the suspended impurities and, if possible, some of the impurities in solution.

PHOSPHATATION

The commonest defecation is by means of phosphoric acid and lime. The phosphoric acid was formerly made in the bone-black houses by treating the spent char or the char dust with either hydrochloric or sulfuric acid. At the present time it is largely sold already made up in pure form, and is so used in Louisiana. The amount to be added depends upon whether or not the soluble monocalcium phosphate or pure phosphoric acid is used. The usual size for defecating tanks is 2500 gals., which at 55 Brix means about 15,000 lbs. raws for the tank. At the beginning of the season 0.25 lb. of P_2O_5 per 1000 lbs. of sugar was generally added, though this amount varied somewhat with the type of sugar melted. This, with the residual acidity of the raws, gives an acidity of about 0.6 cc. 0.1 *N* for 10 cc. of liquor, using phenolphthalein as an indicator. If to this solution we add about 0.25 lb. of CaO per 1000 raws we get a residual acidity of about 0.35 cc. Inasmuch as commercial preparations of lime and of phosphoric acid are not of constant composition, it is advisable to control the defecation by determining acidities. The final acidity of 0.35 cc. to phenolphthalein is practically neutral to litmus. In phosphatation, to the melted sugar, heated to about 195° to 200° F., there is added, first the phosphoric acid and then immediately the lime, and the mixture is blown up for about 10 min. The defecated liquor is next sent to the bag filters. None of the Louisiana houses were provided with any other kind of filter than the bag. The Greenwood type with movable head gave considerably better satisfaction than the old type of Taylor filter. One house ordered Daneks for secondary filtration; another house tried out the Williamson aërating defecator, which works admirably on these liquors; still others ordered the Sweetland type of leaf press, and the Martel type which works on the same principle, but these installations were not finished before melting stopped.

In refinery practice this first liquor goes direct to the char filter. In Louisiana, no char filters are used, so it is considered good practice to sulfur to 0.8 cc. before sending to the pan. This sulfuring is thought to give better molasses. Towards the end of the season several houses had modified the above procedure. The acidity was brought to 0.6 cc. with phosphoric acid and then limed back to an alkalinity of 0.1 cc. After passing through the bags this liquor usually showed 0.1 cc. acidity, due to the acetic acidity of the bags after they had been washed and allowed to stand for a few hours. It was then sulfured a very little, to about 0.2 cc. acidity. With this procedure there was absolutely no rise in glucose ratio and the yield of granulated sugar was better, with no gain in color.

CARBONATION

Several years ago quite a quantity of raw sugar was refined at one factory by a carbonation process which was as follows: The washed raws were melted to 28° Bé. and cooled to 35° C. At this point hydrated lime was added, 2 per cent $Ca(OH)_2$ on weight of sugar, the sirup carbonated cold to phenolphthalein neutrality, heated to 93° C., carbonated again, and filtered. It was claimed for the process that it was about 10 cents per hundred cheaper than the bone-black process and gave nearly a pound more sugar. The sugar actually produced was of fairly good quality, but the cost of the process was not satisfactory to the company, and it was abandoned at the end of a few months. Probably, however, defecation, adding lime, first to the cold juice, following with carbon dioxide and finishing up with a little sulfur dioxide, that is, the so-called sulfo-carbonation process, might prove both cheap and effective. This latter defecation was practiced for many years at Belle Alliance, Louisiana, and gave good results.

SULFATATION

A third process tried out this season at several places was the substitution of sulfur dioxide for phosphoric acid, the acidities ranging about as for phosphatation. This process has given excellent results in some hands and not so good in others. The author would suggest the following procedure: The clear liquor is heated to 70° and forced hot at fairly high speed through a pipe emptying into the blow-up tank. A few feet away from this tank a pipe introducing sulfur dioxide under pressure is led into the juice pipe. Along beside it another pipe enters, introducing milk of lime. The amount of both the lime and the sulfur can be thus regulated with exactness. When the sulfite of calcium is formed at advanced temperature, it filters more readily and is more effective as a defecating agent. Sulfurous acid has the advantage over phosphoric acid that is not cumulative, and will give better molasses. The sugar also is generally whiter.

The foregoing methods employ the three commonest and cheapest acids which will give insoluble precipitates with lime, that is, phosphoric, carbonic, and sulfurous. In so far as the writer has been able to see, there is little difference in the quality of the products. The cost of the acid used per 100 lbs. raws is, of course, negligible. The remaining processes, however, are based on an entirely different principle, that is, on purely mechanical filtration.

KIESELGUHR

It has been known for a long time that if a melted raw sugar liquor be passed through a high-speed centrifuge, it can be separated into a clear liquid and a precipitate which contains not only most of the particles held in suspension, but also most of the germs present and some of the gums. A few years ago the eastern refineries began to filter their juices through kieselguhr. Kieselguhr is a thin, porous, fossil shell of microscopic size, shaped like a shallow boat or disk and composed mainly of silica. It is in consequence exceedingly light and exposes a great surface in filtration. Previous to the war this could be bought f. o. b. New Orleans for about $22 per ton. At present the price is about $50. This increase in price may affect its use in the sugar industry, but at a reasonable figure it has unquestionably a part to play. It was found that if a leaf press was precoated with kieselguhr the filtered liquor was practically clear and the leaves could be sweetened off and washed with great ease. Filtration is rather slow, but if kieselguhr is added to the melted sugars at the rate of about 12 to 16 lbs. to the ton of raws and this fed properly to the precoated press, filtration is exceedingly rapid and the filtrate bright. This system of clarification was tried out at several sugar houses in Louisiana with varying success. It has been materially improved, however, by a very simple change of procedure. The washed sugar is dropped from the centrifugal to a conveyor which carries it to a mingler. In this mingler a slurry of kieselguhr and water of about 12° Bé. is added at the rate of 12 to 16 lbs. of kieselguhr per ton of raw. This brings the kieselguhr into intimate contact with the molasses film on the sugars. The mingler discharges into the melters, where the sugar is melted, preferably with pure water. Filtered river water answers admirably. The melt then goes to the filter press or the bags, and the result is excellent in every respect. First liquors clarified in this way are practically as bright and as light in color as those clarified by phosphoric acid and lime, and the molasses of course has considerably less ash. For this reason a better grade of product is obtained all the way down to the final molasses, and the yield seems to be increased about 0.3 lb. Whereas in refineries this liquor goes to the char filter, in sugar-house practice it can go straight to the pan in a usual way, but the writer is inclined to think a brighter sugar would be obtained if it were sulfured slightly, say, to about 0.2 cc. This would serve to reduce any ferric iron which might be present, and to give a brighter granulated product.

The cost of the kieselguhr at 2.5 cents per pound is about 30 cents per ton. This can be cut down greatly by recovering the kieselguhr. The cake consists mainly of organic matter, a little silica, a little calcium carbonate, and the unaltered kieselguhr. This can be burned at a low temperature for less than $5 per ton, we estimate, and the ash is nearly as good a filter aid as the original. We have recovered it five times and could notice no difference in the filtering effect. The ash is washed by decantation and does not have to be reground. We tried digesting it with dilute hydrochloric acid, but noticed no good effect. It is not necessary to burn off all the carbon, as what remains is also a good filter aid, though it seems to have no decolorizing power. Burned in a closed retort, the ash carried considerable carbon. It filtered well, but showed no decolorizing power. This recovering process we intend trying next fall on cane juice by heating the cake in a closed retort, in the hope that the carbon thus made may also show decolorizing power. In this process the tubes of the heaters are scoured bright, and but little scale forms on the tubes either of the effects or the pan. The filtration, however, presents certain mechanical difficulties which have not yet been completely overcome.

ACTIVATED CHARS

A fourth method of defecation which is now attracting widespread attention is by the use of activated carbons. These carbons have from 50 to 70 times the decolorizing power of ordinary bone-black. They are made by various processes from wood, peat, and other organic materials. Four of these carbons, which may be referred to here as A, B, C, and D, have been tried in Louisiana.

A—On one of these, A, or rice hull carbon the patents are still in litigation. The Louisiana Sugar Experiment Station has secured patents on this product and has dedicated them to the public. These patents are contested at present by several other claimants. This is quite unfortunate, in my opinion, for the rice hull carbon is fully equal in quality to any other and would probably be cheaper to prepare. As matters stand there is none of it on the market, but a company is now being organized to make it.

B—The most exhaustive experiments have been made with the use of B. These indeed may fairly be said to be no longer experiments, though the procedure is doubtless still open to improvement.

C—Certain large-scale experiments recently made with C seem to show it slightly superior in decolorizing power to B and slightly inferior in filtering qualities. C is much heavier than A and finer grained. Its filtering qualities would probably be improved by making the grain somewhat larger and this I judge would make it about equal to B.

D—This char is lighter than B, but not quite so good either in decolorizing or in filtering qualities.

Different samples of each of these chars differed considerably. Using total decolorizing power alone as the standard, B ranged from 75 to 90 per cent; C from 70 to 95 per cent; D from 50 to 80 per cent. This would indicate that the processes of manufacture are not quite standardized as yet. If all were made under equally careful supervision, there would probably be little difference between them. Many other activated chars, equal or in some cases far superior to any of the above, have been prepared in the laboratories of the Louisiana State University and the Sugar Experiment Station, but these have not been made on a commercial scale. Other commercial activated chars have not yet reached Louisiana.

The melted sugars are best first clarified with kieselguhr as just described. This is not necessary, but it prolongs the life of the char.

Several processes were used in applying these chars separately, some quite elaborate and expensive, others very simple, and installed at a minimum cost. The latter type seemed to work as well as the former, as far as yields were concerned, while the quality of the product was in all cases uniformly excellent. The following process is, in the main, that carried out in one of the less elaborate installations, modified by the writer to accord with his experience in various other plants.

The melted raws, without defecation of any sort, are brought to an average concentration of 20° Bé.

Twenty-two hundred gallons of the liquor containing 8673 lbs. of solids are run into a 2600-gal. tank, and 400 lbs. of char added. The amount of char depends somewhat on the character of the raws, but runs between 4 and 5 per cent. The char is first mixed in a closed trough by screw conveyor with some liquor into a magma which is fed to the tanks by compressed air. Some trouble was experienced at first in getting a good mixture, as it tended to float on the surface. This could doubtless be overcome by steaming the char before adding it. It is then blown up thoroughly and circulated between the tank and the heater and back for about 5 min. until the temperature is about 200° F., then passed to the receiving tank and pumping station for the press. From here it is sent at about 8 lbs. pressure to the plate and frame press. This pressure is subsequently increased slowly to maintain about a constant rate of flow. Char filtration is very rapid, owing to the decreased viscosity of the filtrate. The filtered liquor is water-white and absolutely clear, but inasmuch as the presses may occasionally leak, for safety's sake it is sent through a second plate and frame press which catches any char which may have leaked through the first. This second press may be run for several days, if desired, without cleaning. It might advantageously be replaced by a leaf type press, which should give thoroughly satisfactory results. This liquor goes to the charging tanks for the effects or the pan.

The press cake, without washing, is dropped and sent back to a second melted sugar tank, where it is used again. This may be repeated from 3 to 5 times, the number depending upon the weight of char used, and partly upon the quality of the sugars melted. Before returning to the tank, the cake passes through a mingler where about 10 per cent of fresh char are added, and the mass reduced to a magma. When the filtrate begins to run yellow the char is washed to zero Brix, dropped, and sent to the revivifying tank. Here it is treated in 800-lb. batches. To each batch 500 gal. of 4 per cent hydrochloric acid are added in a wooden tank provided with a perforated copper coil, and digested with live steam for about 1 hr. It then passes to the acid press, is washed to neutrality, and cut down into another wooden cistern, with 500 gal. of 5 per cent solution of caustic soda, digested with live steam for 1 hr., sent to the alkali press, and washed to neutrality. The char is then made into a magma with melted raws made faintly acid, and returned to process. The cycle takes about 18 hrs. After the first revivifying the char is used three times, again revivified and used two times, making a total use without burning of between 9 and 10 times for each pound of char. Special char kilns were installed in several sugar houses, but proved of much too small capacity, so the exhausted char was placed in piles for storage. It will be noted that these chars serve both as a filtering medium and as a decolorant. For this reason the following experiment was tried, and seemed thoroughly successful. The greens or affination liquor from the washed sugar are dark in color and turbid. They should undoubtedly be defecated before being taken back into the process, but owing to lack of filtering capacity this was not done in Louisiana sugar houses. This liquor was brought to 60 Brix, boiled up with about 10 per cent of the exhausted char, and sent through a plate and frame press. The filtrate was found to have lost 60 per cent of its color, and was perfectly bright. The char had lost all of its decolorizing properties. The filtrate worked well in process. Towards the last of the season the following method of using the char was tried out with satisfactory results. Five per cent of char on sugar melted was added in the blow-ups, and heated for about 5 min. This went to the press and was followed by successive portions of filtered clear liquor until the color was not materially changed. The char was then dropped and sent to the kiln. This simulated the ordinary bone-black process, the partly decolorized liquor going back to the blow-ups and being treated with fresh char. No acids or alkalies were used, and good results were claimed, the yields being considerably higher than before. Data on this procedure were not sufficient, and the process may be regarded as tentative only.

Owing to conditions which are well known, the difficulties of installing new machinery delayed the installations of the elaborate char plants. The quality of the product is beyond criticism and fully equal in every respect to standard granulated. Yields, however, seem to be no better than those obtained by phosphoric acid and lime or by sulfurous acid and lime. The cost of operation seems to be higher than that of a bone-black plant. The author sees no reason why the process cannot be made fully the equal of bone-black in yield and cost of operation, as soon as the usual chemical and mechanical difficulties attending a new sugar-house process have been overcome. It has been claimed that there was loss by inversion. This was true at the beginning of the season, but when the acidities were kept at the points previously indicated, of about 0.2 to 0.3 cc., the most careful tests showed no rise in glucose ratio whatsoever.

Activated chars cost at present from 15 to 25 cents per pound. Possibly rice hull carbon could be put on the market at 10 cents a pound, but in any case it should be kept in mind that we are dealing with an expensive reagent in char and an expensive raw product in sugar. This means that the process should be under the control of the best man available. It is easy to lose at least 1 per cent in yield. If 400,000 lbs. of raws are melted a day, 1 per cent is 4000 lbs., which, at 10 cents a pound, is $400.00. $400.00 a day for a few days will go quite a distance towards paying the salary of a high-grade man, and in our opinion no other type of men should touch the process at all. In fact, the writer believes that many of the best qualities of activated chars will be developed after they have been used for several years under expert management.

BOILING

The boiling systems in Louisiana differ in each house. Melted sugar is much less viscous and boils much more freely than cane sirup. It is necessary to grain high in the pan in order to give a hard, small, even grain to the sugar, but a pan which ordinarily would boil in 4.5 hrs. with cane sirup will be finished in 1.5 hrs. with melted sugars. This means a very considerable increase in the velocity of vapors through the catchall, and there has been unquestionably a loss of sugar by entrainment. It would seem that this loss is greatest for a short interval of time just before graining. In order to prevent this, new systems of baffles have been installed in the catchalls and the top coil has been cut out in some cases.

Entrainment has thus been largely overcome, but in handling the pans there are several things which raw sugar boilers have had to learn. Even the slightest leak in an exposed coil will cause the sirup to stick and caramelize. This will darken the molasses and also the sugar. The valves should be carefully inspected to guard against this danger. In addition, when the strike is finished and the massecuite is being discharged, any leak whatsoever in any of the coils will have a tendency to caramelize more sugar. For this reason it is not a bad idea to instal a master valve and cut the pan out completely, this in addition to the separate coil valves.

The massecuite ordinarily falls into a mixer. A crystallizer is not practicable for the first massecuites, which would get too stiff to be handled, for which reason they are spun as quickly as possible. It is at this point that the equipment of most Louisiana sugar houses fails. Rarely have there been enough centrifugals to handle the house, when it runs at full capacity, and in consequence the boiling system must be adjusted to suit the centrifugal capacity which is, to say the least, unfortunate.

The run-off must be carefully separated from the wash, which, being very high in purity, is returned to the first liquor. Most centrifugal crews are careless in the matter of separating wash from run-off. Steam is not used at all in washing, but the author believes it could be advantageously employed and would give a brighter sugar.

The washed sugar which generally carries about 1.5 per cent moisture goes to the granulator, of which there are three makes in the state, the Hersey, the Harry, and the Louisville, all working on what is practically the old Hersey principle, and all doing efficient work when run right. It is quite easy to get them too hot, however, and scorch the sugar, and this is difficult to avoid when a steam drum is used in the cooler. The newer machines have no steam drum in the cooler, but in some of the older machines as much as 20 lbs. of steam are occasionally carried on this drum. The manufacturers used to call for 5 lbs. and are now cutting it out altogether. The sugar is weighed automatically into 100-lb. bags which are also sewed automatically. These machines do their work admirably.

The first massecuite has a purity of about 99 or even higher, the melted raws with 98.5 purity rising over 0.5 per cent during defecation. The run-off from the first massecuite, therefore, together with the wash, is grained a second time, the massecuite having a purity of about 97, and the run-off from this, with a purity of about 93 or 94, is grained a third time. These three sugars are mixed in the granulator and are practically indistinguishable from one another. The run-off from the third massecuite has a purity of about 88 to 90. On occasions this also may be grained and give a merchantable sugar, but ordinarily the sugar is light yellow and is remelted. The wash from the bags, the presses, and all other sources goes to a blow-up tank, where it is sometimes defecated and sometimes mixed with the greens and grained for 96 test sugar. Massecuites of about 60 to 65 purity are grained and go to the crystallizers where they stay from 48 to 72 hrs. The run-offs from these crystallizer massecuites should show about 38 to 40 purity in ordinary sugar-house practice, but as a rule in melting raws the purity is closer to 43. This is not so much difference, however, as might be imagined, for the true purities of the run-off from raw sugar crystallizer massecuites are about three to four points higher than the apparent purities, which is not the case with melted sugar. This should be borne in mind in making comparisons. Sometimes the final molasses shows a purity of about 50, in which case it is boiled to string proof and sent to the magma tanks with the idea that it will yield a third sugar and a run-off of about 28 to 30. The only figure we have for molasses of this type shows a purity of 30, but with present prices for high purity molasses the procedure is of doubtful financial value. Yields in all cases have been lower than were anticipated.

TABLE II

No.	Average Polarization	Process	Yield in Granulated Bagged	Yield in 2nds	Total Yield	Pounds Mol.	Purity Mol.	Loss Sucrose Per cent Raws
1	95.7	SO_2	85.75	3.48	89.23	9.4	45	2.36
2	95.7	Kieselguhr	85	3.0	88	11.8	30	4.16
3	95.2	P_2O_5	85.5	3.7	89.1	10	43	1.7
4	95.5	P_2O_5	88	1.3	89.3	8	43	3.06
5	95.8	P_2O_5	90	0.8	90.8	7.8	43	1.65
6	95.6	P_2O_5	87.5	2.1	89.6	8.3	46.7	3.4
7	95.4	Act. Char	86	3.9	89.9	9	40	1.9
8	95.8	Act. Char	89.6	..	89.6	7.9	41.5	3.03
9	95.9	Act. Char	85.6	3.00	88.6	11.5	34.3	3.4

The figures in Table II represent the results obtained by different sugar houses or, in one case, by different processes at the same sugar house. In all cases they include a small quantity of estimated sugar and an average purity for final molasses. In some cases the sugar house was hardly equipped to obtain accurate measurements. They are, therefore, only nearly correct, but they represent a fair average of the results obtained during the season. In No. 3 yields in seconds and in molasses were figured rather too high, and the loss in sucrose would probably have been nearly 1 per cent more. No. 5 gives the figures for a special run, and in the calculations there were items of doubtful accuracy. On the whole, one may say that where all seconds were melted back into granulated, as in No. 8, the amount of granulated actually bagged would be close to 89 lbs. with from 8 to 8.5 gal. of molasses, and about 3 lbs. of sucrose lost in process. The differences in individual cases may sometimes be ascribed to errors in taking stock, or to incorrect assumptions as to final purities, but, in spite of this, and making possible allowances, there seems to be about 3 lbs. loss of sucrose, whereas in good refinery practice the loss unaccounted for ranges from 0.8 to 1.2, of which a great portion is known to be due to the action of bone-black. On the face of things, there should be a smaller loss of solids in sugar-house practice than in the bone-black refinery, but as a matter of fact the loss is about 2 lbs. greater, and the yield in granulated sugar about 3 lbs. less. Inasmuch as the figures available are neither accurate nor complete, it is impossible to explain these facts with absolute assurance, but the discrepancy may be due to any or all of the following causes:

1—Shortage of weight in the raw sugars received. If the original shipping weights only are used, the sugar house cannot be certain that no error has been made, and nothing lost in transit. In one case where this error was checked up by reweighing, a considerable deficit in sugars received was noticed, and the apparent yield rose accordingly.

2—The quality of the raw sugar received this year was such as to make accurate sampling difficult. Moreover, it was stored under such conditions as to make deteriorations probable and considerable. Ninety-six test sugar has on occasions dropped two points by the time it reached New York and two more by the time it reached the manufacturer or refinery.

3—There can be little doubt that a sugar boiler accustomed to boiling cane sirup will have to readjust himself considerably in boiling melted raws. The viscosity is so small, the sirup boils so freely, and the grain must be struck so high in the pan that there is danger of the rapid bubbles bursting into small particles practically like a fog and being carried away by the high velocity of the vapor. This point has already been discussed. It is always a danger point, and in refineries it is guarded against in several different ways. The usual sugar-house method of analyzing the condenser water is not satisfactory, first, because of the great dilution, and, second, because it is essential to know at what stage, if any, entrainment takes place. As a matter of fact entrainment in well-run refineries has been reduced practically to zero. In the newer types of condenser where a surface condenser is interposed between the catchall and the ordinary condenser, the surface condenser takes out most of the vapor and at the same time acts as a catchall itself. This water can be caught separately and analyzed whenever necessary, but there is no such condenser as this installed in any of the Louisiana sugar houses at present. If entrainment occurs it would naturally be most rapid at the moment of maximum viscosity, which would be the period of maximum supersaturation just before graining. At the beginning of the season it was thought that most of the loss went down the water leg of the condenser. Some sugar is lost this way of course, but the writer doubts that it is a dominant factor in houses which endeavor to prevent it.

4—On the other hand, mechanical loss seemed to have been pretty well guarded against, but here again eternal vigilance proved to be necessary. Good press work was the exception rather than the rule, particularly with activated chars, which showed a strong disposition to channel in washing. In one case a char cake showed 20 per cent sucrose in one portion, and 0.5 in another.

5—Whenever a sugar solution is boiled there is, of course, inversion, but this inversion is small. With the acidities used in lime-phosphoric acid defecation there should be negligibly little inversion. The same thing is true of defecation with lime and sulfur dioxide. Where only kieselguhr is used one can see no reason why any inversion at all should take place. Where activated chars are used there may be a slight loss of sucrose, and if the char be not carefully washed there may be also slight inversion brought about by the hydrochloric acid retained in the pores of the char. Inversion was tested for repeatedly. In a few cases there were found slight increases in the glucose ratio, but in most tests this had not changed. Under any circumstances we do not believe the amount lost by inversion would be material. On the other hand, there might be a loss by fermentation, but this should not exist in a clean house. Some years ago, it was known to make a difference of over 1 lb. in yield.

6—Some of the loss may well be due to errors in calculation and, therefore, only apparent. These losses should be eliminated when the house is cleaned up at the end of the season. They may consist in improper weights of molasses and in the improper purities of product.

7—In most cases the ordinary sugar-house equipment was not properly balanced for melting raws. Many more centrifugals were needed in order to instal double purging where possible for economy's sake. Better filtering devices were needed in all cases, and greater steam economy in most. About twice the amount of fuel was used that the refiner requires; about 6.5 gal. of oil compared with 3.5 gal. per 100 lbs. raws melted. On the whole, however, no difficulties have been encountered which cannot be overcome. Processes have been fairly well standardized, and are improving, so it may be said that both the cane-sugar house and the beet-sugar house can be utilized profitably during the off season in refining raw sugars whenever the margin between raws and granulated passes a certain well-defined point.

RESEARCH PROBLEMS IN COLLOID CHEMISTRY

By Wilder D. Bancroft

Cornell University, Ithaca, N. Y.

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(*Continued*)

ADSORPTION OF SOLID BY SOLID

(46) ANALYSIS OF OXIDE ON PASSIVE IRON—It has been shown by Bennett and Burnham[1] that passive iron owes its properties to an adsorbed and stabilized oxide of iron containing more oxygen than ferric oxide; but they could not tell whether it was FeO_2 or FeO_3. Müller and Spitzer[2] appear to have found that platinum stabilizes the higher oxide because they precipitate a higher oxide of iron on a platinum anode from a strongly alkaline ferric tartrate solution. An analysis of this precipitate would probably settle the question. Owing to the small amount of the precipitate such an analysis would be extremely difficult but probably not beyond the skill of an expert analyst. It is possible that better results could be obtained by using a platinized anode. It is also possible that one might precipitate a very thin film of iron on a platinum cathode and then oxidize it completely with nitrogen peroxide.

(47) STUDY RELATION BETWEEN SIZE OF PARTICLES AND TEMPERATURE DIFFERENCE SUFFICIENT TO CAUSE HOT PARTICLES TO STICK TO A COLD ROD—When a fine powder is added to a coarser one, the former tends to coat the latter[3] instead of going into the voids. A glass rod can be considered as an extreme case of a coarse powder and consequently it is not surprising that a very fine powder will stick to a glass rod even when both are at the same temperature. Coarser particles fall off when the powder and rod are at the same temperature; but may adhere when the powder is hotter than the rod.[4] No experiments have yet been made to determine the relation between the size of particles and the temperature difference necessary to cause adherence. It is probable that the nature and pressure of the gas enveloping the rod and the particles are factors, but these points have not been worked out.

(48) PORTLAND CEMENT AND GYPSUM—The addition of small amounts of gypsum to cement increases the setting time. It has been suggested that the portland cement grains become coated with a film of gypsum; but Kühl and Knothe[5] rule this explanation out on the ground that no such coating can possibly be formed either during grinding or on addition of water. Since gypsum is softer than clinker, it is probable that the gypsum particles are distinctly finer than the cement particles. The work of Fink[6] and of Briggs[7] proves that under these conditions the fine gypsum particles would coat the coarser cement particles. It is, therefore, a question of fact whether this happens or not, and the modern microscopist ought to be able to answer this question one way or the other.

Lime and barium carbonate powders are said to stick to charcoal while calcium carbonate and barium sulfate do not. This should be confirmed or disproved and experiments should be made to determine how far the chemical nature of the powders is a factor, and to formulate the laws.

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[1] *J. Phys. Chem.*, **21** (1917), 107.

[2] *Z. anorg. Chem.*, **50** (1906), 351.

[3] Fink, *J. Phys. Chem.*, **21** (1917), 32; Briggs, *Ibid.*, **22** (1918), 216.

[4] Aitken, *Trans. Roy. Soc. Edinburgh*, **32** (1884), 239; Tammann, *Drude's Ann.*, **18** (1905), 865.

[5] "Die Chemie der hydraulischen Bindemittel," **1915**, p. 252.

[6] *J. Phys. Chem.*, **21** (1917), 32.

[7] *Ibid.*, **22** (1918), 216.

(49) BEHAVIOR OF FINE AND COARSE POWDERS IN LIQUIDS—When fine and coarse powders are shaken up together in a liquid, do the fine powders tend to coat the coarser ones? There is some evidence to show that when a colloidal solution is precipitated[1] the finer particles attach themselves to the coarser ones. Owens[2] showed that a dilute suspension of whiting leaves the supernatant liquid cloudy as it settles, whereas a more concentrated one leaves the supernatant liquid clear. Free[3] has obtained similar results with kaolin in water. It has been shown by Deane[4] that clear settling occurs when the coarse particles are so numerous that they sweep down the finer particles with them. In the case of clear settling, each apparent grain should really be an agglomeration of finer grains. While this is undoubtedly true, it has not yet been confirmed by direct observation.[5]

(50) AGGREGATION OF SMALL PARTICLES—Hilgard[6] has described the coagulation of fine suspended particles in a current of water, the resulting flakes consisting of twenty or thirty of the original particles agglomerated together. Hilgard says that the tendency towards agglomeration varies inversely with the size of the particles and the temperature. Alcohol, ether, caustic or carbonated alkalies tend to retard agglomeration, while neutral salts and acids tend to promote it. These experiments should be repeated and extended, and then interpreted from the viewpoint of the colloid chemist.

ADSORPTION OF SOLID BY LIQUID

(51) REVERSIBILITY OF CALOMEL ELECTRODE—It is usually assumed that the calomel electrode is reversible, but there is no experimental proof of this. When mercury is made anode in a potassium chloride or hydrochloric acid solution, the mercury becomes coated with a black film, possibly of oxychloride,[7] which offers a high resistance to the passage of the current. When the mercury anode is covered with mercurous chloride, the black precipitate is not formed, and the mercurous chloride is converted into mercuric chloride which reacts slowly with mercury to regenerate mercurous chloride. It is quite probable that a platinum electrode coated with mercurous chloride would show the same anode decomposition voltage as the calomel electrode.

ADSORPTION FROM SOLUTION BY SOLID

(52) ADSORPTION AND ABNORMAL DENSITY—When making density determinations[8] by weighing a solid in a solution, an error may be introduced because of the solid adsorbing some of the salt. This error is likely to be larger the finer the particles of the solid, because the ratio of surface to mass increases with increasing subdivision. With grains of quartz or glass varying in diameter from 0.015 mm. to 0.9 mm., placed in solution of iodides, the specific gravity of the latter can be adjusted so that the smaller particles will sink while the larger will float.

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[1] Burton, "The Physical Properties of Colloidal Solutions," **1916**, p. 160.

[2] *Geographical J.*, **37** (1911), 71.

[3] *Eng. Mining J.*, **101** (1916), 684.

[4] *Trans. Am. Electrochem. Soc.*, **37** (1920).

[5] See, however, Hilgard, *J. Chem. Soc.*, **40** (1881), 970.

[6] *Ibid.*, **40** (1881), 970.

[7] Cf. Hittorf, *Pogg. Ann.*, **106** (1859), 344; Paschen, *Wied. Ann.*, **34**, (1890), 62.

[8] Thoulet *Compt. rend.*, **99** (1884), 1072; *J. Chem. Soc.*, **48** (1885), 476

Marble is so porous that its surface is almost proportional to its volume, and consequently grains of marble do not show this phenomenon.

It would be instructive to determine the amount of error which would be introduced if instead of weighing in water one were to weigh in a solution of which one component was known to be adsorbed strongly. A distinctly interesting case would be to do such experiments with charcoal and the solutions studied by Osaka.[1]

(53) ADSORPTION OF IODINE BY RED PHOSPHORUS—Sestini[2] states that red phosphorus will decolorize a solution of iodine in carbon bisulfide or of aniline red in ether. It would be interesting to determine adsorption isotherms in these two cases. Since the apparent density of red phosphorus varies with the temperature to which it has been heated, it is probable that a whole series of results could be obtained.

(54) ADSORPTION OF IODINE FROM DIFFERENT SOLVENTS BY SILVER IODIDE—Carey Lea[3] has shown that silver iodide adsorbs iodine strongly. This adsorption should be studied with iodine dissolved in different solvents, so that the results could be compared with those of Davis[4] on the adsorption of iodine by charcoal.

(55) ADSORPTION BY CHARCOAL FROM DIFFERENT SOLVENTS OF SOLUTES OTHER THAN IODINE—Davis[5] found that the order of adsorption of iodine from different liquids was not the same with different kinds of charcoal. With animal charcoal there was decreasing adsorption in the order: chloroform, alcohol, ethyl acetate, benzene, and toluene; with sugar charcoal the adsorption decreased in the order: chloroform, toluene, ethyl acetate, benzene, and alcohol; whereas for coconut charcoal, the order was toluene, chloroform, benzene, alcohol, and ethyl acetate. There are at least two factors governing the effect of the solvent. The more soluble the dissolved substance is in a given solvent, the less readily will it be adsorbed, provided we can neglect the adsorption of the solvent itself by the solid. There are many illustrations, but one will suffice. Charcoal will decolorize aqueous solutions of iodine or of methyl violet, but alcohol will extract the color from the charcoal. The solubility cannot be the sole factor, however, because then the solvents could always be arranged in the same order for the same solute, regardless of the nature of the adsorbing agent. This is disproved absolutely by the experiments of Davis. One other factor is the adsorption of the solvent by the adsorbing agent. This factor was not taken into account at all by Davis, whose data are, therefore, not sufficient to enable us to tell whether there are other factors to be considered. In order to check these results, isotherms should be determined with solutes other than iodine. It is possible that the different impurities in the two charcoals account wholly or in part for the different results.

(56) QUANTITATIVE ADSORPTION OF DYES BY ALUMINA, STANNIC ACID, ETC., WITH SPECIAL REFERENCE TO HYDROGEN-ION CONCENTRATION—All the work on dyes should be repeated, paying close attention to the actual hydrogen-ion concentration. This is more important than ever in view of the recent experiments by Jacques Loeb.

(57) COMPARATIVE STUDY OF ADSORPTION BY ALUMINA, SILICA, KAOLIN, FULLER'S EARTH, AND THE SO-CALLED ALUMINIUM SILICATES MADE IN THE WET WAY—As a help to the study of the constitution of the silicates we ought to have comparative measurements on adsorption by alumina-silica substances, paying attention to impurities such as iron. While the absolute value will vary very much with the structure, it seems probable that a study of the relative values would be very helpful.

(58) EFFECT OF HEAT TREATMENT ON THE ADSORPTION BY THE PRECEDING MATERIALS—Heating fuller's earth to about 600° will destroy most of its adsorbing power. The experiments under No. 57 should be repeated with the same materials after they have undergone a definite heat treatment.

(59) EFFECT OF HYDROCHLORIC ACID ON FILTER PAPER—Miss Murray[1] found that the adsorption of hydrochloric acid by filter paper was practically the same at the end of 3 days as at the end of one hour. When the filter paper was left for 10 days in contact with the acid, there was a marked change, the adsorption dropping to less than half the previous value. This should be repeated so as to determine what physical or chemical change the paper undergoes.

(60) MATHEMATICAL TREATMENT OF WATER-RINGS—Various people have commented on the sharpness of the water-ring when a drop of a colored solution spreads in a piece of filter paper. Since the water-ring is due to adsorption, the changes in concentration as the solution passes out from the center must correspond to an adsorption isotherm; but nobody has ever shown that one can deduce the phenomena of the water-rings quantitatively from the adsorption isotherm. It seems reasonably certain that it is merely a very sudden adsorption of color; but this has not been proved.

(61) THEORY OF CONDITIONS UNDER WHICH ALUMINA ADSORBS BASES PREFERENTIALLY—Alumina is usually considered to adsorb acid dyes rather than basic dyes; but Weber[2] states that the reverse is true, and Pelet-Jolivet[3] says that alumina adsorbs methylene blue and not crystal ponceau. This is said to be due to a difference in the adsorbed ions. This matter should be cleared up.

(62) QUANTITATIVE STUDY OF DECOMPOSITION OF SALTS BY CHARCOAL, ETC.—If we knew the adsorption of a base, an acid, and the undissociated salt by charcoal, it would be possible to calculate the amount of decomposition which should be caused by the action of charcoal on an aqueous solution of a salt. The first two can be determined readily; but we have no way at present to determine the adsorption of the undissociated salt, though one could probably make a guess at it from coagulation experiments.[4] It would be possible to measure the decomposition[5] and calculate the adsorption of the undissociated salt. At present we have no comparable quantitative data on the adsorption of acid and base or on the percentage decomposition. Results could certainly be obtained with aniline acetate[6] or benzoate and charcoal with organic solvents.

(63) BEHAVIOR OF CALCIUM STEARATE—Those who believe that acid soils are due to organic acids postulate the existence of an insoluble acid which forms insoluble salts. Instead of working with ill-defined substances, the thing to do is to take solid stearic acid and treat it with varying concentrations of barium, calcium, and sodium hydroxides and barium, calcium, or sodium salts, making careful quantitative determination of what happens.

(64) DYEING WITH MINERAL COLORS—It is probable that the dyeing with Prussian blue, chrome yellow, iron buff, and manganese brown is due to adsorption and is something more than a mechanical precipitation of the pigment on the fiber. This could be tested by seeing whether the fiber will adsorb Prussian blue from a colloidal solution of this substance.

(65) QUANTITATIVE EXPERIMENTS ON DYEING WITH MORDANTS—Adsorption isotherms should be determined for a number of typical dyes with the mordants which can be used with them.

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[1] *Mem. Coll. Sci. Kyoto Imp. Univ.*, **1** (1912), 257.

[2] *Gazz. chim. ital.*, **1** (1871), 266.

[3] *Am. J. Sci.*, [3] **33** (1887), 492.

[4] See No. 55.

[5] *J. Chem. Soc.*, **91** (1907), 1682.

[1] *J. Phys. Chem.*, **20** (1916), 621.

[2] *Dingler's polytech. J.*, **283** (1892), 158.

[3] "Die Theorie des Färbeprozesses," **1910**, pp. 61, 138.

[4] Weiser and Sherrick, *J. Phys. Chem.*, **23** (1919), 305; Weiser and Middleton, *Ibid.*, **24** (1920), 30.

[5] Liebermann, *Sitzb. Akad. Wiss., Wien.*, **74** (1876), 331; Skraup, *Z. Kolloidchem.*, **6** (1910), 253.

[6] Freundlich and Masius, "Van Bemmelen Gedenkboek," **1910**, p. 100.

We do not know whether the adsorption of the mordant by the fiber results in a somewhat decreased adsorption of the dye by the mordant. More brilliant colors are obtained with a stannic oxide mordant[1] than with an alumina mordant. We do not know whether this is a question of transparency, of refractive index, or of both.

(66) EFFECT OF TEMPERATURE ON ADSORPTION OF ARSENIOUS ACID—Lockemann and Paucke[2] find that more arsenic is carried down by hydrous aluminium oxide when precipitated by ammonia from a hot solution than from a cold one. While this is probably due to the form in which the alumina precipitates, this has not been shown. The matter could be tested by precipitating the alumina separately hot and cold and then shaking the resulting precipitates with the solution of arsenious acid.

(67) DECOLORIZING ACTION OF BONE-BLACK—Patterson[3] believes that the efficiency of bone-black is due in large part to the presence of nitrogenous compounds, and he claims to have extracted substances having 16 to 40 times as much decolorizing action on a standard caramel solution as an equal weight of good bone-black. This work has never been repeated. This should be done. If Patterson's results are confirmed, the peptized material should be precipitated on wood charcoal to see what kind of a product that would give. It would be interesting also to precipitate the peptized material or gelatin on porous calcium phosphate, both with and without the addition of colloidal carbon.[4]

(68) ADSORPTION BY CHARCOAL FROM SUGAR SOLUTIONS—"Bone-black is said to adsorb lime from sugar solutions,[5] and lime salts equally well if an alkali be present. Potash salts are easily adsorbed, especially in presence of lime." This does not seem clear, and experiments should be made to show why alkali increases the adsorption of lime salts and why lime increases the adsorption of potash salts.

(69) ADSORPTION AND CHEMICAL POTENTIAL—If alcohol is added to an unsaturated solution of a salt which is not soluble in alcohol, the chemical potential of the salt is raised, as is shown by the fact that addition of enough alcohol will cause the precipitation of the salt.[6] The experiments of Osaka[7] on the adsorption of salts by charcoal should be repeated after adding organic liquids to the solutions. A correction would have to be made in case there were marked adsorption of the organic liquid.

(70) ACTION OF HYDROCHLORIC ACID ON HIDE POWDER—Kubelka[8] found that the amount of hydrochloric acid taken up by hide powder was 0.74 milli-equivalent of hydrochloric acid per gram of dry hide powder, regardless of the concentration in the solution, at least from 0.01 *N* HCl up. This should mean that a definite chloride or hydrochloride is formed which shows no appreciable hydrolysis or dissociation when in contact with 0.01 *N* HCl. This might be true; but Kubelka says that it is obvious that hide powder will fix more acid in presence of sodium chloride. When he takes a 10 per cent sodium chloride plus hydrochloric acid he finds that the amount of acid fixed is independent of the concentration of the acid as before, and that the total amount is now 0.97 milli-equivalent of hydrochloric acid per gram of dry hide powder. As a matter of fact, there is no reason why addition of sodium chloride should increase the amount of hydrochloric acid fixed by hide powder for the case where there is only one compound and it is not appreciably dissociated or hydrolyzed. Kubelka's results are, therefore, contradictory and must be repeated. To make matters worse, Kubelka finds that, with a 20 per cent sodium chloride solution, the amount of acid taken up increases with the concentration of the acid.

(71) ADSORPTION OF LIQUIDS FROM BINARY AND TERNARY SYSTEMS—With two liquids miscible in all proportions, it is not possible to determine directly which displaces the other in contact with a solid. Results can be obtained by measuring adsorption from binary or ternary solutions just as we are in the habit of doing when studying adsorption from salt solutions by charcoal, etc. There has been almost no work[1] done along this line.

SURFACE TENSION

(72) SURFACE TENSION OF MERCURY BY DYNAMIC METHODS—Rapid measurements of the surface tension of mercury in the presence of gases give higher values than do slower methods, while the same values are obtained by both methods for mercury in a vacuum.[2] This is qualitatively what one would expect if the mercury adsorbed the gas; but unfortunately the rapid readings are higher than the readings in a vacuum and the slow readings are about equal to the vacuum readings. Lenard[3] has brought up a point which may have a bearing on this. If we have a partially polymerized liquid such as water, the modification having the lower surface tension will concentrate in the surface. If we form a new surface suddenly, we shall then get a higher concentration, temporarily, of the higher modification having the higher surface tension. If equilibrium is reached relatively slowly, the dynamic method will give a higher value for the surface tension than the static methods. If equilibrium is reached instantaneously, there will be no difference. We can account for the facts observed with mercury if we make the assumption that mercury is a partially polymerized liquid, that equilibrium between the modifications is reached practically instantaneously in a vacuum, and that equilibrium is reached relatively slowly in presence of gases. The difficulty with this is that we have no independent proof of these assumptions. The specific heat of mercury decreases with rising temperature and so does that of water, at any rate up to about 30°; but we do not know that this is because both liquids are polymerized, nor is it known whether all polymerized liquids show the same phenomenon over some temperature range.

Another hypothetical explanation becomes possible, if we assume that there is no sharp discontinuity at the surface between liquid and vapor. The Laplace theory of surface tension assumes that there is a perfectly sharp line of demarcation between the two media bounding the surface, for instance,[4] between liquid and air, while van der Waals postulates a continuous transition.

According to the latter way of looking at things, mercury in a vacuum adsorbs its own vapor, forming a thin transition layer varying from the density of vapor at one side to the density of mercury at the other side. If this transition film forms instantaneously in a vacuum and relatively slowly in presence of a gas, the surface tension of a fresh surface of mercury in presence of a gas will be higher than the equilibrium surface tension of mercury in a vacuum, and this higher surface tension thus measured will decrease, if the surface is not renewed, down to the equilibrium surface tension of mercury in a vacuum, or below it if the gas is adsorbed markedly at the mercury surface. This explanation seems somewhat more plausible than that of Lenard; but it is open to the same objection that there is as yet no independent proof of the assumptions involved. The whole problem calls for further study.

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[1] Herzfeld, "Das Färben und Bleichen des Textilfasern," **1** (1900), 73.

[2] *Z. Kolloidchem.*, **8** (1911), 273.

[3] *J. Soc. Chem. Ind.*, **22** (1903), 608.

[4] Bancroft, *J. Phys. Chem.*, **24** (1920), 211, 348.

[5] Pellet, *J. Chem. Soc.*, **38** (1880), 834.

[6] Miller, *J. Phys. Chem.*, **1** (1897), 633.

[7] *Mem. Coll. Sci., Kyoto Imp. Univ.*, **1** (1912), 257.

[8] *Z. Kolloidchem.*, **23** (1918), 57.

[1] Mathers, *Trans. Am. Electrochem. Soc.*, **31** (1917), 271.

[2] Stöckle, *Wied. Ann.*, **66** (1898), 49; Meyer, *Ibid.*, **66** (1898), 523.

[3] Cf. Aganin, *Drude's Ann.*, **45** (1914), 1020.

[4] Willows and Hatschek, "Surface Tension and Surface Energy," **1915**, p. 33; Hulshof, *Drude's Ann.*, **1** (1901), 165; Lewis, *Z. Kolloidchem.*, **7** (1910), 197.

(73) SURFACE TENSION PHENOMENA IN TERNARY SYSTEMS—Worley[1] has discovered an interesting fact. Although sodium chloride increases the surface tension of water, the addition of salt to a solution of aniline in water decreases the surface tension. The sodium chloride decreases the solubility of aniline in water and, therefore, increases the partial pressure of the aniline vapor. The vapor pressures, therefore, correspond to solutions richer in aniline than that actually present, and the surface tension relations run approximately parallel with the vapor pressures. Worley noticed another curious thing in regard to change of surface tensions of solutions with rising temperature. Since liquid and vapor are identical at the critical temperature, the surface tension becomes zero at the critical point, and the surface tension of pure liquids, therefore, decreases with rising temperature. One might reasonably have expected that the surface tension curves for solution would run somewhere near parallel to the corresponding curves for the pure constituents, but this is not the case for mixtures of water with aniline or phenol. The surface tensions of the phenol-rich solutions vary relatively little with rising temperature, while the corresponding aniline solutions actually show an increase of surface tension with rising temperature. The explanation seems to be that the ratio of water to aniline or phenol in the vapor increases with rising temperature, and that the solutions, therefore, show surface tensions corresponding to what one might expect of solutions richer in water than they actually are. It is a pity that Worley did not also study some such case as ether and water, where the partially miscible liquid with the lower surface tension has the higher vapor pressure.

These experiments of Worley's should be extended and taken up systematically for a number of cases, such as salt, phenol, and water,[2] and others in which two of the components are practically nonmiscible at the temperature of the experiment.

(74) SURFACE TENSION OF GELATIN AND GUM ARABIC SOLS—Zlobicki[3] states that addition of gelatin to water lowers the surface tension until the concentration reaches 0.5 to 0.8 g. per 100 cc., after which it remains practically constant. If this observation is correct, this limiting concentration must have some physical significance, such as true solubility of gelatin or something. The experiments should be repeated with carefully purified, ash-free gelatin. It is quite possible that the results obtained by Zlobicki really depend on peptization of the gelatin by some of the impurities.

Zlobicki[4] also found that small additions of gum arabic raise the surface tension of water, after which further additions have no effect. This seems very improbable and the experiments should be repeated. It would be desirable to check the results by rapid methods of measuring the surface tension of fresh surfaces.

(75) MOLECULAR WEIGHTS OF LIQUIDS—So many liquids have given "normal" values for the temperature coefficient of the molecular surface energy that we have come to consider the surface tension method a satisfactory one for determining molecular weights. On the other hand, there are a number of liquids which give abnormally high temperature coefficients running above three. Since it seems impossible that these liquids should be dissociated to the extent necessary to make the temperature coefficients normal, Walden[5] rejects the whole method. This does not seem reasonable and it is more probable that some factor has been overlooked which becomes important in some cases.[1] We know that the van't Hoff-Raoult formula gives abnormal results whenever the heat of dilution is large; but that does not worry us because the formula is deduced explicitly on the assumption that the heat of dilution is negligible. Any discussion of the Ramsay-Eötvös formula should take into account the paper by Schames.[2] He believes that the molecular weights of the "normal" liquids are twice the formula weight, which makes the true value for the temperature coefficient 3.36. This would make the abnormal cases, studied by Walden, the normal ones, an interesting possibility for which there is no independent proof at present.

(76) RATE OF EVAPORATION—Schall and Kossakowsky[3] have studied the rate of evaporation of different liquids under comparable conditions and get comparable results for sixteen esters, benzene, toluene, xylene, ethylene chloride, chloroform, carbon tetrachloride, acetone, and ether; but water and ethyl alcohol evaporate about half as rapidly as they should, and methanol less than one-fifth as rapidly. These variations are evidently a result of the polymerization of these liquids; but no attempt has been made to express the disturbing factors quantitatively.

(77) CAPILLARY ACTION IN VERY NARROW TUBES—Thomson[4] has deduced a formula for the change of vapor pressure of a drop with changing diameter; but he states explicitly that he does not consider the formula accurate when the radius of curvature is less than 1.2μ. He considers that the formula is not applicable to the vapor pressure of water adsorbed by such substances as cotton cloth and oatmeal at temperatures far above the dew-point of the surrounding atmosphere. He believes, however, that the difference is one of degree and not of principle; that the adsorption of water vapor by fibrous and cellular organic structures is a property of matter continuous with the adsorption of vapor into a capillary tube.

It seems probable that the formula for the rise of a liquid in a capillary tube can hold accurately only so long as the radius of the tube is distinctly larger than the thickness of the adsorbed film. Since it is a common practice nowadays to calculate pore diameters from the lowering of the vapor pressure, it is very desirable that some mathematical physicist should go over the whole question and determine if possible at what point the formulas become untrustworthy.

(78) CRYSTALLIZATION OF GRAPE SUGAR AS AN ADSORPTION PHENOMENON—According to Seyberlich and Trampedach,[5] grape sugar crystallizes in interlacing needles from acid solution and in smooth plates from an alkaline solution. This difference must be due in some way to a difference in adsorption and the problem should be studied from this point of view.

(79) CRYSTALLIZATION OF SODIUM CHLORIDE IN CUBES AND OCTAHEDRA—Sodium chloride crystallizes in cubes from pure water and in octahedra[6] from solutions of urea, boric acid, caustic soda, etc. This should be studied as a case of adsorption.

BROWNIAN MOVEMENTS

(80) DISTRIBUTION OF COLLOIDAL PARTICLES UNDER THE INFLUENCE OF GRAVITY—Perrin[7] found that, with gamboge particles a little over 0.4μ in diameter, each rise of 30μ caused the equilibrium concentration to fall to one-half its previous value, while a difference of 6μ produced the same effect when the gamboge particles were about 1.0μ in diameter. On this basis the concentration at the top of a beaker 6 cm. high would be only $^{1}/_{2^{2000}}$ of that at the bottom in the case of the fine particles. This does not harmonize at all with the fact that the color of a

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[1] *J. Chem. Soc.*, **105** (1914), 260, 273.

[2] Miller, *J. Phys. Chem.*, **24** (1920), 562; Steubing, *Ibid.*, **1** (1897), 643; Kablukow, Solomonow and Galine, *Z. physik. Chem.*, **46** (1903), 399; Rozsa, *Ibid.*, **24** (1897), 13; *Z. Elektrochem.*, **17** (1911), 934; McIntosh, *J. Phys. Chem.*, **1** (1897), 474; Waddell, *Ibid.*, **3** (1899), 160; Osaka, *Z. physik. Chem.*, **41** (1902), 560; Roth, *Ibid.*, **43** (1903), 539.

[3] *Bull. acad. sci. Cracovie*, **1906**, 497.

[4] *Loc. cit.*

[5] Walden, *Z. physik. Chem.*, **75** (1910), 555; Walden and Swinne, *Ibid.*, **79** (1912), 700; **82** (1913), 271.

[1] Cf. Harkins, *Proc. Nat. Acad. Sci.*, **5** (1919), 539.

[2] *Drude's Ann.*, **38** (1912), 830.

[3] *Z. physik. Chem.*, **8** (1891), 158, 241.

[4] *Phil. Mag.*, [4] **42** (1871), 448.

[5] *J. Soc. Chem. Ind.*, **6** (1887), 46.

[6] Dammer's "Handbuch der anorganischen Chemie," [2] **2** (1894), 127..

[7] "Brownian Movements and Molecular Reality," **1910**, p. 43.

colloidal gold solution is nearly uniform over the whole height. Either the gold solution will settle in time, or there is something wrong with Perrin's mathematics.' Professor Burton, of Toronto University, suggests that perhaps the concentration increases under the influence of gravity as lower levels are reached in the beaker, up to a certain value, after which the concentration remains practically uniform. It is very desirable that the actual facts should be determined and that the mathematical theory should be revised in case it proves to be wrong.

Since this was written, Professor Burton, of Toronto, has found an explanation for the discrepancy. More experiments will be needed to give a broader experimental foundation to Professor Burton's theory.

(81) DETERMINE CHANGE IN EINSTEIN'S FORMULA FOR THE BROWNIAN MOVEMENTS DUE TO THE ADSORBED LIQUID FILM—Einstein[1] has made a study of the so-called movements of colloidal particles suspended in a liquid and has deduced formulas that lead to a very interesting set of relations, which are apparently confirmed fairly well by the experiments. He has not considered the possibility of an adsorbed film on the particles, and it seems very desirable that some mathematician or mathematical physicist should go over his work and see to what extent the assumption of an adsorbed film of some definite thickness would modify the conclusions reached. The error was so serious in the case of the formula for the viscosity that it is not safe to assume that it will be negligible in the equations for the Brownian movements.

COALESCENCE OF SOLIDS

(82) COALESCENCE OF RUBBER—Since two surfaces of raw rubber unite readily and vulcanized rubber acts differently, it should follow that vulcanized rubber adsorbs air more strongly than raw rubber; but this lacks experimental confirmation.

(83) ADHESION OF CLAY TO STEEL—Rice[2] reports that certain clays, one of them containing 76.8 per cent silica, stick very firmly to steel; but there is nothing to show what it is in the clay which produces this result. This should be determined.

(84) SYNTHETIC HARDPAN—It is known that sodium salts promote the formation of hardpan.[3] This should be studied more in detail as it might be possible and desirable to produce synthetic hardpan as a sub-base for roads.

PLASTICITY

(85) STUDY OF RELATION BETWEEN APPARENT VOIDS AND POINT OF ZERO FLUIDITY—Bingham[4] has made a preliminary study of the concentration at which plasticity begins or ends. If a finely powdered solid is added to a liquid, the viscosity of the liquid is increased or the fluidity, which is the reciprocal of the viscosity, is decreased. The fluidity was calculated from the rate of flow of the liquid through a viscosimeter. At temperatures between 25° and 60° the fluidity dropped to zero at the same concentration, so that the concentration of zero fluidity is independent of the temperature over the range studied. With infusorial earth in water, zero fluidity was reached at a volume concentration of about 87 per cent water; with China clay at about 96 per cent; with the graphite used in Acheson's aquadag zero fluidity was reached at a volume concentration of about 94.5 per cent water; and with an unspecified clay at about 80.5 per cent. With infusorial earth in alcohol the zero fluidity was reached at a volume concentration of about 88 per cent alcohol. The mixtures having zero fluidity are not stiff and will not maintain their shape. At higher concentrations there is a change from viscous flow to plastic flow. The distinction made by Bingham is that with viscous flow any shearing force—no matter how small—will produce permanent deformation, whereas in the case of plastic flow, it is necessary to use a shearing force of finite magnitude in order to produce a permanent deformation. It seems reasonable to assume that we reach zero fluidity when liquid enough is added to the solid to begin to scatter the particles, in other words, when about enough liquid is added to fill the voids. This is true in the one case studied by Bingham. The clay referred to contained 81.6 per cent voids and required 80.5 volume per cent of water to bring it to zero fluidity. Of course this very important generalization of Bingham's must be tested in more cases before it can be considered as definitely established; but it is so obvious, after it has been pointed out, that it must be approximately true. This discovery of Bingham's may be of distinct importance in the paint industry. The oil requirement for a given pigment is a very arbitrary amount and experts often differ widely in their values. Reproducible figures could be obtained if in each case there was determined the amount of oil necessary to give zero fluidity. Since this is more oil than painters wish to use, it might be advisable to adopt as the standard some definite fraction of the amount of oil necessary to produce zero fluidity.

(86) FONDANT—If the grain of powdered sugar is as fine as that of fondant, as I have been told it is, it should be possible to make fondant without any cooking, by adding a glucose sirup to powdered sugar.

(87) ARE SAND RIPPLES IN CLOSE PILING OR NOT?—We know that the wet sand on the sea beach is in close piling because the pressure of the foot causes it to dilate and appear dry. We also know that a retreating wave leaves sand ripples on the beach; but the people who have been interested in ripples were not interested in close piling and there seems to be no statement whether the sand in the ripples is or is not in close piling. When a steam roller is sent over a macadam road before the road is dried out sufficiently, transverse ripples or ridges are formed. It would be interesting to know whether any portion of such a road is in open piling.

(88) THE THEORY OF QUICKSANDS—It seems to be quite certain that a quicksand is a mixture of sand and water in which the sand is in open piling and in which the sand grains are sufficiently small or sufficiently lubricated so that the frictional resistance to displacement is not too great. Unfortunately this has not yet been proved experimentally to the satisfaction of anybody.

(89) TO WHAT EXTENT IS MAXIMUM DENSITY BENEFICIAL TO PLASTICITY?—Some experimental studies by Professor E. B. Mathews, of the Johns Hopkins University, seem to indicate that plastic clays contain particles of different sizes in about the proportions to give maximum density. It is not unreasonable to assume that such a mixture would give zero fluidity with less water than any other. This matter should receive further study.

TYPES OF PRECIPITATES

(90) PRODUCTION OF CRYSTALS—Geologists have prepared certain substances in distinct crystals by arranging for the slow diffusion of dilute solutions of two salts which form the desired substance by metathetical reaction. Johnston[1] has improved on the technique by allowing the two solutions to diffuse into a large vessel containing water, causing a further dilution. Dreaper[2] obtained distinct crystals by letting solutions diffuse through sand, the rate of diffusion being relatively slow on account of the capillary spaces. Holmes[3] obtained crystals of silver bichromate in flat needles one centimeter long by this method, substituting aluminium powder for sand. He also filled a small test tube full of $0.1\ N$ potassium iodide, covered the mouth of the tube with gold-beater's skin, and immersed

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[1] *Drude's Ann.*, **17** (1905), 549; **19** (1906), 280, 371; see also Smoluchowski, *Ibid.*, **21** (1906), 756.

[2] *Trans. Am. Ceram. Soc.*, **14** (1912), 610.

[3] Hilgard, "Soils," **1906**, p. 62; Ehrenberg, "Die Bodenkolloide," **1915**, p. 293.

[4] *Am. Chem. J.*, **46** (1911), 278; *J. Frank. Inst.*, **181** (1916), 845.

[1] *J. Am. Chem. Soc.*, **36** (1914), 16.

[2] *J. Soc. Chem. Ind.*, **32** (1913), 678.

[3] *J. Phys. Chem.*, **21** (1917), 709.

the tube in a small beaker containing a saturated lead acetate solution. At once an almost amorphous precipitate of lead iodide appeared on the under side of the membrane and in less than a minute crystals of lead iodide fell in a gleaming shower to the bottom of the test tube. If the same solutions are mixed in a test tube without using a membrane, a yellow powder is obtained and no easily recognized crystals. This method as developed by Holmes seems the most promising of any because it appears to give results with more concentrated solutions and would presumably work even better with more dilute solutions. This method of Holmes should be tested in a number of cases so as to see whether it really is as effective as it seems to be. Perhaps by some modification of the process it might be possible to make dolomite synthetically.

(91) EFFECT OF TEMPERATURE ON CRYSTAL SIZE—In general a precipitate like barium sulfate comes down more coarsely crystalline at higher temperatures than at lower temperatures. This is due in part to the increased solubility at higher temperatures. If this is the sole factor, mixing hot solutions of caustic soda and sulfuric acid, so as to give a precipitate of sodium sulfate, should give finer crystals than mixing the same solutions so that precipitation occurs just above 33°. This has never been tested.

(92) PRECIPITATION OF ALUMINA AT DIFFERENT TEMPERATURES—Since precipitates are less gelatinous and more crystalline the higher the temperature of formation, a series should be run on the precipitation of alumina at different temperatures. The results might be of distinct importance in their bearing on the precipitation of rare earth oxides.

(93) THE PHYSICAL CHARACTER OF MAGNESIUM AMMONIUM PHOSPHATE—The conversion of magnesium ammonium phosphate to pyrophosphate sometimes is and sometimes is not accompanied by incandescence. The pyrophosphate formed with incandescence is gray to black, while that formed without incandescence is white.[1] It is suggested that the incandescence on ignition is most marked the smaller the crystal size, which in turn is determined by the conditions of precipitation. If this is true, rapid precipitation in the cold in the presence of excess of strongly adsorbed phosphate ion[2] should favor incandescence. The darkening of the pyrophosphate formed with incandescence may possibly be traced to impurities adsorbed by very finely divided magnesium ammonium phosphate.[3]

(To be continued)

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[1] Karaoglanov and Dinitrov, *Z. anal. Chem.*, **57** (1918), 353.

[2] See Weiser's discussion of the effect of adsorption on crystal size, *J. Phys. Chem.*, **21** (1917), 314.

[3] Cf. Weiser, *Ibid.*, **20** (1916), 640.

PERKIN MEDAL AWARD

The Perkin Medal, well characterized as the "Badge of Knighthood in American Chemistry," was awarded to Dr. Willis R. Whitney of Schenectady, N. Y., at a meeting of the American Section of the Society of Chemical Industry held Friday evening, January 14, 1921, in Rumford Hall at the Chemists' Club of New York City.

Dr. Whitney was the fourteenth recipient of this high honor, and the applause which greeted him as he accepted the medal from the hand of Dr. Charles F. Chandler, dean of American chemists and senior past president of the American Section of the Society of Chemical Industry, fully demonstrated the unanimous feeling of the assembled chemists that the award was richly deserved and that Whitney the man, as well as Whitney the scientist, was being honored on this occasion.

In opening the meeting, Mr. S. R. Church, chairman of the Section, spoke briefly of the history of the Perkin Medal Award, and then called upon Dr. Allen Rogers to explain certain changes in the manner of making the award which had been adopted recently.

Briefly these changes provide that the medal committee which selects the recipient shall be organized as follows: The chairman, secretary, and treasurer of the American Section of the Society of Chemical Industry shall act as chairman, secretary, and treasurer, respectively, of the medal committee. The members of the committee in addition to the above shall include all past presidents of the Society of Chemical Industry residing in the United States; all past chairmen of the American Section of the Society of Chemical Industry; the vice chairman of the American Section of the Society of Chemical Industry; the presidents, vice presidents and secretaries of the American Chemical Society, of the American Electrochemical Society, of the American Institute of Chemical Engineers, and of the American Section of the Société de Chimie Industrielle, respectively. Any of these members who are unable to attend the meeting may be represented by a proxy. The call for nominees to receive the award is to be sent out to the various societies in April in place of October, thus giving more time for consideration by the committee and preparation by the recipient.

Those attending the meeting of the committee shall constitute a quorum, but no member on the committee shall represent more than one society, except in the case of ex-officio, when he shall indicate the society he desires to represent.

The effect of these changes is to make the committee of award more nearly a national body, rather than one consisting largely of residents of New York City or vicinity.

Before introducing the speakers of the evening, Mr. Church referred to the unanimity of opinion on the part of the medal committee in selecting Dr. Whitney for the honor to be conferred and the universal approval with which this selection has been received.

Prof. Elihu Thomson, who has been intimately connected with the development of many of Dr. Whitney's researches, was called upon by the chairman, and gave a detailed account of Dr. Whitney's career as a scientist and investigator. He paid a splendid tribute to the medalist's organizing ability and his early conception of the value of pure research in solving the problems of commerce and everyday life. Dr. Thomson predicted that we are on the threshold of great developments in thermionic engineering, due largely to the pioneer work of Dr. Whitney and his co-workers. Dr. Thomson also referred feelingly to the unselfish attitude which Dr. Whitney always displayed toward the workers in his organization, his integrity of purpose, his modesty, his ability to inspire young men, and his willingness at all times to lend a helping hand.

Following Professor Thomson, Dr. A. D. Little reviewed some of Dr. Whitney's achievements, touching upon many personal phases of his career. Dr. Little's presentation, in substance, follows.

WILLIS R. WHITNEY

By A. D. Little

CAMBRIDGE, MASSACHUSETTS

The career of Dr. Willis R. Whitney, his contributions to science, and his influence upon research and industry have been set forth so adequately and with such sympathy and understanding by the speakers who have preceded me, that I can hardly hope to do more than review them briefly from what is perhaps another angle and a more directly personal one.

Someone has said that an institution is the elongated shadow of a man. Never was this more true than in the case of the General Electric Laboratory. Its achievements have been itemized with authority by Professor Thomson. They are the work of many men to whom they have brought deserved distinction. None the less, the laboratory, as the entity and organization which has made this achievement possible, is a projection of the personality of Willis R. Whitney, and in this sense its achievements are his achievements.

Whitney returned from Europe in 1896 with a Ph.D. from Leipzig. He had left home a good American and he came back a better one. He had absorbed in Germany what were then advanced and difficult theories in chemistry and physics, and to their application to the solution of chemical and industrial problems he now brought vision and a contagious inspiration. To him a problem was an opportunity, and his reaction to it was as reflex and immediate as a knee jerk. I remember that he once told me after a pleasant dinner in Syracuse, when the conversation had reached the eternal verities, that he didn't want to go to Heaven unless there were problems there.

Naturally, therefore, he began at once the brilliant experimental work which has added much to our knowledge of solubility, colloids, and the corrosion of metals. His fundamental research demonstrated the effect of the positive and negative ions on the precipitation of colloids. He found that the corrosion of metals was an electrochemical process and he was, perhaps, the first to focus public attention upon the great economic wastes resulting from preventable corrosion.

Willis Rodney Whitney, Perkin Medalist, 1921

Whitney is a pragmatic scientist, and the essential and innate practicality of his mental processes found early expression in the successful method which he developed in association with Dr. A. A. Noyes for the recovery of ether and alcohol from collodion, a process which assured the commercial position of the photographic film.

One very conspicuous element in Whitney's character is the sincerity of his indifference to monetary rewards. It is the more striking because of the clarity with which he visualizes the economic aspects of research results.

I happen to know, for I had the honor of making the bid, that prior to 1900 he refused a doubled salary and remained an instructor at Technology, because he "would rather teach than be President." At the time I thought it an extraordinary example of devoted self-denial, but since then I have seen what happens to our Presidents and I would, without self-adulation, take the same position myself, much as I hate teaching.

He went to the General Electric Company, as I confidently believe, not for money, but because it offered an environment and opportunity for broader and more effective service. I am no less confident that he would return to "Tech" to-morrow and readjust his expenditure within the narrow boundaries of a professor's salary if he felt that there he could do a better job.

I wonder how many of you have realized how closely in appearance Whitney resembles Liszt. One expects of him—and is not disappointed—the same fire and enthusiasm, a kindred brilliancy of performance, a similar exothermic quality. Whitney can talk to a man three minutes and inject into him enough enthusiasm to last three months. He can recognize genius, and he is big enough to allow the man of genius to develop at his side. He has no wish and makes no effort to dominate. He scrupulously apportions credit where it belongs. Jealousy is alien to his nature. These are the characteristics of the ideal director of research, and it is because they are possessed in superlative measure by Willis R. Whitney that we are present here to-night.

Willis R. Whitney is a great scientist, but he is not the scientist of fiction or of the stage. He is an intensely human individual. He is extremely fond of out-door life, and it keeps him sane and wholesome. He is a farmer, not a gentleman farmer, but a dirt farmer who knows hog cholera and manure, and what to do when his hens have the pip. He has hobbies and rides them. He can tell you more about arrowheads than an Algonquin Indian ever knew, and if necessary he can make them. He usually prefers to pick them up in Central Park or Longacre Square, or at church. He can find them anywhere. He enjoys the lighter things of life and has even been known to side-step a meeting of the American Academy of Arts and Sciences, and go to a girl-and-music show instead. Biological subjects (and I am not now referring to those just mentioned in association with music) interest him keenly. He raises flies and kills them with X-rays to cure their cancer. Some day he may kill the cancer first. He is a serious student of heredity and knows exactly how much red hair is required to tint a large family unto the third and fourth generation. But do not let me convey the impression that Whitney approaches these avocational interests in the spirit of the dilettante. His knowledge of them is not broad and thin: it is both broad and deep. When he cultivates a subject, he does it intensively with all the energy in him. Better than all this, however, Whitney has a genius for friendship. He values it and holds it. He knows you but likes you.

With this interest in his fellowmen so dominant and characteristic, it is not surprising that Whitney should have proved an ideal teacher or that no later absorption has turned his thought from education. He inspires whole departments in the Massachusetts Institute of Technology; he is the prime mover of Albany Medical College, and as trustee of Union College at Schenectady has so tied his laboratory to the college that they constitute a joint educational institution.

In a very striking way and more nearly, as it seems to me, than any of his contemporaries, Whitney has the mental attitude and scientific breadth of an earlier generation in the scientific world, the ability to correlate and integrate observations and deductions in wide and different fields.

In 1909 Whitney was honored by election to the presidency of the American Chemical Society, then, as now, the largest organization of chemists in the world. Under his administration the Society enjoyed a year of continued growth and success. Several new divisions were organized and four new sections. Many of the sections were visited by the president and always with a gain to their enthusiasm and *esprit.* Two years later he was similarly distinguished by the American Electrochemical Society. For its Toronto meeting he organized a notable symposium on electric furnaces and for the Boston meeting another on electrical conduction, the subject of his presidential address in which he brought out many interesting points. He directed attention to the fact that whereas the resistance of pure metals disappears at absolute zero, that of alloys does not; that we cannot predict at all the conductivity of definite compounds such as Cu_3Sn; that no poor conductor is ductile; that if electrical apparatus were made with copper having only 2 per cent higher resistance, it would involve, on the 1912 basis of consumption, about $2,500,000 added cost for power; that in the arc the consumption of the positive electrode is apparently secondary, and that we know nothing about the theory of magnetism.

During the war Whitney was ubiquitous and untiring as a member of the Naval Advisory Board, where perhaps his most important contribution was a method for the detection of submarines.

The Perkin Medal is the badge of knighthood in American chemistry. It has never been more worthily bestowed. Its latest recipient has inspired numberless young men; he has brought distinction to a great corporation and proved to financiers that research pays; he has added new luster to American chemistry. The spirit of research has laid her hands upon him, and the spirit of youth as well.

PRESENTATION ADDRESS

By Charles F. Chandler

New York, N. Y.

It is my privilege and very pleasant duty as Senior Past President of the Society of Chemical Industry, residing in this country, to present to Willis R. Whitney, B.S. and Ph.D., the fourteenth impression of the Perkin Medal, in recognition of his most original and valuable work in applied chemistry.

Dr. Willis R. Whitney was born in Jamestown, N. Y., August 22, 1868, and was the son of John and Agnes (Reynolds) Whitney. He was graduated from the Massachusetts Institute of Technology with the degree of S.B. in 1890, and in 1896 received the degree of Ph.D. from Leipzig.

He held the following positions at the Institute of Technology following his graduation: Assistant, Sanitary Chemistry, 1890 to 1892; Instructor, Sanitary Chemistry, 1892 to 1894; Instructor, Theoretical Chemistry and Proximate Analysis, 1898 to 1901; Assistant Professor, Theoretical Chemistry, 1901 to 1904; Non-resident Associate Professor, Theoretical Chemistry, 1904 to 1908; Non-resident Professor, Chemical Research 1908—.

Since 1900 Dr. Whitney has been Director of the Research Laboratory of the General Electric Company at Schenectady, N. Y.

Among his early work, Dr. Whitney, in conjunction with Professor A. A. Noyes, successfully developed a recovery process for alcohol and ether from collodion which insured the commercial practicability of the present photographic film.

His most notable achievement has been the creation and development of the Research Laboratory of the General Electric Company at Schenectady. This laboratory, one of the earliest of its kind in this country, the embodiment of the application of science to industry, has gained a world-wide reputation by the quality of its work and the importance of its results. These results speak for themselves, but only those associated in the laboratory with Dr. Whitney can realize to what extent they are due to him personally, or how truly the story of the laboratory, from its inception with a small staff, to its present development with 275 people on its payroll, has been the story of his personal achievement. Its growth has followed naturally from the value of its accomplishment, but its accomplishment has been due primarily to him. His broad scientific knowledge, his ability as a chemist, his resourcefulness in experiment, his energy, enthusiasm, and optimism, combined with a clear sense of proportionate values, laid the foundation for, and guided and inspired all the work of the laboratory, while his democratic and magnetic personality created an *esprit de corps* in his staff which has been a powerful factor for success. It is necessary to realize this fully in order that his personal achievements may be justly appraised in considering the successes of the laboratory.

These successes have often been recited specifically, to prove the value of the application of organized research to industry. In electric lighting, the first radical improvement in the carbon incandescent filament, since Edison first produced it, was due to Dr. Whitney's personal work. The "metalized" filament, or "GEM" lamp, which he developed, and which embodied a new form of carbon, gave 25 per cent more light for the same wattage than the standard carbon filament lamp. Millions of these new lamps were sold in a single year. A little later the laboratory made a still greater contribution to electric lighting by solving the problem of mechanically working tungsten, and taught the world how to make the drawn wire which has given the tungsten lamp its universal application. The latest achievement of the laboratory in incandescent lighting is the gas-filled or half-watt lamp, which, in its larger sizes, has twice the efficiency of the vacuum lamp, and nearly equals the most efficient arcs. In arc lighting, the laboratory developed the magnetite electrode, and thereby produced the most successful arc lamp of to-day.

The laboratory has produced many new and useful forms of insulations and molded compounds, many new alloys, for resistance units and other purposes, new processes, like "Calorizing," for giving metals protective coatings, new articles of manufacture like "sheath wire," with its core of resistance alloy, its mineral insulation, and its metal sheath, adapted for heating devices, new materials like "water japan" and "Genelite," new electric furnace products, like boron carbide, useful as a flux for casting copper, and titanium carbide for arc lamp electrodes, new laboratory tools, such as the Arsem vacuum furnace, the tungsten tube furnace, and the Langmuir condensation vacuum pump, high resistance units for lightning arresters, improved carbon and graphite brushes, and brushes of new and special composition, such as "Metite."

The development of wrought tungsten has been followed by several important applications worked out entirely in the laboratory. Tungsten contacts have practically replaced platinum in spark coils, magnetos, and relays, and tungsten targets have replaced platinum in X-ray tubes.

As a result of a study of high vacuum, the laboratory devised means and methods for producing much higher vacua than before obtained, and the study of the phenomenon of electron discharge in high vacuum has produced a number of new types of vacuum tubes which have revolutionized more than one art. The

Coolidge X-ray tube was the earliest result of this investigation and has practically displaced all other types of X-ray tubes. It has made possible many results not otherwise obtainable, as, for instance, the development of a truly portable X-ray outfit. Another result was the pliotron, the first real power tube suitable for radio transmission. The pliotron practically created radiotelephony, and has revolutionized radiotelegraphy. Other types of these tubes resulting from this investigation are the dynatron, magnetron, pliodynatron, etc.

The contributions of the laboratory to pure science have been numerous, varied, and important, as is indicated by the titles taken from the list of laboratory publications:

Factors Affecting Relation between Photo-electric Current and Illumination
Structure of the Atom
Theory and Use of the Molecular Gage
Theory of Unimolecular Reaction Velocities
Absorption and Scattering of X-Rays
New Method of X-Ray Chemical Analysis
New Method of X-Ray Crystal Analysis
Roentgen-Ray Spectra
High Frequency Spectrum of Tungsten
Arrangement of Electron in Atoms and Molecules
Chemical Reactions at Low Pressures
Constitution and Fundamental Properties of Solids and Liquids
Dissociation of Hydrogen into Atoms
Effect of Space Charge and Residual Gases on Thermionic Currents in High Vacuum
Evaporation, Condensation, and Reflection of Gas Molecules
Fundamental Phenomena in Electron Tubes Having Tungsten Cathodes
Isomorphism, Isosterism, and Covalence
Mechanism of the Surface Phenomena of Flotation
Octet Theory of Valence and Its Applications with Special Reference to the Organic Nitrogen Compounds
Properties of the Electron as Derived from the Chemical Properties of the Elements
Structure of the Helium Atom
Structure of the Hydrogen Molecule and the Hydrogen Ion

Dr. Whitney is a trustee of the Albany Medical College and of Union College, and a member of the Corporation of Massachusetts Institute of Technology. He is a member of the U. S. Naval Consulting Board, National Research Council, American Chemical Society (president in 1910), American Electrochemical Society (president in 1911), American Institute of Mining and Metallurgical Engineers, American Institute of Electrical Engineers, American Association for the Advancement of Science, American Academy of Arts and Sciences, American Physical Society, and British Institute of Metals. He received the Willard Gibbs Medal in 1916 and the Chandler Medal in 1920.

Dr. Whitney's translation of Le Blanc's textbook of electrochemistry is well known.

Among the papers which he has personally published are the following:

1—"The Rate of Solution of Solid Substances in Their Own Solutions" (with A. A. Noyes). *J. Am. Chem. Soc.*, **19** (1897), 930.

2—"The Nature of the Change from Violet to Green in Solutions of Chromium Salts." *J. Am. Chem. Soc.*, **21** (1899), 1075.

3—"The Precipitation of Colloids by Electrolytes" (with J. E. Ober). *J. Am. Chem. Soc.*, **23** (1901), 842.

4—"An Investigation of Ammonio-Silver Compounds in Solution" (with A. C. Melcher). *J. Am. Chem. Soc.*, **25** (1903), 69.

5—"The Corrosion of Iron." *J. Am. Chem. Soc.*, **25** (1903), 394.

6—"Electrolysis of Water." *J. Phys. Chem.*, **7** (1903), 190.

7—"The Migration of Colloids" (with J. C. Blake). *J. Am. Chem. Soc.*, **26** (1904), 1339.

8—"Colloids." *Trans. Am. Electrochem. Soc.*, **7** (1905), 225.

9—"Arcs." *Trans. Am. Electrochem. Soc.*, **7** (1905), 291.

10—"Suspensions in Dilute Alkaline Solutions" (with Alonzo Straw). *J. Am. Chem. Soc.*, **29** (1907), 325.

11—"Organization of Industrial Research." *J. Am. Chem. Soc.*, **32** (1910), 71.

12—"Some Chemistry of Light" (Presidential Address, American Chemical Society, Dec. 29, 1909). *J. Am. Chem. Soc.*, **32** (1910), 147.

13—"Alloys." *Am. Foundrymen's Assoc.*, **1910**.

14—"Chemistry of Luminous Sources." Johns Hopkins Univ., **1910**. *Lectures on Illuminating Engineering*, Vol. 2.

15—"Research as a Financial Asset" (Congress of Technology). *Elec. World*, **57** (1911), 828; *J. Ind. Eng. Chem.*, **3** (1911), 429; *Science*, **33** (1911), 673.

16—"Mental Catalysis" (Opening Chemists' Building, N. Y.). *Met. & Chem. Eng.*, **9** (1911), 179.

17—"Theory of the Mercury Arc Rectifier." *G. E. Review*, **14** (1911), 619.

18—"Carbon Brushes." *J. Ind. Eng. Chem.*, **4** (1912), 242; *J. Frank. Inst.*, **176** (1912), 239.

19—"Electrical Conduction" (Presidential Address, American Electrochemical Society, April 19, 1912). *Trans. Am. Electrochem. Soc.*, **21** (1912), 19.

20—"Some Uses of Metals." *N. E. L. A. 35th Convention*, **1**, (1912), 336. *Publications of the Research Laboratory*, Vol. 1.

21—"Vacua." *Trans. Am. Inst. Elec. Eng.*, [1] **31** (1912), 1207. *Publications of the Research Laboratory*, Vol. 1.

22—"Phenomena of Catalysis." *Science Conspectus*, **3** (1913), 84.

23—"Light." *G. E. Review*, **17** (1914), 171.

24—"Relation of Research to the Progress of Manufacturing Industries." *Annals Am. Acad. Political and Social Science*, **870** (1915).

25—"Research." *G. E. Review*, **18** (1915), 1012.

26—"The Corporation." *Trans. Am. Electrochem. Soc.*, **29** (1916), 36.

27—"Preparedness." *J. Ind. Eng. Chem.*, **8** (1916), 298.

28—"Water Power and Defense." *Amer. Inst. Elec. Eng.* (Advance Paper), **1916**.

29—Two untitled papers. One was published in *American Defense*.

30—"The Call for Research." *National Defense Digest*, **1916**.

31—"Research and the Newlands Bill." *Met. & Chem. Eng.*, **14** (1916), 565.

32—"Research as a National Duty." *Science*, **43** (1916), 629; *J. Ind. Eng. Chem.*, **8** (1916), 533.

33—"Incidents of Applied Research" (Willard Gibbs Medal Address). *J. Ind. Eng. Chem.*, **8** (1916), 560.

34—"Research Organization." *G. E. Review*, **19** (1916), 572.

35—"The Newlands Bill and National Research." *Met. & Chem. Eng.*, **14** (1916), 621.

36—"Practical Significance of Pure Research." Paper for American Mining Congress, Chicago, November **1916**.

37—"The Undeveloped Powers of the South." *Manufacturers Record*, **70** (1916), 58.

38—"The Great Need of Promoting Research in America." *Elec. World*, **69** (1917), 12.

39—"Research" (Address at Alumni Dinner of Massachusetts Institute of Technology, Jan. 6, 1917). *G. E. Review*, **20** (1917), 114.

40—"National Need of Scientific Research." *Yale Review*, April **1917**.

41—"American Engineering Research." *Proc. Am. Inst. Elec. Eng.* **37** (1918), 115.

42—"Patent Renewal Fees," *J. Ind. Eng. Chem.*, **11** (1919), 936.

43—"What Is Needed to Develop Good Research Workers." *Elec. World*, **75** (1920), 151.

44—"The Littlest Things in Chemistry" (Chandler Medal Address). *J. Ind. Eng. Chem.*, **12** (1920), 599.

CONFERRING OF THE MEDAL

Willis R. Whitney, Bachelor of Science and Doctor of Philosophy:

It gives me the greatest pleasure, as the representative of the Affiliated Chemical and Electrochemical Societies of America, to place in your hands this beautiful Perkin Medal, as a token of the appreciation and affection of your fellow-chemists.

THE BIGGEST THINGS IN CHEMISTRY

By Willis R. Whitney

General Electric Company, Schenectady, N. Y.

If I were to try to justify my receiving the Perkin Medal, I think I would begin by assuming that now good intentions are being rewarded. As the aim of the award is to promote or stimulate research, I must find the ways by which I can most directly do so, and so I ought to say something about the biggest things in chemistry. No matter how irrelevant some of my remarks may seem, I hope you will believe that they are aimed with that high intent. While it is a great honor, it is also a wonderful opportunity to write something which may be read by 15,000 or more American chemists.

In America, patents are granted to individuals for their new disclosures. Such patents are not granted to organizations, to companies, or even to laboratories. This is really an antique limitation, for discoveries are often the result of combined efforts. And so I look at the Perkin Medal, in my case, as an award directed to me, but belonging to the Research Laboratory to which I belong, it having not yet become customary to award such medals to laboratories. In any case, I heartily thank the various men and organizations which made this Medal possible, and the Committee of Award who have chosen that my name shall stand on that honor list headed by Perkin.

I am not going to tell of the specific researches in which I may have coöperated, nor of the good fellows who have carried them out in our laboratory, though I should like to do so. One reason is that this is, to a considerable extent, being done all the time, through our laboratory system. We have always followed the plan of individual publication as completely as seemed desirable from the scientific point of view and as rapidly as consistent with fair commercial conditions. Moreover, I, being almost the only man in our laboratory who does not often personally carry through separate researches, have already summarized the work of others until it is overdone.

What I have to say oscillates about a central point. This point I see so well that I am surprised that every one does not see it too, and make more use of it. I am also at a loss to know why so many men go through college keeping their eyes mainly on a ball of some kind or other, when the world is so full of greater interest. Perkin's life contains all the data which we need in analyzing scientific research, and shows at once what I shall repeat throughout this paper, that our great advances are usually made by men who are trained in their particular line of work and are working diligently just beyond the boundaries of the known.

Perkin was a student of chemistry in one of the best college laboratories in England, under a great teacher (Hofmann), who was so imbued with the chemical research spirit that he tried to keep Perkin from stopping to develop technically his discovery of mauve. He actually left such an impression on this young man's mind that, after years of commercial success, Perkin returned to pure scientific research and enjoyed it for the rest of his life.

The essentials appear to be: first, the teacher, enthusiastic pioneer, hunting, and fishing along that ever-expanding outer rim of knowledge; then the laboratory and equipment, supported by some far-sighted government, individual, or organization; and then the school boy, with shining morning face. Don't say it can't be done, and that Perkins, Faradays, and Pasteurs are born, not made, for the process is entirely standardized. We in our schools have not realized the proper sequence, because we have used so much of our energy in bringing large numbers of men part of the way only.

On receiving the first Perkin Medal at the time of the Jubilee Celebration, Sir William Perkin said that he had all his life insisted on the importance of research, and that this medal would accomplish a valuable result if it helped to encourage and stimulate activity in that direction. He then proceeded to tell the interesting story of his subsequent discoveries. Such a story is the strongest force he could have used to support his wish to promote research, and it is true that, although it would have been more agreeable to him if some one else could have told the story, everyone who heard it, and the countless chemists who live to read it, are glad that no one else did tell it.

PERSONAL EXPERIENCE

No greater satisfaction in connection with my own life's work could come to me than to contribute to the encouragement and stimulation of research. If I can help it to an appreciable extent by telling any unpublished portions of my own story, I will willingly disregard for a few moments a natural reluctance to talk about myself.

I learned that Professor Perkin became a chemist through the influence of an Englishman named Hall, with whom he came into contact when under 15 yrs. of age, and, moreover, an event which increased his desire to become a chemist was seeing an experiment showing the growth of certain crystals. I have the honor to have started as a chemist in this identical manner, and I will tell a little more about it, because I have always wished I had some way of expressing my gratitude to my particular Mr. Hall. When I was about 15 yrs. old, an English mill owner and one of the leading citizens of my home town, Mr. William C. J. Hall, assisted in establishing a Young Men's Christian Association. He had also long been interested in the microscope, and was a scientist such as we seldom find among business men to-day. He formed a free evening class for about half a dozen boys—all that could work together around the rotating table on which he placed his immense microscope. This was so arranged that specimen, instrument and illuminating system did not have to be disturbed as they passed from one boy to another for observation. He did not merely show his specimens, of which he had thousands, but taught us how to prepare them in all the various ways now more or less common. They were all wonderful to me, and still are. My mother gave me some money which, combined with that of one of the other boys, purchased a small microtome, and my father gave me $75.00 for a microscope. Under Mr. Hall's guidance I bought the instrument, with the understanding that whenever I wanted a better one, the old one would be taken back at the original price. I later procured one for $250 which, throughout 35 yrs., I have used almost daily. One of the first experiments I tried with the microscope was to precipitate metallic silver from silver nitrate solution onto a speck of copper filings. Anyone who has watched these beautiful crystals grow knows that they are surpassingly wonderful. They constituted my first chemistry. It was those little bottles of salts and bugs in alcohol that led someone to call me a chemist, and it apparently determined my future work. It does not seem now as though anyone else ever enjoyed a tenth of the pleasures my old microscope introduced to me. I find them inseparably interwoven with about everything I know. Even the barren North Pole reminds me of Andrée and Amundsen and microscopic algae which drifted across the polar circle from the Lena delta. The equally barren Sahara reminds me of Darwin and De Vries and the diatoms which were carried by the wind from central Africa and fell on the deck of the Beagle, hundreds of miles away.

In trying to put the truthful personal and human element into these notes, as previous Perkin medalists have done for the help of would-be research men, I find I cannot lay valid claim to the insurmountable difficulties or to especially commendable early struggles which have helped so many others. Perhaps even this admission, however, may have its place for the encouragement of some research man. I was early taught that a dollar a day was a fair wage and that frequently this was unearned, and I quit worrying about pay so long ago that the date is not important. I once asked the president of a large technical school for a salary increase of $75 a year and was shown that it could not be done. Perhaps that wise president convinced me that financial rewards are not the main thing. At any rate, I believe it.

In mapping milestones not mentioned before, I want to express my indebtedness to Professor A. A. Noyes, who showed me some of the interesting things in the science of chemistry. He let me work with him on some physicochemical researches, and this work was responsible for my later spending two years with Ostwald in Leipzig, and a summer with Friedel in Paris. Work with these men gave me a feeling of surety in chemistry that no mere talk could ever have done. I ought to say that one of our first joint researches, so far as publication was concerned, had the peculiar effect of freeing me forever from the wiles of college football, and if that is a defect, make the most of it! Dr. Noyes and I conceived an idea on sodium aluminate solutions on the morning of the day of a Princeton-Harvard game (as I recall it) that we had planned to attend. It looked as though a few days' work on freezing-point determinations and electrical conductivities would answer the question. We could not wait, so we gave up the game and stayed in the laboratory. Our experiments were successful. I think that this was the last game I have ever cared about seeing. I mention this as a warning, because this immunity might attack anyone. I find that I still complainingly wonder at the present position of football in American education.

BIGGER THINGS

I would prefer now to talk about the biggest things in chemistry, not so that I may be facetious, nor yet to form a companion piece to a talk on the "Littlest Things." Far from it. In fact, so far from it that after having some of my thoughts in preliminary notes for years, with a conviction that they ought to be expressed, I have always deferred it. I feared that I was not just the man to say it.

We are all interested in the detailed and specific advances which constitute our science. We know that it is from these little things that the largest ones grow. We see a certain similarity between the history of Professor Perkin's mauve, with its subsequent enormous development of the dye, medicine, and explosive industries, and the development of the living acorn into the spreading oak tree. But we should sometimes look at the forests from the plains, without obstructions. And we want to know our chemistry, too, in its relation to the general landscape. Some kind of an inner man advises us not to think exclusively of the littlest things, the parts of some whole, but sometimes to give constructive thought to the ultimate objects, to our aims at large, our chief pretensions, our real ambitions, our main direction of motion. Are these consistent with, or independent of, our temporary and apparently vacillating movements?

I know from experiment (as we usually say) that no two chemists would agree at first as to what constitute the most important things of chemistry. I have found, however, that if we say that the "possibilities" are the biggest things, then to-day there is some agreement between experts.

TESTED LAWS—Chemistry is one of those branches of human knowledge which has built itself upon methods and instruments by which truth can presumably be determined. It has survived and grown because all its precepts and principles can be re-tested at any time and anywhere. So long as it remained the mysterious alchemy by which a few devotees, by devious and dubious means, presumed to change baser metals into gold, it did not flourish, but when it dealt with the fact that 56 g. of fine iron, when heated with 32 g. of flowers of sulfur, generated extra heat and gave exactly 88 g. of an entirely new substance, then additional steps could be taken by anyone. Scientific research in chemistry, since the birth of the balance and the thermometer, has been a steady growth of test and observation. It has disclosed a finite number of elementary reagents composing an infinite universe, and it is devoted to their interreaction for the benefit of mankind. The rate of this advance in chemistry is in our day almost incredibly great.

Mark Twain's little history game has given me a view of our rate of development, and particularly of modern as compared with ancient affairs, that I want to pass along to you. Possibly some of you have thought of the rate of mental development, of material development, and of power developments as involving only a fairly uniform change through all time. This is not so at all. But to shorten this story: I started from a certain point in the woods with a measuring tape and marking tools, and laid out a winding path 1000 ft. long. I cut smooth marking places on all trees along the way and on some large rocks. I appropriated one foot length of this patch for each year's history since William the Conqueror (the year 1000), and spent the rest of my time properly locating prominent events along the path, down to 1920 ft. I was impressed by the 45-ft. length of Queen Elizabeth's reign, near the middle of the way, and such a short distance from Columbus and the discovery of America. Stockings and pins and sugar (except as medicine) came into the path about there. But of interest to us particularly is that all the great chemists began to arrive together near the 1850-ft. point. This seemed very recent. It meant that most of the superstitions about matter began to disappear only about 250 ft. back, so to speak. You all know the story, but for 75 or 80 per cent of my measured path, and for the interminable portion representing all time prior to 1000 A. D. (which I let wind, without construction or destruction, back the mile or more which might still have been historically illustrated), there had been no need for more than four supposed elements: earth, air, fire, and water. It was not the old facts, but the dimensions which impressed me. While a foot is ample space in which to erect monuments to everything we know about any year chosen in the fifteenth century, and a single tree could be sign-post for all the cards on events for any century a little earlier, there was great lack of space for descriptive matter beyond the 1800-ft. point. All down the line, to within a stone's throw of the end, individual man-power had been the important energy, and then, as power, it almost disappeared. Within 200 ft. of the end, which stood for the present day, steam had been put to use, and there came in turn the myriads of machines which multiplied a thousand-fold the previous constant and limited muscular power of man. No one can accurately determine the added spread of effort, due to this substitution of coal for human strength, and then of machines, one for another.

Within 30 ft. of the end of the path, a score of new chemistries had grown into activity, and every single one seems more promising than the original stem: physical, colloidal, subatomic and radio, metabolic, biologic, enzymic, piezo, therapeutic—all growing infants. Thus the time seems almost near when, to quote Carnegie, "the mind, like the body, can be moved from the shade into the sunshine."

This interesting game of Mark Twain's actually chokes itself off mechanically when one tries to post modern chemical work at one foot per year. New facts now take about that space when posted edgewise in abstract journals, a dozen items per page. What this game, applied to chemistry, has done for me is to show me the almost inconceivably great strides in countless lines which constitute our modern chemistry, and it leaves me with the feeling that no one in the world has ever had such possibilities open to him as the present-day student of chemistry.

Perkin was a well-prepared research chemist when he made his discoveries. He was just the kind of man of which we produce too few. Only a very small number of our students get so far in the science as he went under Professor Hofmann, and nowadays, in order to go so far, one must go much farther, for, as Wendell Phillips said, "to be as good as our fathers were, we must be a good deal better." The process Perkin followed is the same one which has led to most of our discoveries. It is the encouragement of natural inquisitiveness under the best conditions. It is using the newest knowledge and best tools in exacting pieces of work. No short-cut and easy process would have produced dyes from tar. Such efforts could not even find a way to make tar acceptable for road material.

One of the biggest things in chemistry for us to-day is to learn how to bring about the productive teaching of chemistry. The desirable qualities are illustrated by the life of Wöhler, who prepared the first organic compound, when the consensus of opinion (and infinite argument) favored the theory that organic compounds were producible only through a mysterious vital force. Pasteur's work is another case of a trained research chemist, and every American should learn his ways. What such explorers seek are not imaginary points on a drifting field of perpetual ice in an uninhabitable world, but something which may possibly help every individual who lives after them.

We might have similar results developing in chemistry to-day, but they call for the good teachers and the highly trained observer, with well-backed faith. These two, high training and faith, are an uncommon pair with us. They seldom grow within the same Yankee.

INORGANIC CHEMISTRY—I need not repeat what is known about the many disclosures of inorganic chemistry. How, within the past few years, chemical science has at least doubled the number of available metals, and so raised to the *n*th power the possible alloys. All these new metals are gradually coming into use, as you know.

I am often reminded of metallic calcium in this connection, because it is really still being born, but the process is the old one. It was produced by high-grade electrochemical research, and the discoverer, in describing the process, said, "We do not know now of any use for this new metal, but when its properties and production are understood, it will probably find its place." It is almost useless to think otherwise. Here is a chemical element the compounds of which are as numerous and whose ores are as rich as those of any element known. The isolation of the metal is not so simple as in the case of zinc, copper, iron, or tin, and its properties are different, but, as usual, it is differing properties which determine the new use. It is worth telling in passing that, during the war, we made this metallic calcium and found two widely different uses for it. One was as a suitable generator of hydrogen to maintain very high pressure of this gas inside certain deep-sea sound detecting devices, where the sea water itself was the other reagent. The reaction was slow and well suited for this work. The other use is as a continuously reacting purifier for argon in the tungar rectifier. This latter is now the basis of a considerable manufacturing business. It is interesting, from the chemical research standpoint, because it consists of a bulb made of a special new glass, a tungsten wire spiral, an artificial graphite electrode, a little argon gas, and some metallic calcium. Within the spread of my brief experience, there was a time when any part of this combination would have been an impossibility from lack of every one of these chemical materials. And so I note such researches as Professor Lehner's, on selenium oxychloride, and I say to myself, "Watch it grow." To add such a liquid to our little category will prove an ever-growing utility.

ORGANIC CHEMISTRY—We ask ourselves: Can there be greater fields of new organic chemical research than that which met Perkin as a student? Is not tar the last big raw material? The answer is simple. New fields are greater in number because the territory of chemical knowledge is so greatly broadened and the new tools are so numerous. The results will depend solely on mentality—not tar. Is it not within reason that another as great a field as dyestuffs will be developed directly from carbon itself, for example? The entering gates to organic chemistry, reached by the shortest road, were apparently opened when calcium carbide was first made. Thus, starting with two of our most abundant mineral products, coal and limestone, and adding water alone, we are supplied with the endothermic gas, acetylene. From this point, almost anything organic seems possible. When we realize that the manufacture of acetone, alcohol, etc., has been thus made possible from these inorganic raw materials, we might as well expect, by the same road, useful food as certainly as medicaments.

I am repeatedly pointing to need in our country for the highest class of chemical preparation. It is not enough to talk of the importance of fuel, of the conservation of coal, of the possible use of benzene or alcohol in our motors. Such have already become engineering problems, and we have a hundred thousand engineers in the country capable of solving them. Some of these men have already carried out the manufacture and use of hexahydrobenzene in motors, for example, but the chemistry itself, as a science, though still infinitely promising, is relatively neglected.

AGRICULTURE—Possibly one of the biggest things in chemistry lies in agriculture, but it would be futile for me to treat of its research by the modern truthful, but standardized, method. It is admitted that we need more and better fertilizers. We now use nearly $200,000,000 worth annually. It is true that we have recently spent many million dollars on nitrate plants. We also think we need half a million tons of potash annually, and of this we can see how to produce locally only about 10 per cent. We want synthetic ammonia and we can get it, because, during the war, we were forced to adopt production methods derived from foreign chemical research.

I do not need to go further with agriculture in order to prove that I am not a real farmer, but I insist on doing so because I want to make clear the thought that possibly our troubles in general with Nature are sometimes due to our personal limitations, not to the limitations of Nature.

It looks to me as though possibly man had developed most of the cultivated fruits of the field along the line of maximum human exertion and immunized them to everything else. I draw this hasty conclusion from a single experiment of my own. Last year I procured some special high-grade seed corn and treated portions of it in widely different ways. In one case the kernels were planted, properly spaced, through holes in large sheets of paper placed on new ground which had had its grass killed by a year's covering with gravel, which was then removed. The paper was to discourage the weeds and make hoeing unnecessary. Other hills were planted without the paper, and still others in which the soil was taken up, softened, and replaced. None of these new-type gardens was disturbed during the summer. Less radical experiments, including nothing at all but muscular effort, were tried on other hills in an old-type garden. Knowing how corn had been produced through thousands of years of applied work, the results could have been foreseen. All that grown on new soil, protected by paper from weeds and from evaporating winds, took the whole summer to grow about a foot high. It looked very mature, but didn't bother to produce any ears. That which had been about buried in modern artificial fertilizer, and well hoed, pulled through somehow, and that which had been manured and most energetically hoed did the best and gave a normal corn crop.

The growing of corn and grain is an older process than making wire nails, and cannot so easily be improved. It has developed with no fair regard to human labor, and will take more novelty of effort to change it than was employed in freeing manual labor from nail, screw, and bolt making, or from the production of artificial indigo or synthetic camphor.

When one reads of the experiments of Loeb on the rate of growth of bryophyllum shoots as influenced by various schemes of cutting leaf from stem, etc., one can hardly doubt that new truth, learned for itself alone, in some such way, may at least rearrange some parts of future agricultural research. Anyone who has annually tried to kill a burdock by any means short of complete eradication, or who has watched the persistency with which a lot of wild chicory will grow to maturity in the almost imaginary crack between a reinforced concrete roadbed and the adjoining separate curbstone, will appreciate the thought that some time, somehow, man may successfully direct his researches towards the growth of useful vegetation with reduced, not increased, human labor.

MEDICAL RESEARCH—Many biggest things in chemistry are coming from chemical research in the field of life and health. When I recall the Rockefeller Institute for Medical Research and think of the international character of its men and work, I incline to the belief that, through such researches in chemistry and allied sciences, the countries of our world may be more certainly finally allied than by the system of countless peaceful words coupled with increasing arguments. There I have seen Carrel, French scientist of the purest type, keeping chicken tissues growing on microscope slides for nearly a decade, in order that he may carry out those quantitative experiments which lead to exact medical science. In such an institution a class of refined and exhaustive work can be done whose results stand as foundation stones on which doctors and surgeons of all lands may build at once. The diplomacy of such institutions leaves room for no international spies. The results, as soon as verified, are published to all quarters of the globe. Jacques Loeb, studying the amphoteric properties of gelatin or the temperature coefficient of the life-reactions of fruit flies, is putting permanent points of observation on the graph of human knowledge where all may see, confirm, and use them. The little Jap, Noguchi, a most attractive enthusiast and a co-worker of Dr. Flexner's for nearly 20 yrs., is now all wrapped up in yellow fever work. He has isolated the germ and prepared the preventive vaccine and the immunizing sera. Thus he adds some of the finishing touches to that story of a fight which has been under way since 1900, when Dr. Lazear knowingly risked and lost his life by letting a certain mosquito bite him.

BRAIN—If we think of the brain as the workshop of the mind and then look back over the history of the growth of brains, we find that this workshop first appeared as a relatively *very* small portion of the mass of the early animals. All the prodigious vertebrates of the mesozoic period had exceedingly small brains in proportion to their bodies. The brain size in comparison to the size of the animal has always been on the increase. In man and his forerunners this is also well known. But it is significant that, even with man, there is no continuing brain growth when he is kept from doing or thinking something new. The Egyptian fellaheen, who were kept at unchanging labor for many centuries, possessed the same size brain cavity at the end as at the beginning of that period. But the diameters of the brain cavities of the early man-forms after the chimpanzee (the Trinil, Piltdown, and Neanderthal men) stand to man as at present in about the relation of the numbers 12, 13, 14, and 15.

And yet, in this most modern workshop, the energy which is consumed is so small, when compared to the work done by other organs of the body, that it cannot be measured as energy at all. It is easy to measure the work done by the little finger and express it in calories consumed from the food eaten. The most extensive mental exercise is much more economical of energy. In other words, we have not yet taxed the mind's workshop from the energy or work point of view. All this means that, following the direction of natural development, there need be no lack of that brain power or mentality which is needed to handle all that he may wish to know and think.

MIND—The biggest thing of all in research is the mental effect, the projecting of a beam of light into the infinite and the growth of man's appreciation. I can scarcely touch the many connections here. But in delicacy and sensitiveness, the mind far transcends the wireless receivers which yet read, half around the world, a message sent by a few watts of energy. And I need say nothing about its possibilities as a power producer or controller. In coöperative work, minds multiply, instead of adding together, and growth of mind depends on the experiments or the reactions with things. Whether mind is a polarized energy, or merely a long habit, may still be in doubt, but there can be little doubt as to what expands it.

Not very long ago it was safer to conceal new truths than to disclose them. If a man wished to die by some horribly ingenious method, he had but to discover something like the rotundity or mobility of the earth and insist on it. For advocating justification by faith alone, he would be burned alive. Dabbling with intangible matters which led only to disputation was gradually replaced by increased attention to immediate surroundings.

Is it too much to say that, through research into materials, the main advances in physical and mental welfare take place? Where do we meet contradiction if we say that, except for research, or experimental study of matter, we stand still or mill about in circles filled with superstitions? Particular attributes of the human mind may well have reached higher altitudes in some previous age, as is usually claimed. In specific lines of human undertaking we can but accept this as true. We have no Homer among our poets, no Cellini nor Angelo nor De Vinci among our artists. Plato and Aristotle and many others ages ago equaled our present-day logicians. Such are the nuggets of truth which the seeker for values in history is apt to dig up. As architects or sculptors or hewers of stone we may be retrogressing, and in any selected development we may have passed the zenith, but all the time the knowledge of the universe and of each atom of it, from the tiny flower of the crannied wall to the sun which brings it forth, and the stars which so immensely exceed this, has been rapidly increasing. The only perpetual motion is the growth of truth. Possibly faith, hope, and love are not at a maximum in our age, but they may be, and through all ages there seems to run Tennyson's one "increasing purpose." Only one sure line of continuing increments can be traced. It is not the line of the search for waters of eternal youth. It is not the series of philosopher-stone experiments, though a few of them contributed to the steady growth of our horizon. It is not the line of ascetism, stoicism, religious tolerance, or intolerance of any form, nor yet the political systems of the widest variety. They are now useless except as they added to the accumulating mass of truth. Appreciation of environment has always increased.

RELIGION—The natural desire for religious truth has been responsible for most colleges and universities. They served first to encourage learning and prepare religious teachers, but only recently has it become the recognized duty of universities to seek truth by investigations of material things. Goldwin Smith wrote of Oxford in the early days that:

> For the real university students, the dominant study was that of the school of philosophy, logical and philosophical, with its strange jargon; an immense attempt to extract knowledge from consciousness by syllogistic reasoning instead of gathering it from observation, experience, and research, mocking by its barrenness of fruit the faith of the enthusiastic student. * * The great instrument of high education was disputation, often repeated, and conducted with the most elaborate forms in the tournament of the schools, which might beget readiness of wit and promptness of elocution, but could hardly beget habits of calm investigation or paramount love of truth.

The uptrending curve of recognized facts might be called Nature's appreciation curve, or the growth of mind. While cattle eat, drink, and die with no more appreciative attitude towards their surroundings than shown in previous ages, mankind has accumulated, by experiment, everything that distinguishes him. But certainly the end of this growth is far away and still out of sight. When men can talk so glibly about their closeness to a Creator and yet uniformly show, by destructive warfare, their extreme remoteness, surely the great undertaking, whatever it means, is not nearly complete. We have much to learn.

May it not be possible that the human urge for new truth, the world trend for clearness of vision in material things, will be justified? Can there be a better way of appreciating the wonders of creation than by looking into them, uncovering, understanding, and appreciating them?

I should identify all search for scientific truth with the highest religious aim, no matter what the cult. I would point out here that our inactivity and inappreciation in the presence of infinite, undeveloped truth is the most inexcusable type of error and unfaithfulness. It is intense faithlessness, no matter what conception of a Creator we adopt.

There is no better (perhaps no other) way of going forward in the new paths which instinctively attract us than by using new material knowledge. Is it not possible that words of affection, of sympathy and promise of all kinds, helpful, heartfelt, and beautiful as they may be, are only the paper money of our transactions, and that, behind them, there should be gold of service, in which to pay the promises?

I do not look at this as crass materialism. We all know that the mere chemical reactions of the brain are not the whole story. A measuring machine, repeating automatically all the motions of the scientist, would not interest us at all. Appreciation of the infinite is not mechanical, but truth is necessary for appreciation. John Burroughs has said:

> Every day is a Sabbath day to me. All pure water is Holy Water, and *this* earth is a celestial abode. It has not entered into the mind of any man to see and feel the wonders and mysteries and the heavenly character of this world.

Yet most of what even John Burroughs sees and appreciates is outside of the infinitely beautiful and orderly realm of modern chemistry. When we are first old enough to ask ourselves questions, we are so mature that we seem already surrounded by an infinitely complex and interesting environment. A persistent and age-old instinct makes us want to wander

> Into regions yet untrod
> And read what is still unread
> In the manuscripts of God.

And it has developed that in no other way may we hope to understand and appreciate. Chemists should naturally be the first and greatest appreciators. Research is appreciation.

SCIENTIFIC SOCIETIES

PLANS FOR THE SPRING MEETING

Preliminary plans for the big Spring Meeting of the American Chemical Society to be held in Rochester, N. Y., from April 26 to 29, 1921, are already under way.

The Council Meeting, on the day previous to the regular meeting, will be held at the Rochester Club. The General Meeting is to utilize the Central Presbyterian Church in order to give room for the large crowds. At this time the address of welcome will be given by a man whose name is on every tongue, but whose identity we are not now allowed to divulge.

The various Sectional meetings will be held at Mechanics Institute, where there will be hung charts illustrative of the methods and productions of all our most important home industries. Parallel to this, there is to be a series of personally conducted trips through the following large manufacturing plants: Eastman Kodak, Pfaudler, Bausch & Lomb, Taylor Instrument, and Vacuum Oil Companies.

It is also planned that during the Sectional meetings a master of ceremonies will be in instant communication with all Sections through an intricate system of intercommunicating telephones. Thus any hitches in the program which usually occur will be at once alleviated.

The piece de resistance will be the banquet, free to members, to be held at Bausch & Lomb's, after which this company will furnish a high-class entertainment. At this banquet it is hoped much of the formality will be dispensed with, and the ladies will be in evidence.

CELLULOSE SECTION

At the Cellulose Symposium held by the Industrial Division at the meeting in Chicago it was voted to form a permanent Cellulose Section. The necessary steps for organization were taken, and President Noyes appointed Professor Harold Hibbert of Yale University, chairman of the new Section, with Gustavus J. Esselen, Jr., secretary. One of the objects of the Section is to provide an opportunity for those interested in the practical applications of cellulose to get together with those concerned with the more strictly scientific aspects of cellulose chemistry, thus affording an opportunity for discussion which should prove mutually helpful.

An interesting program is being arranged for the first meeting of the new Section in connection with the Spring Meeting. Those having papers which they would like to present before the Section are requested to send title and abstract before April 1, 1921, to the secretary, G. J. Esselen, Jr., care Arthur D. Little, Inc., 30 Charles River Road, Cambridge, 39, Massachusetts.

CENTENARY OF THE FOUNDING OF THE SCIENCES OF ELECTROMAGNETISM AND ELECTRODYNAMICS

On December 4, 1920, electrical engineers, chemists, and men of affairs gathered at Ampere, New Jersey, on the invitation of the Crocker-Wheeler Company, to do honor to the memorable discoveries of André Marie Ampère.

The meeting was not held on September 18, the exact date of the anniversary of Ampère's first memoir to the Académie des Sciences, on account of Ambassador Jusserand's absence abroad. Although back in this country, diplomatic matters prevented his unveiling the bronze wreath placed above the tablet bearing Ampère's features, which he had unveiled in October 1908. However, his Chargé d'Affaires, Prince de Béarn, made a felicitous address, and later unveiled the wreath.

Dr. Schuyler Skaats Wheeler, president of the Crocker-Wheeler Company, introduced the speakers and welcomed the guests.

Dr. M. I. Pupin spoke of Ampère, "The Man and Genius." His account of the philosopher's life, his struggles against adversities, his remarkable mathematical gifts, and wide acquaintance with all departments of learning was brought to a close by a glowing peroration in which he eulogized Ampère as typical of France, now emerging from imminent disaster to win the plaudits of the world.

Dr. C. O. Mailloux, officially representing the Académie des Sciences, devoted a part of his address to a description of the rapidity with which Ampère developed the basic principles upon which our electrical knowledge and engineering depend, and then gracefully thanked the donors of the wreath in the name of the Académie.

A series of letters by eminent scientists reprinted in pamphlet form, from the *Electrical World* of September 18, and October 9, 1920, was distributed to the guests. The short genealogical trees, drawn up by Prof. R. A. Millikan of the Ryerson Physical Laboratory of the University of Chicago, illustrate admirably the relationship of Ampère's work, founded on the experiments of Oersted, to our present electrical developments:

"Electronic Amplification—De Forest, Richardson, Thomson, Roentgen, Lenard, Hertz, Maxwell, Faraday, Ampère, Oersted.

Relativity—Einstein, Lorenz, Becquerel, Roentgen, Lenard, Hertz, Maxwell, Faraday, Ampère, Oersted.

Radiotherapy—Rutherford, Curie, Roentgen, Ampère, Oersted.

Subatomic Structure—Sommerfield, Bohr, Rutherford, Thompson, Roentgen, Lenard, Hertz, Maxwell, Faraday, Ampère, Oersted.

"These are merely illustrative of what might be done presumably in scores of other fields. They illustrate also the immeasurable value to mankind of the work of the pure scientist and the imperative necessity of stimulating and supporting him. With one single exception all of the foregoing names belong to men who devoted their whole lives to pure science."

Charles A. Doremus

DR. HENRY A. BUMSTEAD

The following resolution on the death of Dr. Bumstead was adopted at a special meeting of the Interim Committee of the National Research Council, January 3, 1921.

Resolved, That the National Research Council learns of the death of Dr. Henry A. Bumstead, Chairman of the Council, with great sorrow and profound sense of loss. Dr. Bumstead in his association with the Council had revealed to its officers and members not only a high capacity for administration, and a most loyal fidelity to the aims and work of the Council, but also a sweetness of disposition and personal attractiveness which had won for him the devoted and affectionate regard of all of his colleagues in the Council. In his death the Council and the scientific world lose a man of most eminent attainments, highest character, and lovable personality.

The National Research Council extends to the bereaved wife and family its deepest sympathy and condolence and wishes to express to them its full appreciation of the great value of the services which Dr. Bumstead rendered it in the period of his association with it and the great loss which it suffers by his untimely death. But may we all remember that "that life is long that answers life's great ends."

NICHOLS MEDAL AWARD

The William H. Nichols Medal for 1920 has been awarded to Dr. Gilbert N. Lewis, of the University of California, for his paper on the "Third Law of Thermodynamics and the Entropy of Solutions and of Liquids," published in the *Journal of the American Chemical Society*, **42** (1920), 1529.

The presentation of the medal will take place at the meeting of the New York Section of the Society, in Rumford Hall, Chemists' Club, New York City, May 6, 1921.

JOHN SCOTT MEDAL AWARD

Dr. C. E. Kenneth Mees has recently been awarded a John Scott Medal and Premium by the City of Philadelphia, on the recommendation of the Franklin Institute. The award was made for special researches on the structure of photograph images, which form part of the systematic investigation of photographic theory undertaken by the research laboratory of the Eastman Kodak Co., of which Dr. Mees is director.

RUMFORD MEDAL PRESENTATION

The Rumford Medal of the American Academy of Arts and Sciences was presented on Wednesday, January 12, 1921, to Dr. Irving Langmuir, of the General Electric Research Laboratory.

PRESIDENT SMITH ADDRESSES JOINT MEETING

President Edgar Fahs Smith, of the American Chemical Society, will deliver an address at the joint meeting of the New York Section of the American Electrochemical Society with the New York Sections of the American Chemical Society and the Société de Chimie Industrielle and the American Section of the Society of Chemical Industry, to be held in Rumford Hall, Chemists' Club, New York City, on February 11, 1921.

CALENDAR OF MEETINGS

American Ceramic Society—Annual Meeting, Deschler Hotel, Columbus, Ohio, February 21 to 24, 1921.

American Paper and Pulp Association—Annual Meeting, Waldorf-Astoria and Hotel Astor, New York, N. Y., April 11 to 15, 1921.

American Electrochemical Society—Spring Meeting, Hotel Chalfonte, Atlantic City, N. J., April 21 to 23, 1921.

American Chemical Society—Sixty-first Meeting, Rochester, N. Y., April 26 to 29, 1921.

NOTES AND CORRESPONDENCE

HISTORY OF THE PREPARATION AND PROPERTIES OF PURE PHTHALIC ANHYDRIDE

Editor of the Journal of Industrial and Engineering Chemistry:

An article on this subject was published in This Journal, **12** (1920), 1017, by H. D. Gibbs of E. I. du Pont de Nemours & Company. As this article adds nothing to scientific knowledge and also varies somewhat from being an accurate statement of the facts, it was thought appropriate to present the following correction in order that a proper understanding might be reached.

The matter under discussion is U. S. Patent 1,336,182, which claims as an article of manufacture, "phthalic anhydride being substantially chemically pure and having a melting point above 130° C. (corrected)" and "phthalic anhydride in the form of colorless needle-like crystals substantially chemically pure and having a melting point above 130° C. (corrected)."

It is pointed out by Gibbs that Monroe[1] prepared and described phthalic anhydride of a degree of purity which undoubtedly exceeds that of the product described in this patent in 1919 prior to the date of filing of this patent. Monroe[2] states in this article that "the resublimed phthalic anhydride produced by the air oxidation process was of a high degree of purity but it was determined to subject it to a more rigorous purification." He found the equilibrium temperature of liquid and crystals when this especially purified material was used to be 130.84°. Quoting from his article, "A melting point identical within experimental error was obtained under similar conditions for the original anhydride which was the source of the carefully purified material confirming the previous conclusion that no more than traces of impurities were contained in this." It can be definitely proved that this original anhydride was a sample of the anhydride produced as described in the patent under discussion (U. S. Patent 1,336,182) and was sent to the Color Investigation Laboratory of the Bureau of Chemistry for investigational purposes. From this there would seem to be no doubt about the priority of the product described in the patent.

It seems quite probable that the anhydride described in this patent is a new commercial article of manufacture. Monroe[1] investigated samples of Kahlbaum's "Phthalsäure Anhydrid" and found the equilibrium point of solid and liquid to be 129.6°. When this material was subjected to purification, as in the case of the product obtained by air oxidation, he obtained a constant freezing point of 130.8°, which is the same as obtained from the latter material. He suggests that the original samples obtained contained a considerable admixture of phthalic acid. Certainly the material put on the market by Kahlbaum must have been as good as that sold in commercial quantities.

Gibbs states that "a process of manufacture by air oxidation (using vanadium and molybdenum oxides as catalysts) which yields a product in the form of 'long, colorless, glistening needles' substantially chemically pure and having a melting point above 130° C. (corrected) has been described and patented" by himself and C. Conover. The patents referred to are U. S. Patents 1,285,117 and 1,284,888. The essential claim of both of these patents is as follows: "A process for the manufacture of phthalic anhydride, phthalic acid, benzoic acid, and naphthaquinones, which process consists in subjecting naphthalene in

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[1] This Journal, **11** (1919), 1116

[2] *Loc. cit.*

[1] *Loc. cit.*

the gaseous state and mixed with an oxygen-containing gas mixture, to the action of vanadium (molybdenum) oxides heated to temperatures ranging from 250° to 650° C. When the process is carried out according to the above claims either on a laboratory or commercial scale, phthalic anhydride is produced which may consist of long, glistening needles, but it is always far from colorless and anything but substantially chemically pure, and having a melting point above 130° C. (corrected). The color ranges from a light yellow to black and the melting point never is as high as 130° C. There is no mention made in either of the Gibbs-Conover patents as to the purity of the product, but Gibbs bases the disclosure of the remarkable purity of the product on Monroe's work and an article published by him.[1] It has been shown that Monroe carried out his work with material made according to U. S. Patent 1,336,182, which is the one under discussion. The article entitled "Phthalic Anhydride. I—Introduction," just mentioned, was received for publication August 19, 1919, which was approximately two months earlier than the filing date of U. S. Patent 1,336,182. It will be evident to those who have had charge of similar problems that two months is a very short time for the development of a manufacturing process for the product in question. In addition to this it can be definitely proved that this product was produced according to the claims of the patent in large quantities at a much earlier date than either of these disclosures.

It is evident also that Gibbs has neglected to consider the judgment reached by the examiners of the Patent Office after a very careful search of the Patent Office records as well as the literature on the subject.

In view of the above facts it does not seem impossible to conceive the grounds upon which such a patent was granted.

THE SELDEN COMPANY
PITTSBURGH, PA.
November 15, 1920

C. E. ANDREWS

THE IGNITION OF FIRE ENGINE HOSE WHEN IN USE

Editor of the Journal of Industrial and Engineering Chemistry:

Boston papers of November last had a most astonishing tale of the spontaneous ignition of fire hose when in service. The facts in the case are as follows:

It was a new 50-ft. length of the usual 2.5-in. hose consisting of a simple rubber lining inside a heavy cotton jacket. Outside this was drawn a similar cotton jacket. The hose was used in a test made on the new pumping engines, and the stream was throttled down about 45 per cent, discharging about 250 gal. per min. Notwithstanding the fact that this quantity of cold water from the Charles River was used, the hose took fire *between the cotton jackets.* A spot 2 in. long by 1.12 in. wide was burned clear through each. Careful examination reveals the fact that on each side of the burned hole the inner casings or jackets are very severely chafed. This chafing coming from the vibration produced in the hose by the pump was in my opinion, sufficient to produce great heat and finally active combustion. I found also a similar state of things in another sample of hose used at a later test. The chemical composition of the rubber, in my opinion, had nothing to do with the case.

I am of the opinion that the occurrence was due to excessive friction between the cotton casings produced by the vibration of the hose in service.

It is interesting to note that these results have been confirmed by Mr. J. S. Caldwell, chief engineer of the N. E. Insurance Exchange, with three different types of engines and three different makes of high-grade, standard hose. The experiments were made in Portland, New Bedford, and Boston, and in some cases the cotton was charred in about 15 min.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS
January 13, 1921

A. H. GILL

REPAIRING IRON LEACHING VATS

Editor of the Journal of Industrial and Engineering Chemistry:

Herewith I should like to communicate an experience in repairing leaching vats which may be helpful to others.

The bottom of a 5.5 ft. by 22 ft. circular cyanide leaching vat contained numerous holes, and some parts were so badly worn out that a needle could be passed through without effort.

At first the leaks were calked with coal-tar soaked cotton waste. This method proved to be inefficient. Then a 2-in. cement bottom was laid on the inside of the tank, but pressure variations during charge and discharge, causing various bendings of the bottom, broke the cement layer in no time. This observation led to the construction of a more flexible bottom, built as follows:

Over the whole defective bottom was laid a 0.25-in. asphalt layer, covered with a layer of canvas (in our case old filter leaves). Care was taken that the canvas was pressed on the asphalt while the latter was still hot, in order to secure a close contact. Finally the canvas was covered with asphalt 0.25 in. thick.

After 24 hrs. the tank was filled with water, held under water pressure for 72 hrs., discharged, filled again, and held under pressure again for 72 hrs. During this experiment not the slightest leaking could be observed.

The total repair cost amounted to approximately $92, whereas a new tank was quoted at $750. To put a new iron bottom in was impossible, owing to the fact that the bottom ends of the mantel-pieces would not stand a new riveting.

As your Journal, which I receive as a member of the AMERICAN CHEMICAL SOCIETY, often gives me helpful suggestions, I should like to help someone who is in trouble.

FRENCH MINES
TAIYUDONG, KOREA, JAPAN
October 13, 1920

C. FLURY

VAPOR COMPOSITION OF ALCOHOL-WATER MIXTURES

Editor of the Journal of Industrial and Engineering Chemistry:

Under the above heading in THIS JOURNAL, **12** (1920), 296 W. K. Lewis disposes of the writer's earlier results on the same subject [THIS JOURNAL, 8 (1916), 261] with the statement that "The work of Evans is obviously unreliable in view of the fact that he finds the composition of vapor and liquid identical at 92 per cent by weight."

This statement of Lewis is incorrect, as the writer's experiments did not extend beyond 91.1 per cent in the liquid, which corresponded to 91.8 per cent in the vapor. In correspondence Lewis says that he obtained the "92 per cent" by slightly extending the writer's curves beyond the experimental region—graphic extrapolation. In view of the admitted experimental error of possibly 1 per cent and the absence of evidence of the character of the curves beyond this region, this is manifestly unjustified, especially as the writer expressly accepted 96 per cent alcohol by weight, as found by others, as the constant boiling mixture.

Lewis' results are not experimentally obtained by him, but are graphically extrapolated (again) by him from experimental results of Wrewsky, the extrapolation being for as much as 25° beyond the actual observations! Surely experimental confirmation of results obtained in this way might be expected, and would be more convincing than Lewis' belief that they are "by far the most accurate available."

A comparison of the curves obtained from Lewis' extrapolated and the writer's experimental results, plotting alcohol per cent against boiling point, leaves the probability in favor of the writer, as judged from the form of the curves, especially for boiling points between 90° and 97°, where they most diverge, Lewis' curve showing an improbable bulge in this region.

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[1] THIS JOURNAL, **11** (1919), 1031.

In correspondence with the writer, Lewis claims that means should have been adopted to prevent any condensation in the top of the distilling flask and also to prevent any superheating of the vapor—a difficult matter. The conditions were intentionally those usually obtaining in a distilling flask in which a slow distillation of a considerable quantity of the mixture is taking place, and therefore easily duplicated in practice, and it is to such usual conditions that the results are still believed to apply within the limits of error originally stated.

P. N. Evans

Purdue University
Lafayette, Indiana
October 23, 1920

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Editor of the Journal of Industrial and Engineering Chemistry:

Professor Evans desires experimental confirmation of the data as to vapor compositions of alcohol-water mixtures calculated by the writer. He will find such confirmation in the direct experimental determinations of Lord Rayleigh,[1] to which reference should have been made originally. The average difference between the twelve determinations of vapor composition reported by Lord Rayleigh and the curves of the writer (based on the data of Wrewsky) is 2 per cent. Excluding two points, the deviations of which are 6 and 7 per cent, respectively, the average difference between Lord Rayleigh's results and the curves is less than 1 per cent. The average difference between the results of Professor Evans and the curves is 3.6 per cent.

The admitted failure of Professor Evans to provide against partial condensation of vapor in the top of the flask is probably the major source of error. This is especially serious in dilute liquids. Thus for liquids of less than 5 per cent alcohol, the average difference between the vapor compositions determined by Professor Evans and those read from the curve is over 9 per cent, while the deviations of the results of Lord Rayleigh from the curve within this same range average less than 1 per cent. Moreover, with the exception of two points in forty-two, all vapor compositions determined by Professor Evans are higher than those read from the curves. This is to be expected where partial cooling of the vapors occurs in the top of the flask. On the other hand, ten of the twelve points of Lord Rayleigh fall below the curve.

The data of Wrewsky were used because they seemed accurate, and especially because no other data gave information on the important questions of change of vapor composition and of vapor pressure with change in temperature. When more accurate data become available, it is not improbable that the vapor-composition curve calculated from Wrewsky will be found too high rather than too low.

W. K. Lewis

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts
January 9, 1921

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[1] *Phil. Mag.*, [6] **4** (1902), 529.

THE BRITISH DYE BILL

A Bill to Regulate the Importation of Dyestuffs

Be it enacted by the King's most Excellent Majesty, by and with the advice and consent of the Lords Spiritual and Temporal, and Commons, in this present Parliament assembled, and by the authority of the same, as follows:

1—(1) With a view to the safe-guarding of the dye-making industry, the importation into the United Kingdom of the following goods, that is to say, all synthetic organic dyestuffs, colours and colouring matters, and all organic intermediate products used in the manufacture of any such dyestuffs, colours, or colouring matters shall be prohibited.

(2) Goods prohibited to be imported by virtue of this Act shall be deemed to be included among the goods enumerated and described in the Table of Prohibitions and Restrictions Inwards contained in section forty-two of the Customs Consolidation Act, 1876, and the provisions of that Act and of any Act amending or extending that Act shall apply accordingly.

2—(1) The Board of Trade have power by licence to authorise, either generally or in any particular case, the importation of any of the goods, or any class or description of the goods, prohibited to be imported by virtue of this Act.

(2) For the purpose of advising them with respect to the granting of licences the Board shall constitute a committee consisting of five persons concerned in the trades in which goods of the class prohibited to be imported by this Act are used, three persons concerned in the manufacture of such goods, and three other persons not directly concerned as aforesaid.

Such one of the three last-mentioned persons as the Board shall appoint shall be chairman of the committee.

(3) For the purpose of providing for the expenses incurred by the Board in carrying this Act into execution, the Board may charge in respect of a licence a fee not exceeding five pounds.

3—Subject to compliance with such conditions as to security for the re-exportation of the goods as the Commissioners of Customs and Excise may impose, this Act shall not apply to goods imported for exportation after transit through the United Kingdom or by way of transhipment.

4—Anything authorised under this Act to be done by the Board of Trade may be done by the President or a secretary or Assistant Secretary of the Board or by any person authorised in that behalf by the President of the Board.

5—(1) The provisions of this Act shall continue in force for a period of ten years from the commencement thereof and no longer.

(2) This Act may be cited as the Dyestuffs (Import Regulation) Act, 1920.

EUROPEAN RELIEF COUNCIL

Everybody in the country by this time knows of the work of the European Relief Council headed by Mr. Hoover, and the "Invisible Guests" which they are struggling to entertain until the next harvest. I am sure that everyone of the members of the American Chemical Society wants to take part in this splendid work, but some may be so situated that they do not know where to send their contribution. In case no local committee is functioning, such contributions may be sent to me at 61 Broadway, New York, N. Y. At Mr. Hoover's request, I am acting as chairman of the Chemicals Division in this city, and all such contributions would naturally be credited to the chemical industry. A word should be sufficient to bring a prompt response from any who have not already contributed to this magnificent work.

Wm. H. Nichols

January 20, 1921

WASHINGTON LETTER

THE FORDNEY TARIFF BILL

Washington has been concerned of late with the amusing and not too difficult task of muddying the waters. It is easy to muddy the waters, and who is to reprove a senator for doing so, especially if he has handy a semi-plausible excuse?

There has been much fuss and feathers flung round the Fordney emergency tariff measure by various members of the Senate, both Democrats and Republicans, and that measure has been dignified with a favorable report from the Senate Finance Committee, the members of which sat for several days hearing pilgrims gathered to the Mecca tell of their dire straits brought about by the squeezing pincers of economic forces.

There was not any doubt that the bill would pass the House when it was reported from the House Ways and Means Committee, but in the Senate the situation is different, and there are few members of the Finance Committee who expect the bill to be enacted into law.

The bowing of the representatives of powerful manufacturing districts to what they believe to be the dictate of the voting farmer is par excellence an example of the psychology of the lawmakers of the great United States. They know not wisdom, and principle is a word they wot not of. Force—the fear of defeat and the threat of defeat in votes—is understood. That is heeded. And the Senate committee throws to the American farmer the sop of a measure that it knows full well will never be enacted into law.

There has been some talk of attaching the dye bill as an amendment to the emergency tariff measure, but that would avail little and will not seriously be attempted. Senator Pat Harrison, Democrat, of Mississippi, has succeeded in having attached to the emergency tariff measure as an amendment irrelevant laws that alone will take the reading clerk of the Senate a week to read.

Chairman Fordney's denunciation of a licensing system for the protection of the dyestuffs industry and championing of an embargo for potash when the Longworth bill was passed by the House is recalled by Senator Smoot, of Utah. The old saw to the effect that it depends upon whose ox is gored is perhaps apropos. The wool growers of the West have been hard hit by the disappearance of their market. This was evidently well impressed upon Senator Smoot during the time he spent in Utah when elections were uppermost in the minds of senators, for immediately upon his return to Washington he announced that nothing less than an absolute embargo against all importations of wool would save the great wool and cattle industries of the Nation. Unfortunately, perhaps, there are no manufacturers of dyestuffs among Senator Smoot's constituents.

THE DYE BILL

Careful survey of the situation in the Senate has convinced friends of the vital dyestuffs industry that there is practically no hope for enactment of a licensing bill protecting the industry at this session. This is due to the determined opposition of Senators Moses and Thomas and the apathy existing in the ranks of the Republicans who profess their desire to see the measure enacted into law. Behind this apathy upon the part of the Republicans there is to be found a peculiar chain of reasoning. With protection the by-word of their party, Republican senators are anxious that it be understood that protection is spelled in only one way, *viz.*, tariff. If a tariff is insufficient to protect a vital industry, that is too bad, but—let's try it anyhow; the embargo is a Democratic measure.

Tear camouflage and political pretense aside, and in the last analysis the secret lies in the fact that the Republican leaders in the Senate are convinced that whatever they give to the American dye industry it must be content and lend their party support, because the industry cannot expect to get as much from the Democratic party.

Because of the existing situation it is understood that a measure providing a system of tariffs for protection of the dye industry may be introduced in the near future by a member of the Finance Committee who is friendly to the Longworth bill. Such a measure will, of course, not be opposed by the dye producers. The attitude of the dye men, so far as can be ascertained, has not changed. The smaller manufacturers are particularly insistent that more than a tariff is needed for their protection. The measure, which is understood to be under preparation by Senator Knox, of Pennsylvania, will be built along the general lines of the Moses amendment. Such a measure may enable the assembling of solid Republican support for passage at this session. Senator Thomas, Democrat, has been absent from the Senate because of the illness of his wife, but now is back in his seat. Such a measure as outlined will certainly not meet with his approval, however, and he probably will be joined by a considerable number of other Democratic senators who would vote for the Longworth bill.

Unless the improbable occurs and some measure protecting the dye industry is passed this session, an effort will be made to extend the life of the War Trade Board Section of the Department of State. Funds for carrying on the work of this organization also are needed.

THE NITRATE BILL

Assailed as a socialist measure, the nitrate bill has been passed by the Senate by a vote of 34 to 29 and sent to the House, where there will be made another determined effort on the part of Republican members to kill it. The bill as passed by the Senate provides for a federal corporation, capitalized at $12,500,000, to develop the nitrate plant erected at Muscle Shoals, Alabama. Expenditure of $140,000,000 for water-power development is also authorized by the measure.

Passage of the bill by the Senate followed lengthy and bitter debate, with opponents just falling short by a few votes in their efforts to defeat or emasculate it. Opponents of the measure object to it as an entering wedge for the entry of the Government into a field that should be left to business. Supporters declare that the need for the product of the plant is great, but business has not seen fit to undertake the work of supplying the needs of the country.

Senator Wadsworth, of New York, succeeded in having several amendments of a technical nature accepted, and several important changes in the provisions of the measure were made as a result of the efforts of the New York senator. An effort was made to attach the measure as an amendment to the sundry civil appropriation bill early in January, but this was defeated. The fight on the bill developed along party lines, with several Republican senators supposed to be opposed to it absent and not paired when the vote came. Senator Poindexter, Republican, of Washington, made a last effort to have the bill sent to the Military Affairs Committee, but was unable to carry his motion. Senator Smoot was particularly active against the measure and declared that it was not in reality a proposition for the production of fertilizer, but was "for the development of power in the interest of utilities."

THE NOLAN BILL

The Nolan patent office reorganization bill is still in conference between House and Senate, and apparently an agreement on a report back from conference is not a prospect of the next few days. The conferees have held generally to their lines of difference previously outlined, and the section of the Senate bill providing for the turning of patents over to the Federal Trade Commission is the principal bone of contention. There seems to be little question but that there will be material amendments to the Senate bill, and increased personnel and pay will be granted the Patent Office by the measure which eventually will come from the conference.

An agreement has been reached for a vote on the bill regulating the meat packers. This vote is to be taken on January 24, and debate is to be held on the measure. Senator Penrose, chairman of the Finance Committee, has declared that he wants to make the emergency tariff measure the unfinished business of the Senate, and the Senate still has to consider many appropriation bills that are to come from the House.

CHEMICAL WARFARE SERVICE

Hampered continually by the General Staff controlled by General March, Chief of Staff of the Army, General Amos A. Fries, Chief of the Chemical Warfare Service, has made public a statement in which he outlined the difficulties that have been placed in the way of proper development of the Service by the Chief of Staff. General Fries, it will be recalled, was hardly back in the United States from France where he was in charge of the Chemical Warfare Service of the American Expeditionary Forces when he was reduced to his pre-war rank of Lieutenant Colonel. General March and Secretary of War Baker strongly opposed creation of the Chemical Warfare Service as a separate department of the Army, and endeavored to have it submerged under another department. This, however, was defeated when the army reorganization bill, fathered by Senator Wadsworth and Representative Kahn, of California, was passed by Congress. The opposition in Congress to Secretary Baker and General March perhaps resulted in Congress taking a more favorable attitude toward the Service as a separate branch than if they had supported such a proposal.

General Fries charged that the development of the Service was being continually hampered and restricted by General March, and that plans worked out by the officers in charge of the work had been interfered with and could not be carried out. Training of proper personnel, which will be needed, was not permitted, he charged, and activities were limited practically to the limited training of an insufficient number of officers without the necessary enlisted personnel.

CENSUS OF DYES

The census of dyes and coal-tar chemicals for 1919, which has been under preparation for some time by the United States Tariff Commission, has now been published. In its report the Commission has this to say with regard to the quality of American dyestuffs:

> As has been pointed out in earlier reports of the Commission, during 1915 and 1916 the new American dye industry naturally sought the line of least resistance by making dyes which were easiest to make, and the consumers used whatever dyes they could get instead of the varieties they preferred. As a result there were many cases of enforced substitutions of both German dyes (available from stocks) and American dyes. This substitution in early years of the war materially damaged the reputation of American dyes. During the succeeding years there has been a steady and progressive improvement in the situation. Although consumers were better supplied with the particular dyes they desired in 1919 than they were in 1918, there were still needed certain types of dyes which could not be supplied from American sources in the quantity desired. Thus in 1919 there was an insufficient domestic output of vat dyes which, on account of their extreme fastness and beauty of shade, are important for cotton shirtings, ginghams, and calicoes. Considerable progress has been made, however, toward supplying these much-needed colors. There is also a demand for many individual dyes of other classes which are not yet available at all or only in inadequate amounts. This is particularly true of alizarin derivatives and of certain other specialties.

Commenting upon the exportation of certain American dyes during the year, the Commission declares that:

> In estimating the significance of this achievement of the domestic industry in the exportation of dyes it should be remembered that domestic manufacturers during 1919 and 1920 have met little competition in foreign markets from German dyes. It should also be pointed out that any deductions as to the competitive strength of the domestic industry which are based on exports of dyes do not take into consideration the fact that the domestic industry is still deficient in the important group of vat and alizarin dyes.

Discussing the condition of the German dye industry, the report says that:

> During February 1920, the quantity of dyes reserved by German plants totaled 876,449 lbs., indicating a total output of over 3,500,000 lbs. for that month. A progressive increase is shown in each succeeding month to a maximum of 3,026,247 lbs. in August, which indicates a total output of over 12,000,000 lbs. monthly. Since August there has been a slight decline in reserved stocks to 2,779,132 lbs. in October. The rate of production from July to October, inclusive, is only about one-third of Germany's pre-war output.

One of the most important features of the report is the detailed table it contains giving figures on dye imports into this country during the fiscal year 1920. This is carried out in detail and gives the same figures in general as were contained in the Norton report early in the war.

TARIFF REVISION

Hearings on general revision of the tariff were begun by the House Ways and Means Committee early this month. Taking up the tariff by schedules in alphabetical order, the committee devoted three days, beginning January 6, to Schedule A (chemicals). Coal-tar chemicals already provided for in the Longworth bill were not touched upon.

There will be, of course, no effort to begin consideration in the House itself of the new tariff law the Republicans propose in place of the Underwood act, now in effect. It is planned to finish hearings on the entire law by the Ways and Means Committee before adjournment of this session of Congress, and to have a new tariff bill ready for introduction in the House early in the next Congress, which will be called in extra session early in April, as Chairman Fordney has announced after a conference with President-elect Harding at Marion, Ohio.

Germany looms as the ghost feared by those seeking tariff protection, although great emphasis is also laid by several industries upon the competition that is to be expected from Japan.

Considerable sentiment exists among Republican members of the committee in favor of temporarily laying aside the new tariff in favor of revenue revision. It is impossible at the present time, they point out, to work out a scientific tariff based upon the difference in costs of production in the United States and abroad. Chairman Fordney, however, has refused to change his plans for continuing hearings on the tariff.

Elimination of the ad valorem in favor of the specific rates of duty has been advocated by Representative Longworth, of Ohio, and this, too, is favored by Chairman Fordney. The question of exchange must necessarily enter into the discussion and several plans have been advanced, none of which so far, however, has been received with any great kindness by the committee. Chairman Fordney has declared that all duties should be assessed upon the American valuation of imported goods. This has been ridiculed by the Democrats as impracticable and described as a camouflage designed to enable the enactment of rates considerably higher than would otherwise be possible. Several Republican members of the committee also are opposed to this scheme.

Hearings on Schedule A were completed within the allotted three days, Chairman Fordney cutting witnesses short at the expiration of their allotted few minutes, and granting permission to file supplemental briefs. Earthenware and glassware representatives were heard by the committee, following the conclusion of hearings on the chemical schedule.

The exchange situation and efforts to ascertain the industrial and commercial conditions in Germany and Japan evidently will be features throughout the hearings.

January 17, 1921

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

THE PAPER SITUATION

The crisis in the chemical industries to which I called attention in my previous letter still continues, more especially in the paper trade: factories are being compelled to dismiss their employees. The Darblay factory at Corbeil-Essonnes, the Etienne factory at Arles, the Papeterie de l'Ouest at Chatenay are cases in point. Scandinavian competition is particularly felt in this industry and the price of wood pulp, the raw material, plays a very important part.

In order to rid ourselves as completely as possible of the necessity of obtaining wood pulp from Scandinavia, we are at present studying its industrial production, on a large scale, from alfa, a product which is very abundant in Morocco and Algeria. The Société des Produits chimiques d'Alais and Camargue, les Papeteries de Rives, les Etablissements Bergès, Outhenin-Chalandre, etc., have had a study made at Seveux (Haute Saône) of all points concerning the manufacture of alfa paper. A factory is to be set up on the banks of the Rhône, near Avignon, in a former gunpowder arsenal which is now lying idle. This factory is to be equipped to treat 30,000 tons, and it is hoped to start work in 6 mos.' time.

The high cost of paper considerably hampers editors and printers, and scientific publications are even threatened with suspension. To avoid this difficulty the Confédération des Sociétés scientifiques françaises, of which the Union Nationale de la Chimie pure et appliquée forms part, has decided to establish a printing and publishing company for scientific works, as well as for the sale of French and foreign books. A special department would keep the French public acquainted with English scientific publications.

THE ALSATIAN POTASH INDUSTRY

At the last meeting of the Société de Chimie Industrielle, Professor Matignon made an important statement on the present situation of the potash industry in Alsace.

The administrative and financial situation of the Alsatian potash mines is not yet settled. A sequestration administrator is controlling them at present. However, the process for extraction and methods of work now adopted by French engineers are different from those formerly employed, and the present returns are greater than those obtained prior to 1914.

The scheme of operation consists in the extraction of salt, leaving pillars, and filling up afterwards. This filling is done with the lime salts left in the residues from manufacture. The potash obtained as chloride is remarkably pure and does not contain magnesium salts.

LIGHT MINERALS

At the same meeting Mr. Bigot opened a discussion on light minerals. Under this heading he described as natural products pumice stone and infusorial silicas or kieselguhr.

Mr. Bigot compared the light pumice stones, obtained in California, with French pumice stones. Their quality is nearly the same. From pumice, pulverized and then agglomerated with silicates, it has been possible to build a new type of furnace for glass works, the radiation of which is very slight, and which consequently allows work to be carried out quite close to the furnace itself, thus reducing the amount of labor necessary.

Following the same line of ideas, Mr. Bigot has obtained, by pyrogenic methods from slate and slaty schists, an extremely light and porous mineral, which is compact and offers the same advantages as the natural pumice stones.

INVAR METAL

Mr. Guillaume, director of the Bureau of Weights and Measures, is continuing his studies of invar metal. He has examined samples of that metal manufactured about 10 yrs. ago, and has discovered small variations in length of about 0.01 mm. per meter. This slight instability of invar he ascribes to the presence of carbon, or rather of the ferrocarbon compound called cementite.

He proposes the addition of chromium or tungsten-vanadium to rectify the invar, and the results obtained show that, thus modified, invar can be used without the necessity of corrective calculations.

THE AGE OF PAINTINGS AS SHOWN BY X-RAYS

Although rather foreign to the sphere of chemistry, a question which is now absorbing the attention of the French scientific world is the diagnosis of the age of pictures by X-rays.

For instance, the artists of the 17th century almost exclusively used mineral colors impervious to X-rays. The modern painting, however, done almost exclusively in colors of organic or vegetable origin, is permeable to X-rays.

The great French physician, Lippmann, has been able, by this method, to determine the age of a picture and ultimately expose to view any superimpositions or fakes. This application of science to an art where, up till now, technical examinations were solely the work of art critics, is of extreme interest.

In my previous letter, I spoke of the petroleum question. I can now inform you of the bringing forward, by the government, of a bill, the principle of which is government-controlled freedom.

In order to compete with the Claude process (fixation of air) a certain number of French banks and factories have acquired the Badische process (Haber patent) and are going to attempt its exploitation in France.

January 7, 1921

INDUSTRIAL NOTES

At a meeting of the directors of The Barrett Company, held December 17, 1920, Eversley Childs, chairman of the Board, and William Hamlin Childs, president, offered their resignations. William N. McIlravy was elected chairman, and Thomas M. Rainhard, president. William Hamlin Childs was elected chairman of the Executive Committee. The following directors presented their resignations: Harry W. Croft, J. H. Fulton, William S. Gray, Alexander C. Humphreys, Isaac B. Johnson, Powell Stackhouse, Hamilton Stewart, J. Harry Staats, H. D. Walbridge, and Horace S. Wilkinson. The following directors were elected: E. L. Pierce, president, Solvay Process Company; W. H. Nichols, Jr., president, General Chemical Company; Orlando F. Weber, president, National Aniline and Chemical Company; Walter B. Harris, sales manager, The Barrett Company; M. H. Phillips, New York manager, The Barrett Company; D. W. Jayne, manager chemical department, The Barrett Company; Clark McKercher, general counsel, The Barrett Company; E. J. Steer, secretary and treasurer, The Barrett Company.

The United States Supreme Court on December 6, 1920, handed down an important decision in favor of the defendant, in the "Hydrogenated Oil Case," of Procter & Gamble *vs.* The Brown Company (formerly Berlin Mills Co.), reversing the Court of Appeals and holding with the District Court that Claims 1 and 2 of the Burchenal Patent No. 1,135,351 assigned to the Procter & Gamble Company are invalid. Procter & Gamble brought suit against the Berlin Mills Company in 1915 for alleged infringement of a product made under the Burchenal patent. The decision of the Supreme Court is based almost exclusively on the belief of the Court that the prior art, especially Normann's British Patent of 1903, described the products obtained sufficiently well so that an oil chemist would understand that they could be used in any of the usual ways that fats are used. Burchenal's contribution "did not rise to the dignity of invention." Both sides were represented by eminent counsel and well-known experts, and the case attracted a great deal of interest on account of the prominence of the litigants and the importance of the decision when it should be rendered.

The following associations of manufacturers have been formed in England to conduct industrial and scientific research in the fields of their industries, and have been given governmental assistance:

British Boot, Shoe, and Allied Trades Research Association
British Cotton Industry Research Association
British Empire Sugar Research Association
British Iron Manufacturers' Research Association
British Photographic Research Association
Research Association of British Motor and Allied Manufacturers
British Portland Cement Research Association
British Research Association for the Woolen and Worsted Industries
British Scientific Instrument Research Association
Research Association of British Rubber and Tire Manufacturers
Linen Industry Research Association
British Nonferrous Metals Research Association
Glass Research Association
British Association of Research for Cocoa, Chocolate, Sugar, Confectionery, and Jam Trades
British Refractories Research Association
Scottish Shale Oil Scientific and Industrial Research Association

Various other research organizations are under consideration for approval, or in process of organization.

Experimental camphor groves which have been planted in Florida are expected to attain commercial importance within a few years. These groves, together with the synthetic camphor now being manufactured in the United States, are expected to make the United States the leading producer of natural and synthetic camphor, and to render it independent of the former sources of supply in China, Japan, and Formosa.

The committee in charge of the consolidation of the General Chemical Co., the Solvay Process Co., the Semet-Solvay Co., The Barrett Co., and the National Aniline and Chemical Company has announced that the new merger plan has become operative, and was carried into effect as of January 1, 1921.

The President of Uruguay has submitted to the National Administration Council a bill providing for the establishment of several government industries under control of the Institute of Industrial Chemistry, with a view to the development of the industry so as to take care of the domestic needs of the country in peace or war. Among the factories to be established are a sulfuric acid factory with a daily production of 25,000 kilos, all of which is expected to be required for domestic use as soon as the country begins production of superphosphates from bones now exported. Raw material for the sulfuric acid can probably be obtained from important iron pyrites deposits which are said to exist. It is planned also to build factories for the production of nitric acid; crude benzene, toluene, xylene, and carbolic acid; electrolytic caustic soda; alcohol and sulfuric ether; acetic acid; glycerol; powder and explosives. The total cost of these works is estimated at 2,180,000 pesos, to be secured through the imposition of an import tax of 1 per cent. 25,000 pesos yearly is to be set aside for the engagement of five foreign technical experts under three-year contracts, at the end of which time it is expected that native experts will be able to take their places.

The Tariff Commission of Canada is to take up the question of a tariff against German dyes which has been laid before the Minister of Finance by British dyestuff manufacturers, five of whom are represented in Canada. Some German firms are already underbidding the British dyers for Canadian business.

The United States Civil Service Commission has announced an examination for laboratory assistants to fill vacancies in the Bureau of Mines at Pittsburgh, Pa., and elsewhere. Salaries are as follows: Senior Grade, $1320 to $1500; Intermediate Grade, $1200 to $1320; Junior Grade, $1080 to $1200. Papers will be rated as received and certification made as the needs of the service require. Applicants will be rated on general education and special training and experience. Applications will be received until the hour of closing, April 5, 1921.

Examinations have also been announced for Associate Chemist at $2500 to $3600 a year; Assistant Chemist at $1800 to $2500 a year; and Junior Chemist at $1200 to $1800 a year. Applicants will be rated on (1) education, training, and experience, and (2) publications or thesis, to be filed with application, and must qualify in one of the following subjects: advanced inorganic, analytical, biological, dairy, explosives, food, fuel, metallurgical, organic, pharmaceutical, physical, soil, petroleum, gas, or ceramic chemistry. Applications will be rated as received until further notice.

Examinations have been announced for Associate Engineer at $2000 to $2800 a year and Assistant Engineer at $1400 to $1800 a year, to fill vacancies in the Bureau of Standards and elsewhere. Applicants must qualify in one of the following subjects: electrical, mechanical, civil, chemical, or ceramic engineering, and will be rated on (1) education in general physics, chemistry, and mathematics, (2) special education and experience in the optional subject; and (3) general education, experience, and fitness. The duties of appointees will be in connection with original investigations in some field of the Bureau's work. Detailed information should be given in applying. Applications will be rated as received until further notice.

The Commission has also announced an examination for Assistant Examiner, Patent Office, at $1500 a year, with $20 monthly increase to appointees who perform satisfactory service. Competitors will be rated on (1) French or German, (2) mechanical drawing, (3) technics, covering the general field of mechanics, mechanic arts, industrial arts and processes, and applied chemistry. In addition, applicants must select two of the following optional subjects: chemistry, civil, electrical, or mechanical engineering, mathematics, physics, experience. Examinations will be given February 9 to 11, 1921, at places named by the Commission. Details concerning the examinations may be obtained from the Civil Service Commission. No credit is given for student work in school or college.

The French Commission in the United States has published information regarding the reconstruction of the French chemical industry. The chemical plants located in the devastated departments, 17 per cent of all chemical plants in France, were almost totally destroyed. On October 1, 1920, 78.1 per cent had resumed operation in whole or in part. On October 1, 1919, only 18.7 per cent of the 1914 personnel were occupied at production, while on October 1, 1920, 54.2 per cent were occupied. The 1914 production of chemical plants was 850,000 tons; the present production is between 200,000 and 300,000 tons.

A new standard sample of electric steel No. 51, 1.2 per cent carbon, and a new standard sample of cast bronze No. 52 (approximate composition: Copper 88 per cent, tin 8 per cent, zinc 2 per cent, lead 1.5 per cent, antimony 0.15 per cent, iron 0.10 per cent and nickel 0.10 per cent) have recently been prepared by the Bureau of Standards, Washington, D. C., and are now ready for distribution with provisional certificates. Standard Sample No. 23*a*, a renewal of the exhausted Sample No. 23, Bessemer Steel, 0.8 carbon, has also been prepared and is now ready for distribution with a provisional certificate.

The Acetate Products, Ltd., has purchased the plant of the Liverpool Cannery at South Westminster, B. C., and will begin installation of an up-to-date methanol plant at once. This is the first methanol plant to be erected on the Canadian Pacific coast, and will produce in addition to methanol, acetate of lime, charcoal, and wood-tar products.

Investigations by the Forest Service of the Department of Agriculture show that the use of wood preservatives has increased to a large extent in this country. In 1919 there were used 65,556,247 gal. of creosote, 2,412,592 gal. of paving oil, 101,011 gal. of miscellaneous preservatives, and 43,482,000 lbs. of zinc chloride. Over 6,000,000 gal. of creosote were imported, practically all from England and Canada. The total amount of wood treated amounted to 139,878,845 ft., covering operations at 108 plants, 17,265,694 ft. more than in 1918.

At a meeting of the Board of Directors of the National Aniline & Chemical Co., Inc., on December 21, 1920, Mr. O. F. Weber offered his resignation as president, and Mr. J. W. Newlean was elected president in his stead. Mr. Weber continues as chairman of the Board of Directors of the National Aniline & Chemical Co., Inc., and has accepted the presidency of the Allied Chemical and Dye Corporation. Mr. F. M. Peters resigned from the Board, and Mr. E. L. Pierce, president of the Solvay Process Co., was elected a director. Mr. B. A. Ludwig, Mr. O. F. Weber, and Dr. L. H. Cone were elected vice presidents.

The Canadian government has withdrawn from sale, lease, or settlement approximately 55,000 acres of land along the Athabasca River in Alberta, subject to leases already issued under the petroleum and natural gas regulation. It is expected that a successful process will soon be evolved for the extraction from the tar sands of oil, bitumen, and other hydrocarbons in commercial quantity. The nearest estimate of tar sands available for reduction runs into billions of tons. The drawback to development is the scarcity of fuel to withdraw the oils, but it is hoped that this may be overcome by finding natural gas.

On December 10, 1920, 500 shares of stock of the J. P. Devine Company, together with letters patent of the United States subject to the right of the company and all interests in an agreement between the company and Joseph P. Devine and Emil Passberg of Berlin, were sold at public sale by the Alien Property Custodian. Mr. J. P. Devine was the highest bidder. The sale, however, has not yet been confirmed by the Alien Property Custodian.

The $4,000,000 by-product plant of the Domestic Coke Corporation, Fairmont, W. Va., has recently begun operations. When running at full capacity, the plant will consume 1100 tons of coal a day. At present only 24-hr. coke is being produced, but when sufficient coal is on hand to assure steady operation, the coke will be produced in from 14 to 15 hrs.

PERSONAL NOTES

Dr. Ira Remsen, for twelve years president of Johns Hopkins University, former professor of chemistry at the institution, discoverer of saccharine and other products, and one of the foremost men in his special field of science in the country, has accepted an offer from the Standard Oil Company to act as consulting chemist for the corporation. Dr. Remsen was associated with Johns Hopkins University since its foundation in 1875. He resigned both the presidency and the chair of chemistry in 1913 to return to private life, and now holds the title of professor emeritus. On December 13, 1920, **Dr. Remsen** gave, under the auspices of Eta Chapter of Phi Lambda Upsilon at Ohio State University, a lecture on "What Chemists Were Thinking About 50 Years Ago."

Dr. F. G. Cottrell resigned December 31 as director of the U. S. Bureau of Mines, and **Mr. H. Foster Bain**, of California, has been named his successor. Dr. Cottrell left the Bureau in order to take up his duties as chairman of the Division of Chemistry and Chemical Technology of the National Research Council.

Dr. Henry A. Bumstead, professor of physics at Yale University, who had been on leave serving as chairman of the National Research Council, died recently on a train from Chicago to Washington. He was graduated from Johns Hopkins University in 1891, and later received his doctor's degree from Yale.

Mr. J. Russell Marble, a native of Smithfield, and prominently identified with the business life of Worcester, died last October at his home in Worcester. Mr. Marble was associated with the Northeastern Section of the American Chemical Society.

Dr. Hugh C. Muldoon has left the position of professor of chemistry at the Albany College of Pharmacy and has accepted the deanship and professorship of chemistry in the School of Pharmacy, Valparaiso University, Valparaiso, Ind.

Mr. James R. Owens has severed his connection with E. I. du Pont de Nemours & Co., and is at present holding an operating position in the wood distillation plant of the Mid-Continent Iron Co., Midco, Carter Co., Missouri.

Mr. Charles Horvath, research chemist for the International Motor Co., New Brunswick, N. J., resigned some months ago from that firm to become chief chemist for the National Metal Reduction Company of Newark, N. J., and the Atlantic Smelting & Refining Works, of New York City, the plants of both firms being located in Newark, N. J.

Mr. William D. Hatfield resigned as assistant professor of chemistry at the Montana State College of Agriculture and Mechanic Arts to accept the position of superintendent of the new water filtration plant at Highland Park, Mich.

Mr. H. L. Lentz has resigned from the U. S. Bureau of Mines, Pittsburgh, Pa., in order to accept the position as chief chemist for the Robinson Milling Co., at Salina, Kan.

Mr. Walter J. Geldard recently resigned as chief of the analytical section, Fixed Nitrogen Research Laboratory, and has accepted a similar position with the International Coal Products Corp., of Newark, N. J.

Mr. Edwin Androvic, formerly with the Cudahy Packing Company of Omaha, Neb., is now taking some special courses in chemical engineering at Johns Hopkins University, Baltimore, Md., and is at the same time working with some oil refining and hydrogenating problems.

Dr. Arnold H. Smith, secretary of the rubber division of the American Chemical Society, resigned his position as research chemist with the Goodyear Tire & Rubber Company to assume the position of chief chemist with the Thermoid Rubber Co., Trenton, N. J.

Mr. Thomas M. Rector, formerly in charge of the division of food technology of the Institute of Industrial Research, Washington, D. C., has been appointed director of the department of industrial chemistry of the Pease Laboratories, Inc., New York City.

Mr. L. J. Waldbauer has left the employ of the Redpath Laboratory of E. I. du Pont de Nemours & Co., and is at present instructor in chemistry at the University of Maine, Orono, Me.

Mr. B. E. Long, who was engaged as sugar factory chemist and superintendent in Cuba and Puerto Rico, now holds a similar position with a new company, the Binalbagan Estates, Inc., Philippine Islands.

Mr. G. H. Cartledge resigned last June as chief for the Island Refining Corp., of New York City, to become associate professor in chemistry at Johns Hopkins University, Baltimore, Md.

Mr. I. E. Cooper, a recent graduate of the University of Illinois, has accepted a position with the Apollo Metal Works, La Salle, Ill., as chemist in charge of the research department and control laboratory.

Mr. Hiller Zobel recently left Death Valley, Cal., where he was engaged in metallurgical and chemical research for the Pacific Coast Borax Co., to assume duties as research chemical engineer at the Bayonne, N. J., plant of the same company.

Mr. Marvin J. Udy was recently transferred to the research department of the Electro Metallurgical Co., at Niagara Falls, N. Y., upon the closing down of the cobalt mines of the Haynes Stellite Co., at Leesburg, Idaho, where he was mine manager.

Mr. J. Howard Roop, formerly chemist for the Noblesville Milling Co., at Noblesville, Ind., has accepted a position as chief chemist for the American Stores Co., at Philadelphia, Pa.

Mr. L. T. Bryson has temporarily left the El Salvador Silver Mines Co., Ltd., and is engaged in analytical research work with the Dearborn Chemical Co., of Chicago, Ill.

Prof. Hermon C. Cooper has been granted leave of absence from the College of the City of New York for the present academic year and is acting as factory manager of the Acids Manufacturing Corp., of New York City.

Dr. E. P. Deatrick, formerly instructor at the Pennsylvania State Forestry Academy, Franklin County, Pa., is at present instructor in the department of soil technology at the College of Agriculture, Ithaca, N. Y.

Mr. J. W. Ziegler, who graduated last June in chemical engineering at the University of Illinois, Champaign, Ill., has entered the employ of the Como Chemical Co., Kokomo, Ind., as foreman of one of their departments.

Mr. Donald E. Cable has become research chemist in the Agricultural Experiment Station of the University of Wyoming, after having spent two years as assistant chemist and engineer at the Forest Products Laboratory, Madison, Wis.

Mr. Bert Russell, who left the Patent Office about a year ago, after extended service in its various chemical divisions, to accept a position with Prindle, Wright & Small, of New York City, is now leaving the latter firm in order to accept employment in the office of Mr. Roy F. Steward, chemist and patent attorney, Washington, D. C.

Mr. Joseph Wertheimer, formerly with the American Borish Co., of Cleveland, Ohio, has been appointed to the position of assistant professor of metallurgy at the University of Kansas, and **Mr. Henry Werner,** formerly with the H. K. Mulford Chemical Co., of Philadelphia, has been made assistant professor of chemistry at the same university.

Mr. James H. Aldred has joined the forces of the Smith Rubber & Tire Co., Inc., of Garfield, N. J., as general superintendent. Mr. Aldred was previously chemist for the Industrial Supervision Company of New York City.

Mr. L. W. Briggs is instructor of inorganic chemistry at Wooster College, Wooster, Ohio. He formerly held a graduate scholarship at the State University of Iowa, Ames, Iowa, for the year 1919 to 1920.

Mr. Carl E. Frick, formerly chemist for the Philadelphia Rubber Works Co., Akron, Ohio, has been made instructor in general chemistry at the University of Wisconsin, Madison, Wis.

Mr. Charles H. Spayd has left the Modoc Company of Pennsylvania, soap powder, cleanser, and boiler composition manufacturers, where he was secretary-treasurer and manager, to reënter the printing ink manufacturing business with the California Ink Co., of San Francisco, Cal.

Mr. John H. Culver has accepted the position of textile expert and chemist for the Firth Carpet Co., of Firthcliffe, N. Y.

Mr. R. R. Bryan until recently engaged with the Sunnyside Mining & Milling Co., at Eureka, Col., as metallurgist, recently went into business as consulting engineer, with offices at Denver, Col.

Mr. C. H. Kerr, research manager of the American Optical Co., Southbridge, Mass., is now associated with Mr. H. L. De Zeng in the management of the De Zeng-Standard Co., Camden, N. J.

Mr. S. M. Oppenheim, formerly connected with the engineering department of the Board of Commissioners of the Port of New Orleans, has returned to the Miles Planting & Manufacturing Co., as superintendent-of-manufacture of their two sugar factories in Louisiana.

Dr. L. A. Mikeska has accepted a position on the staff of the Rockefeller Institute, New York City, having left the Color Laboratory of the Bureau of Chemistry in Washington, D. C., where he was working on photosensitizing dyes.

Mr. Bernard L. Peables, who was associated with the Boston Consolidated Gas Co., as chief inspector in field for the chemical control section, has joined the forces of the Pawtucket Gas Works, for the broadening and intensifying of the chemical control.

Mr. S. H. Champlin is now chemist with the Cape Cod Preserving Corp., at Onset, Mass., his previous position being that of assistant and research chemist with the Loose-Wiles Biscuit Co., of Long Island City.

Mr. George R. Greenbank, formerly employed by the Goodyear Tire & Rubber Company as chemical engineer, is at present acting in the same capacity at Edgewood Arsenal for the Chemical Warfare Service.

Dr. George Borrowman, recently returned from chemical investigations in Europe, has resigned from research work in the laboratory of Dr. J. E. Teeple, and opened his own laboratory in Chicago, Ill.

Mr. Alger L. Ward, who was employed for the past five years as a research chemist by E. I. du Pont de Nemours & Co., has accepted a position as an organic research chemist with the United Gas Improvement Co., and is connected with their laboratories in Philadelphia, Pa.

Mr. G. N. Prentiss has been appointed engineer of tests of the Chicago, Milwaukee & St. Paul Railway Co., with headquarters at Milwaukee Shops, Wis., vice Mr. H. K. Fox, resigned.

Mr. John L. Parsons, formerly instructor in chemistry at Boston University, has been released in order that he may take up industrial research for the Hammermill Paper Co., Erie, Pa.

Mr. George F. Lull has severed his business connections in the East and has been made president of the Trinity Paper Mills with headquarters at Dallas, Texas.

Mr. D. M. Bates, following his resignation last March as agent of the Lewiston Bleachery & Dye Works, Lewiston, Me., became vice president of Day & Zimmermann, Inc., of Philadelphia, Pa.

Mr. Philip A. Kober, formerly with E. R. Squibb & Sons, of New York, is now president for the Kober Chemical Co., Inc., Hastings-on-Hudson, N. Y., which firm intends to manufacture chemically pure arsphenamines, Dakin's chloramines, and dialyzing, ultrafiltering and perevaporation membranes.

Mr. William W. Coblentz, physicist in the Bureau of Standards, Washington, D. C., has been awarded the Janssen Medal by the Academy of Science, for discoveries in connection with rays emanating from the earth and stars.

Mr. Carl Bloess has left the St. Louis branch of the American Cotton Oil Co., which branch has been discontinued, and has become chemist for the Crown Margarin Co., of the same city.

Prof. A. F. Gilman, Ph.D., who has been professor of chemistry at Illinois Wesleyan University, Bloomington, Ill., for the past two years, has been elected head of the chemistry department at Carroll College, Waukesha, Wis.

Dr. J. E. Zanetti, assistant professor of chemistry at Columbia University, has had conferred upon him by the King of Italy the Order of the Crown with the rank of officer, for services rendered during the war as Lieutenant-Colonel in the Chemical Warfare Service. He has also received from the French government the Legion of Honor and from the British government the Distinguished Service Order.

Dr. J. C. Witt, assistant professor of analytical chemistry in the University of Pittsburgh, has resigned to become chief research chemist for the Portland Cement Association with headquarters in Chicago. Dr. Witt has been succeeded in his former position by **Dr. C. J. Engelder,** of Hornell, N. Y.

Mr. Harry E. Wently, formerly with Brown & Co., Inc., Pittsburgh, Pa., is at present associated with the Latrobe Electric Steel Co., Latrobe, Pa.

Mr. W. L. Moyer, while in Youngstown, O., was a chemist in the by-product coke plant of the Youngstown Sheet & Tube Co., and is at present associated with the Pittsburgh Crucible Steel Co., as heater foreman in their coke plant at Midland, Pa.

Mr. Franklin B. Furber, for several years chemist with the U. S. Bureau of Mines and the U. S. Bureau of Chemistry, has resigned from the position of assistant director of the Pease Laboratories, Inc., to become associated with the Research Laboratories, Inc., of New York City.

Mr. N. D. Doane, formerly with the Goodyear Tire & Rubber Co., of Akron, Ohio, is now engaged in chemical and sanitary engineering work for Mr. Charles H. Hurd, consulting engineer, of Indianapolis, Ind.

Mr. Lloyd Platzker, formerly with the American Sugar Refining Co., of Jersey City, is now associated as a chemist with Messrs. Bendiner & Schlessinger, of New York City.

Mr. Lewis O. Bernhagen, until recently a sanitary engineer for the Texas State Board of Health, has accepted the position of director of sanitation for the city of Beaumont, Texas.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

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.

NATIONAL ADVISORY COMMITTEE FOR AËRONAUTICS

Fifth Annual Report of National Advisory Committee for Aeronautics, Fiscal Year 1919. 870 pp. Paper, $1.50. 1920.

GOVERNMENT PRINTING OFFICE

Agricultural Chemistry, Industrial Alcohol, Preservatives: List of Publications for Sale by Superintendent of Documents. 9 pp. Price List 40, 12th edition. 1920.

GENERAL LAND OFFICE

Regulations Concerning Oil and Gas Permits and Leases (Including Relief Measures) and Rights of Way for Oil and Gas Pipe Lines, Authorized by Act of February 25, 1920 (Public 146); approved March 11, 1920. 1920 Reprint as Amended to October 29, 1920. 57 pp. Circular 672.

SMITHSONIAN INSTITUTION

Analyses and Optical Properties of Amesite and Corundophilite from Chester, Mass., and of Chromium-Bearing Chlorites from California and Wyoming. E. V. Shannon. 9 pp. From Proceedings of the National Museum, Volume 58, No. 2342. 1920.

Some Minerals from Old Tungsten Mine at Long Hill in Trumbull, Conn. E. V. Shannon. 14 pp. From Proceedings of the National Museum, Volume 58, No. 2348.

TARIFF COMMISSION

Industrial Readjustments of Certain Mineral Industries Affected by the War, Antimony, Chromite, Graphite, Magnesite, Manganese, Potash, Pyrites, Sulfur, Quicksilver, Tungsten (with Bibliographies). Tariff Information Series 21. 320 pp. 9 maps. Paper, 65 cents. 1920.

WAR DEPARTMENT

Report of Tests of Metals and Other Materials Made in Ordnance Laboratory at Watertown Arsenal, Mass., Fiscal Year 1918. War Department Document 901. 338 pp. Paper, 80 cents. In many cases one side of the leaf only is paged, the unnumbered side usually bearing illustrations, although in some cases it is blank.

PUBLIC HEALTH SERVICE

Recent Experiments in the Control of Air Dustiness. O. M. Spencer. Public Health Reports, 35, 2907–14. The following conclusions are reached as a result of these investigations: (1) The necessity for establishing a "standard dust table" of the number of dust particles of a certain size permissible in all dust-creating or dust-hazardous processes and occupations; (2) The necessity for checking the efficiency of all dust-removing systems or devices at regular intervals by an actual dust count at the place of work and in the workroom, which count must come within the limits prescribed by the "standard dust table" for that particular process.

Sanitary Disposal of Sewage through a Septic Tank. A System of Simple Construction and Inexpensive Operation for Isolated Dwellings. H. R. Crohurst. Public Health Reports, 35, 2959–64.

Supreme Court of the United States Construes Section 2 of the Harrison Antinarcotic Act. Public Health Reports, 35, 3077–9. The Supreme Court of the United States has decided that the issuance of a prescription for a habit-forming drug by a physician not "in the course of his professional practice only" is a sale of the drug and a violation of Section 2 of the Harrison Antinarcotic Act.

The Importance of Tellurium as a Health Hazard in Industry. A Preliminary Report. M. D. Shie and F. E. Deeds. Reprint 590 from Public Health Reports. 18 pp. Paper, 5 cents. 1920.

Studies of Reconstructed Milk. A. F. Stevenson, G. C. Peck and C. P. Rhynus. Reprint 608 from Public Health Reports. 37 pp. Paper, 5 cents. 1920.

Effect of Shaking Alkalinized Aqueous Solutions of Arsphenamine and Aqueous Solutions of Neoarsphenamine in the Presence of Air. G. B. Roth. Reprint 612 from Public Health Reports. 7 pp. Paper, 5 cents. 1920.

Municipal Wastes. Their Character—Collection—Disposal. H. R. Crohurst. Public Health Bulletin 107. 98 pp. Paper, 20 cents.

Digest of Comments on Pharmacopeia of the United States of America (9th Decennial Revision), and National Formulary (4th edition), Calendar Year 1917. A. G. Du Mez. Bulletin 125 of the Hygienic Laboratory. 340 pp. Paper, 25 cents. Also issued as H. Doc. 856, 66th Congress, 3rd Session.

I. Trinitrotoluene Poisoning—Its Nature, Diagnosis, and Prevention. Carl Voegtlin, C. W. Hooper, and J. M. Johnson. **II. The Toxic Action of "Parazol."** Carl Voegtlin, A. E. Livingston and C. W. Hooper. **III. Mercury Fulminate as a Skin Irritant.** A. E. Livingston. Bulletin 126 of the Hygienic Laboratory. 216 pp. Paper, 20 cents. 1920.

GEOLOGICAL SURVEY

Surface Water Supply of the United States, 1917. Part III. Ohio River Basin. N. C. Grover, A. H. Horton and W. E. Hall. Prepared in Coöperation with the states of Illinois and Kentucky. Water-Supply Paper 453. 173 pp. Paper, 15 cents. 1920.

Marble Resources of Southeastern Alaska. E. F. Burchard. With a Section on the Geography and Geology. Theodore Chapin. Bulletin 682. 118 pp. Paper, 30 cents. 1920.

Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1919. J. P. Dunlop. Separate from Mineral Resources of the United States, 1919. Part I. 10 pp. Published November 8, 1920.

The total value of the gold, silver, copper, lead, and zinc mined and sold in the Eastern States in 1919 was $25,110,186, a decrease of about 9 per cent from the corresponding value in 1918. Of this total, gold represented $7,052, silver $117,253, copper $3,086,890, lead $232,034, and zinc $21,666,957.

The output of all metals decreased, though the decreases in quantity of copper, lead, and zinc were comparatively small. The decrease in total value of the metals was caused mainly by the lower price in 1919 for copper, lead, and zinc. The high price of silver caused its value to increase, notwithstanding a decrease in quantity.

Mine Production of Gold, Silver, Copper, Lead, and Zinc in the Appalachian States, 1918 and 1919

	1918	1919	Decrease
Ore sold or treated, short tons	2,355,688	1,930,411	425,277
Gold, dollars	14,352	7,052	7,300
Silver, fine ounces	106,585	104,690	1,895
Copper, pounds	17,858,535	16,596,182	1,262,353
Lead, pounds	5,158,329	4,378,000	780,329
Zinc, pounds	248,563,192	243,558,000	5,005,192
Total value, dollars	27,517,488	25,110,186	2,407,302

Preliminary Report on the Deposits of Manganese Ore in the Batesville District, Arkansas. H. D. Miser. Bulletin 715-G. Separate from Contributions to Economic Geology, 1920, Part I. 32 pp. Published November 15, 1920. The manganese ores may be grouped according to composition into two general classes—high-grade ores and low-grade or ferruginous manganese ores. Most of the high-grade ores contain 45 to 52 per cent of manganese, generally from 3 to 8 per cent of iron, 0.15 to 0.30 per cent of phosphorus, and 2 to 8 per cent of silica. Most of the low-grade ores contain 20 to 35 per cent of manganese, 8 to 20 per cent of iron, and 5 to 26 per cent of silica. The phosphorus content is about the same as that of the high-grade ores. The ore from this district has been used for making ferromanganese, spiegeleisen, and high-manganese pig iron. Very little, if any, of it has been found suitable for chemical uses because the amount of manganese dioxide is, as a rule, less than 80 per cent, and it is not likely that commercial quantities of chemical ore will be discovered.

Sodium Compounds in 1919. R. G. WELLS. Separate from Mineral Resources of the United States, 1919, Part II. 30 pp. Published November 16, 1920. Nearly all the compounds of sodium consumed in the United States except common salt are manufactured products. Even the salts that occur naturally are usually refined before they are used. As the natural salts, however, form only a small part of the annual production, this report deals almost entirely with the manufactured products. The following table summarizes the production of sodium and sodium compounds reported in 1918 and 1919:

SODIUM AND SODIUM COMPOUNDS PRODUCED IN THE UNITED STATES IN 1918 AND 1919

	1918		1919	
	Quantity Short Tons	Value	Quantity Short Tons	Value
Sodium (metal)	264	$153,437	(1)	(1)
Sodium acetate	2,622	460,783	2,426	$311,175
Sodium benzoate	203	886,058	126	230,224
Sodium bicarbonate	118,535	3,293,153	134,962	3,486,635
Sodium bichromate	28,334	9,868,118	26,526	6,233,566
Sodium bisulfite and sodium sulfite	16,362	478,482	11,846	687,750
Sodium bromide	574	438,730	499	493,319
Sodium carbonate:				
Soda ash	1,390,628	35,635,520	981,054	29,895,343
Monohydrate and sesquicarbonate	22,678	482,958	30,796	710,748
Sal soda	82,465	2,020,271	80,090	2,229,994
Sodium chlorate and sodium perborate	2,413	1,004,250	1,210	62,980
Sodium chloride:[2]				
Salt in brine	2,830,600	1,245,265	2,809,000	27,296,000
Rock salt	1,683,941	5,684,661	1,637,300	
Evaporated salt	2,724,203	20,010,435	2,618,200	
Sodium citrate, tartrate and bitartrate	(1)	(1)	33	58,128
Sodium cyanide, peroxide, and iodate	9,077	5,361,000	9,148	4,515,106
Sodium ferrocyanide	4,525	2,690,110	3,437	1,346,285
Sodium fluoride, acid sodium fluoride, and sodium fluosilicate (silicofluoride)	1,879	387,224	811	150,404
Sodium hydroxide (caustic soda)	513,363	31,854,470	355,466	22,196,898
Sodium iodide	(1)	(1)	12	86,985
Sodium nitrate (refined)	...	...	8,040	816,647
Sodium nitrite	1,701	609,779	676	151,621
Sodium phosphate (incl. all sodium phosphates)	15,620	1,427,947	14,760	1,733,996
Sodium silicate	317,161	5,870,973	300,138	5,879,628
Sodium sulfate:				
Salt cake	141,054	2,844,897	134,685	2,035,543
Glauber's salt	50,715	1,041,070	42,087	860,977
Niter cake	143,155	595,660	83,402	271,424
Sodium sulfide	43,490	2,293,304	45,448	2,645,181
Sodium tetraborate (borax)	26,673	3,909,565	28,518	4,351,891
Sodium thiosulfate (hyposulfite)	26,868	1,051,623	32,212	1,709,223
Miscellaneous sodium compounds	390	1,188,792	841	756,548
TOTAL	10,199,493	142,788,535	9,393,749	121,204,219

[1] Included under "Miscellaneous sodium compounds."

[2] Herbert Insley, "Salt, bromine, and calcium chloride." U. S. Geol. Survey Mineral Resources, 1919, pt. 2 (in preparation).

Natural-Gas Resources Available to Dallas and Other Cities of Central North Texas. E. W. SHAW AND P. L. PORTS. Bulletin 716-D. Separate from Contributions to Economic Geology, 1920, Part II. 31 pp. Published November 17, 1920. It seems probable that with rigid economy and scientific conservation the present available supply of natural gas in the region around Dallas may be depended upon to suffice for 6 to 10 yrs., though there will be shortages nearly every winter. Little can be certainly predicted for future developments.

Forty-First Annual Report of the Director of the United States Geological Survey to the Secretary of the Interior for the Fiscal Year Ended June 30, 1920. 180 pp. 1920.

Structure and Oil and Gas Resources of the Osage Reservation, Oklahoma. T. 28 N., RS. 11 and 12 E. M. I. GOLDMAN AND H. M. ROBINSON. Bulletin 686-Y. 36 pp. 1920.

Contributions to Economic Geology (Short Papers and Preliminary Reports) 1919. Part 1. Metals and Nonmetals except Fuels. F. L. RANSOME AND E. F. BURCHARD. Bulletin 710. 248 pp. 1920. The bulletin contains an introduction and the following special papers which have previously been reviewed in THIS JOURNAL: A Reconnaissance of the Pine Creek District, Idaho, by E. L. Jones, Jr. (published August 27, 1919); deposits of manganese ore in New Mexico, by E. L. Jones, Jr. (published October 21, 1919); deposits of manganese ore in Costa Rica, by J. D. Sears (published December 30, 1919); deposits of manganese ore near Boqueron River, Panama, by J. D. Sears (published December 30, 1919); deposits of manganese ore in Arizona, by E. L. Jones, Jr., and F. L. Ransome (published January 29, 1920); deposits of manganese ore in southeastern California, by E. L. Jones, Jr. (published December 30, 1919); deposits of manganese ore in Nevada, by J. T. Pardee and E. L. Jones, Jr. (published February 20, 1920).

The Lance Creek Oil and Gas Field, Niobrara County, Wyoming. E. T. HANCOCK. Bulletin 716-E. Contributions to Economic Geology, 1920, Part II. 32 pp. Published December 13, 1920.

Coal in Eastern Idaho. G. R. MANSFIELD. Bulletin 716-F. Contributions to Economic Geology, 1920, Part II. 31 pp. Published December 14, 1920. The results of the examination are disappointing. The only part of the Teton Basin that is producing coal at the present time is the Horseshoe district. Though conditions in this district are such that large-scale development is probably impracticable, work now in progress will doubtless make possible a somewhat greater yield than that of previous seasons. During the examination of the Teton Basin several reported occurrences of oil were investigated, but these do not indicate the presence of oil in paying quantities.

Potash in 1919. W. B. HICKS AND M. R. NOURSE. Separate from Mineral Resources of the United States, 1919, Part II. 18 pp. Published December 8, 1920. The potash industry of the United States was at a critical period of its history at the beginning of 1919. Developments had progressed under the high war prices until the annual productive capacity of the plants in operation or about ready to operate was estimated at 100,000 short tons of potash, and the capital invested in these plants was reported to be about $25,000,000. Comparatively few of the larger plants had been fully paid for, and many were still under construction or had been operated only a short time. About one-third of the production of 1918 was still in the hands of the producers, prices had dropped about half, and the market for domestic potash was dull even at that price, because lower priced potash was expected from Alsace and Germany. As a result, most of the producers closed their plants, and some of them went out of business. Foreign mines were in a poor state of repair, however, and imports were small, so that a ready market was found for the domestic output. The quantity of potash produced in 1919 fell far short of the production in 1918, and hardly equaled that of 1917, as is shown by the following table:

DOMESTIC POTASH PRODUCED AND SOLD IN THE UNITED STATES IN 1915 TO 1919

		PRODUCTION		SALES		
YEAR	No. of Plants	Crude Potash Short Tons	Available Content of Potash (K_2O) Short Tons	Crude Potash Short Tons	Available Content of Potash (K_2O) Short Tons	Value
1915	5	4,374	1,090	4,374	1,090	$342,000
1916	70	35,739	9,720	35,739	9,720	4,242,730
1917	95	126,961	32,573	126,961	32,573	13,980,577
1918	128	207,686	54,803	140,343	38,580	15,839,618
1919[1]	77	110,243	30,845	173,786	46,732	11,370,445

[1] Production for 1919 includes a quantity of material either utilized by producer or reported as not marketed; sales for 1919 include material produced in 1918 but sold in 1919.

Strontium in 1919. G. W. STOSE. Separate from Mineral Resources of the United States, 1919, Part II. 4 pp. Published December 9, 1920. No domestic strontium ore was mined or sold in the United States in 1919. Crude ore was imported from England by manufacturers of strontium salts, and some manufactured salts were also imported. Strontium nitrate and strontium carbonate were the chief chemicals made.

CRUDE DOMESTIC STRONTIUM ORES PRODUCED AND MARKETED IN THE UNITED STATES, 1916 TO 1919

	1916		1917		1918		1919	
MINERAL	Quantity Short Tons	Value	Quantity Short Tons	Value	Quantity Short Tons	Value	Quantity Short Tons	Value
Celestite	240	(1)	3,630	$72,285	0	0	0	0
Strontianite	10	(1)	405	15,415	400	$20,000	0	0
TOTAL	250	$3,650	4,035	87,700	400	20,000	0	0

[1] Figures not available.

Gypsum in 1919. R. W. STONE. Separate from Mineral Resources of the United States, 1919, Part II. 15 pp. Published December 28, 1920.

Gypsum was mined in the United States in almost continuously increasing quantity for many years up to 1917, when there began a decrease in production that amounted to three-fourths of a million tons in 2 yrs., the production in 1918 being the lowest recorded since 1908. In 1919, however, the quantity mined was 2,420,163 short tons, an increase of 18 per cent over the output in 1918. A similar increase in 1920 would make the production of crude material greater than in any preceding year.

CRUDE GYPSUM MINED IN THE UNITED STATES, 1908–1919, IN SHORT TONS

1908	1,721,829	1912	2,500,757	1916	2,757,730
1909	2,252,785	1913	2,599,508	1917	2,696,226
1910	2,379,057	1914	2,476,465	1918	2,057,015
1911	2,323,970	1915	2,447,611	1919	2,420,163

BUREAU OF MINES

Fees for Testing Explosives and Conditions and Requirements under Which Explosives Are Tested. Schedule 1-A. 13 pp. Paper, 5 cents. 1920. Authorization for the work is cited, permissible explosives are defined, and tests of coal mining explosives, conditions under which tests will be made, test requirements of explosives for admittance to permissible list, prescribed conditions for use of permissible explosives, conditions under which an otherwise permissible explosive is not permissible, explosives not to be considered permanently permissible, manner of making remittances, tests of explosives used in metal mines, tunnels, quarries, and other engineering operations, conditions under which tests will be made, and test requirements of explosives used in metal mines, quarries, and other engineering operations are described.

Stenches for Detecting Leakage of Blue Water Gas and Natural Gas. S. H. KATZ AND V. C. ALLISON. Technical Paper 267. 22 pp. Paper, 5 cents. 1920. The impregnation of natural gas or blue water gas with a stench-imparting chemical provides a means for reducing loss from leakage and for eliminating accidental poisoning and explosions. Stenches that possess a disagreeable odor serve best as warnings. Of those examined, amyl thioether, ethyl mercaptan, phenyl isocyanide, and pyridine present the best possibilities. None of the stenches that contain sulfur, if added to gas in amounts to produce strong odors, would carry sufficient sulfur to inhibit commercial use of the gas.

Miners' Safety and Health Almanac 1921. Published in Coöperation with the United States Public Health Service for the Use of Miners. Compiled by R. C. WILLIAMS. 48 pp. 1920.

Tenth Annual Report of the Director of the Bureau of Mines to the Secretary of the Interior for the Fiscal Year Ended June 30, 1920. 149 pp. Paper, 15 cents. Issued December 1920.

Structure in Paleozoic Bituminous Coals. REINHARDT THIESSEN. Bulletin 117. 296 pp. Paper, 80 cents.

BUREAU OF STANDARDS

Effects of Cal as an Accelerator of the Hardening of Portland Cement Mixtures. R. N. YOUNG. Technologic Paper 174. 24 pp. Paper, 5 cents. 1920. Cal is obtained by pulverizing the dried or undried product resulting from a mixture of either quicklime or hydrated lime, calcium chloride, and water. It is much more convenient to handle and use in making concrete than calcium chloride, either fused or in concentrated solution. The general effect of Cal on portland cement mixtures is the same as might be expected from the use of equivalent amounts of hydrated lime and calcium chloride. The 3-yr. tests by the Bureau of Standards on concrete gaged with a solution of calcium chloride are sufficient grounds for believing that the addition of Cal will not injuriously affect the ultimate strength and integrity of portland cement concrete.

Slushing Oils. P. H. WALKER AND L. L. STEELE. Technologic Paper 176. 23 pp. Paper, 5 cents. 1920. This paper was published to answer inquiries requesting information as to methods of protecting from corrosion metal in storage for rather long periods. The investigations were confined to a consideration of protective coatings which remain in a soft condition so that they can be easily removed at any time.

Pouring and Pressure Tests of Concrete. W. A. SLATER AND A. T. GOLDBECK. Technologic Paper 175. 13 pp. Paper, 5 cents. 1920. These tests suggest the desirability of conducting further tests to determine (1) the relation between the pressure on the forms and the rate of increase in the head of the concrete, and (2) the influence of hardening of the concrete upon the pressure under increasing head.

DEPARTMENT OF AGRICULTURE

The Bureau of Chemistry of the United States Department of Agriculture. Organization, Enforcement of Food and Drugs Act, Enforcement of Tea Act, Research Work. Department Circular 137. 23 pp. Issued 1921.

Peanut Oil. H. C. THOMPSON AND H. S. BAILEY. Farmers' Bulletin 751. Revised December 1920. 18 pp.

The Care of Leather. F. P. VEITCH AND H. P. HOLMAN. Farmers' Bulletin 1183. 18 pp. Issued December 1920. The supply of leather in this country can be made to go much further than is now the case if everyone selects with discrimination and properly cares for their boots and shoes, harness, and machine belts. Not only can personal budgets be cut down in this way, but prices can be brought down to a lower level by giving the supply a chance to catch up with the demand. This bulletin contains suggestions for a judicious selection of articles made from leather and tells how to care for them in order to secure the maximum amount of service.

Articles from Journal of Agricultural Research

Some Changes in Florida Grapefruit in Storage. L. A. HAWKINS AND J. R. MAGNESS. 20 (December 1, 1920), 357–73.

A Bacteriological Study of Canned Ripe Olives. S. A. KOSER. 20 (December 1, 1920), 375–9.

Relation of the Soil Solution to the Soil Extract. D. R. HOAGLAND, J. C. MARTIN AND G. R. STEWART. 20 (December 1, 1920), 381–95.

Effect of Season and Crop Growth on the Physical State of the Soil. D. R. HOAGLAND AND J. C. MARTIN. 20 (December 1, 1920), 397–404.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Import and Export Schedules of Spain. Miscellaneous Series No. 87. 60 pp. Paper, 10 cents. 1920. This bulletin is a translation of the import and export schedules of Spain. Among other things, import schedules are given for mineral fuel, ores, gold, silver and platinum, unmanufactured iron and steel, copper and alloys thereof, other metals and alloys thereof, simple drugs, colors, dyes and varnishes, mineral fertilizers, chemical and pharmaceutical products, and paper pulp. Export schedules are given for minerals, mineral ores, gold and silver, iron and steel, copper and alloys thereof, other metals, simple drugs, coloring materials, chemical products, and oils.

Industrial Machinery in France and Belgium (with Bibliography). C. P. WOOD. Special Agents Series 204. 61 pp. Paper, 10 cents. 1920.

COMMERCE REPORTS—DECEMBER 1920

Recent experiments of the British Department of Scientific and Industrial Research prove that, provided certain precautions are taken, **beef** can be frozen in such a way as to preserve completely the physical and chemical qualities of the fresh meat. The experiments were carried out with small pieces of beef, and the committee states that subsequent attempts to repeat them on a commercial scale have so far failed for lack of adequate apparatus. (P. 970)

As a result of experiments at Bruenn-Koenigsfeld, **turf** treated by a special patented process furnishes a material for insulation and building purposes that is said to be, in most respects, not inferior, and in some, superior, to cork. (P. 978)

Considerable uncertainty exists in Holland as to the future of the **dye** trade. (P. 982)

The **kauri-gum** industry in New Zealand is taking on new impetus since the closing of the war. (Pp. 984–5)

The Argentine market for **drugs** and veterinary remedies is reviewed. (Pp. 990–2)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable oil material by the former German colonies in Africa during the three latest years for which statistics are available. (P. 1004)

A Portuguese decree has been issued removing the license requirements for the exportation of **leather**. (P. 1009)

The **oil, medicinal products, chemical** and **pharmaceutical** products market in Argentine is reviewed. (Pp. 1031–3)

Recent experiments of the British Department of Scientific and Industrial Research show that **strawberries**, when picked ripe, may be held in cold storage (temperature 1° to 2° C.) in a good marketable condition for 6 to 7 days. Unripe strawberries do not ripen normally in cold storage, neither do they ripen when transferred to normal temperatures after a period of cold storage. (P. 1035)

The yield of a good quality of **crude oil** from English shales by means of treatment in specially designed retorts is reported to be satisfactory. (Pp. 1038–9)

Although the production of **rosin** in Spain was less during the fiscal year ended June 30, 1920, than in the preceding year, sales were greater and the profit was the largest that the Union Resinera Española has had in its 22 yrs. of existence. (Pp. 1046–7)

A law of the Dominican Republic provides that all **patent** and **proprietary remedies** must be analyzed and approved by the department of sanitation before being offered for sale in the republic. (P. 1047)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable oil material by Australia during the fiscal years ended June 30, 1916, 1917, 1918, and, when possible, 1919. (Pp. 1054–5)

According to preliminary figures issued by the Tunisian government, the regency's **olive oil** yield for 1920 is given at 40,000,000 kilos, compared with 12,000,000 to 16,000,000 kilos in 1919 and 40,000,000 kilos in 1918. (P. 1064)

An American-owned **manganese** mine, situated on the Gulf of California, is now operating and shipping 200 tons of high-grade ore monthly. The ore extracted averages about 48 per cent manganese. (P. 1066)

A company has been formed in Mexico to develop the **oil wells** in the districts of Bravos, Iturbide, and Camargo. This field, it is said, should prove to be one of the world's great oil fields. (Pp. 1066–7)

Although the imports of **oil** into Czechoslovakia have been large, the domestic production of oil has been appreciable. In Slovakia the finding of rich, new oil wells is reported near Trenčin. (P. 1076)

The **peanut** and peanut oil industry of China is reviewed. (Pp. 1083–5)

The production of **cacao** for 1920 in Tabasco is estimated at 3,300,000 lbs., the largest crop since 1913. Mexican cacao, besides being of superior quality, is far less bitter than other varieties, and hence requires less sugar in the manufacture of chocolates and bonbons. As it is richer in fats and oils, it should be profitable for American manufacturers to import it. (P. 1088)

Australian **dehydrated vegetables** have attained prominence on the local market, as well as abroad. (P. 1096)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable oil material by the Philippine Islands during 1917, 1918, and 1919. (P. 1097)

The **mineral resources** of Slovakia are reviewed. In addition to iron, coal, and oil, the following minerals are of considerable importance in manufacturing and the arts: calciferous rocks, sand, porcelain earth and kaolin, common salt, antimony, copper, manganese, cobalt, nickel, cinnabar, and pyrite. (Pp. 1098–1100)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable oil material by Spanish colonies and by the Belgian Kongo during the only years for which statistics are available. (P. 1102)

The Sicilian **sumac** crop is from one-half to two-thirds of last year's production, which was about 20,000 tons. (P. 1103)

Manila is making plans for greatly enlarging its **water system.** For the purpose of carrying out the improvements, the metropolitan water district has been organized. Two or three experienced engineers have been procured in continental United States for the work, which will probably take 7 yrs. (P. 1116)

One of the most interesting contributions to the chemistry section of the British Association during its annual conference at Cardiff was that which opened up a discussion on the subject of **industrial alcohol.** (Pp. 1118–9)

It is estimated that the 1920 Chinese **peanut oil** for export will be about 84,000 tons. (P. 1121)

A group of German textile manufacturers has established a new company in Prague for the manufacture of **artificial silk.** (P. 1132)

As a result of a general conference of those interested in Czecho-Slovak **mineral waters,** resolutions were prepared petitioning the government to favor the mineral-water trade by a thorough revision of freight rates, special rates for the return of empty bottles, export premiums, arrangements with foreign countries for the importation of Czecho-Slovak mineral waters under more favorable tariff arrangements, and the like. (P. 1136)

During September, the Argentine government **oil wells** at Comodoro Rivadavia produced the largest amount of petroleum for any month up to this date. (P. 1146)

In order to intensify production in the state **oil fields** of Argentina, the Ministry of Agriculture in that republic has under consideration a plan by which it is expected to secure the following production: 1920, 210,000 cubic meters; 1921, 330,000 cubic meters; 1922, 480,000 cubic meters; 1923, 600,000 cubic meters; 1924, 700,000 cubic meters. (P. 1147)

The production of **salt** in Japan is reported to be short of the country's requirements. Government help is being solicited for the protection of the industry. (P. 1150)

The Japanese allotment of **camphor** for the fourth quarter of 1920 gives to the United States the same amount as that of the last quarter. (P. 1153)

The **cacao** growers in Bahia, Brazil, have formed a syndicate for the purpose of fostering the industry. (P. 1163)

The Rubber Producers' Association of Malaya has issued a circular letter to its members in British Malaya urging them to reduce the normal output of **rubber** by 25 per cent because of the depressed condition of the rubber market at the present time. (Pp. 1166–7)

The present condition of the Alsatian **potash mines** is described, and it is claimed that the German salts of Stassfurt are on the average less rich in potash than the Alsatian. (Pp. 1173–5)

Announcement comes from Greece that the Patras consular district is in the market for about 55 tons of **dyestuffs.** (Pp. 1180–1)

Conditions in the German **paper** industry showed a slight improvement during September 1920. (P. 1190)

Analyses of **petroleum gas** at Roma, Queensland, show it to be considerably richer than the gas from most petroleum wells. (P. 1191)

Imports of **oilseeds,** oil nuts, and kernels into the United Kingdom in October aggregated 129,290 tons, as compared with 197,525 tons in October 1919, a decrease of 68,235 tons. (P. 1197)

The greater number of Germany's **chemical plants** are located in Leipzig, Cologne, Berlin, and the Hambur districts. There were 15,204 plants in operation in 1918, while the total has fallen to 15,069 in 1919, a decrease of 1.95 per cent. This decrease is due chiefly to the fact that the chemical plants in Alsace-Lorraine were eliminated from consideration in 1919. (Pp. 1210–1)

The **lime** industry in Finland is considerably handicapped at the present time by having to use wood in place of coal. (P. 1211)

A plant for producing **benzine** and **industrial oils** is under construction at Belgrade, Serbia. A chemical factory is also to be built on the banks of the Danube near there. A plant for the manufacture of chemical products and perfumery is being built at Bjelovatz, Slavonia, and a new tannery is being organized at Vissoko, Bosnia. It is believed that the alcohol distilleries at Zagreb, Croatia, will soon be completed, and that distillation will begin prior to May 1921. (P. 1213)

Licenses for the creation of **alcohol distilleries** will be granted by the Minister of Finance of Jugoslavia in agreement with the Minister of Agriculture. Preparations will be made to abolish, by legal methods, the alcohol monopoly existing in Serbia and in Montenegro, and everything will be done to facilitate the development of alcohol industries in these provinces. (P. 1215)

The **vegetable oil** industry in Marseille, France, is described. During the last 5 mo. the industry was seriously affected by the fluctuations of the oilseed market. There has been a slight improvement of late, and the outlook for the winter months is fairly promising. (Pp. 1222–7)

Report comes from Bradford, England, that a machine has been designed to ascertain the contraction of a **cloth** due to **shrinkage.** The value of the machine may be judged by the results shown in the following tests, which cover a range of cloths varying in shrinkage:

CLOTHS TESTED	Average Calculated Shrinkage Per cent	Actual Shrinkage Per cent
Worsted costume cloth (loose setting)	18.7	18.7
Milled Austrian rug	29.8	31.0
Woolen costume cloth	19.3	19.5
Honeycomb vesting	20.0	19.0
Mixture coating	14.3	14.7
Mixture worsted coating	21.3	23.6

(Pp. 1228–9)

The Chinese **soap** market is described, including native soap substitutes. (Pp. 1229–31)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable oil material by Straits Settlements during the three latest years for which statistics are available. (P. 1238)

The following table shows the output of **minerals** in Mexico during the first 6 mo. of 1920 compared with the corresponding period in 1919:

MINERALS	First 6 mo. of 1919		First 6 mo. of 1920	
	Kilos	Total Value	Kilos	Total Value
Antimony	4,148	$3,434	577,723	$381,875
Arsenic	1,358,860	898,206	770,797	309,860
Commercial copper	21,405,829	17,424,345	23,914,011	19,466,005
Tin	1,588	4,535	......	......
Amorphous graphite	3,686,563	405,522	2,441,240	390,598
Manganese	1,437,495	343,561	31,509	7,531
Mercury	52,094	262,970	42,505	220,218
Molybdenum	1,563	14,891	648	6,173
Gold	10,343	13,790,663	11,775	15,699,996
Silver	954,333	69,666,309	1,029,940	75,824,183
Commercial lead	30,918,282	10,821,399	44,898,902	17,465,673
Tungsten	1,389	11,633	4,471	37,445
Commercial zinc	4,485,115	1,323,109	8,543,132	3,434,339

(P. 1247)

The new Swedish regulations regarding the uses of **artificial leather** in shoes become effective immediately. (P. 1255)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable oil material by Hongkong during the two years for which statistics are available. (P. 1258)

There is reported to be an active demand in Greece for **petroleum** products. (P. 1262)

About 20 tons of **benzidine** are used annually in the Athens consular district. Benzidine has been imported in the past from American and German firms. (P. 1263)

The Italian restrictions on the importation and sale of **mineral oils**, including gasoline, kerosene, and fuel oils, will be removed on or about January 1, 1921. (P. 1265)

The text of the proposed British law for restrictions on the importation of **dyestuffs** into Great Britain, is quoted. (Pp. 1297–8)

The Japanese government is soon to appoint a committee for the disposition of Germany's **reparation dyes** arriving in Japan. Approximately 88 tons of German dyes are in warehouses in Kobe. (P. 1302)

A sample of **tungsten ore** from Argentina has been examined by the Bureau of Mines and found to contain 64.46 per cent wolfram, 10.95 per cent silica plus insoluble matter, and considerable calcium carbonate. (P. 1318)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable oil material by French Colonies and Protectorates in Africa during the three latest years for which statistics are available. (Pp. 1319–26)

Indications of **oil** in various parts of Uruguay have been reported. (P. 1343)

The date on which the new **British Dyestuffs Act** is to become effective has not yet been decided. There is said to be a reasonable probability that a bill for the restriction of inorganic chemicals and pharmaceuticals will be introduced after New Year's Day. (P. 1345)

Announcement is made of the discovery of **lignite** and **iron ore** in Poland. (P. 1348)

A new process has been discovered for **drying turf for fuel** in Finland. (P. 1359)

The output of the **oil fields** at Assam, India, is said to be increasing, and many Indian engineers and chemists are employed under European supervision. (Pp. 1368–9)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable oil material by Portuguese colonies in Africa during the three latest years for which statistics are available. Photostat copies of detailed statistics, showing countries of shipment of imports and destination of exports from Mozambique may be obtained from the Bureau of Foreign and Domestic Commerce for 15 cents a page. (Pp. 1372–3)

SPECIAL SUPPLEMENTS ISSUED

BELGIUM—*2a*
FRANCE—*7c*
GREECE—*9a*
WALES—*22h*
DUBLIN—*22i*
BRITISH WEST INDIES—*25c*
CANADA—*26c*
COSTA RICA—*27b*
DOMINICAN REPUBLIC—*29b*
PANAMA—*38a*
BRAZIL—*43b*
CEYLON—*54a*
CHINA—*55e*
CHINA, SHANGHAI—*55f*
DUTCH EAST INDIES—*56b*
MESOPOTAMIA—*62a*
AUSTRALIA—*63b*
AUSTRALIA—*63c*

STATISTICS OF EXPORTS TO THE UNITED STATES

CHINA—(P. 1085)	BRAZIL (Pp. 1087, 1345)	ALGERIA—(Pp. 1306–7)
Peanut oil	Crude rubber	Oil, geranium Iron ore

BOOK REVIEWS

Soil Alkali. By FRANKLIN STEWART HARRIS, Ph.D., Director and Agronomist, Utah Agricultural Experiment Station. xvi + 258 pp. John Wiley & Sons., Inc., New York, 1920. Price, $2.50, net.

This book is issued in answer to the continued demand for a volume containing a resumé of the important information concerning the subject. An enormous amount of work has been done on "soil alkali" but this is the first effort to correlate it. The term "soil alkali," is perhaps a misnomer, although it is now definitely fixed as applying to any accumulation in the soil of soluble salts in sufficient quantity to be injurious to plant growth. Most of the "alkalies" are salts, namely, chlorides, sulfates, carbonates, and nitrates of sodium, potassium, and magnesium, and the chlorides and nitrates of calcium. Naturally, the accumulation of alkali occurs in arid regions, or under conditions which do not readily admit of the removal of soluble salts from the soil.

The author points out that most of the desirable land of the world has been taken up and about one-half of the area of the earth is in arid regions where drought and alkali are encountered. In the United States about 13 per cent of the irrigated area, or about 9,000,000 acres, contains sufficient alkali to be harmful.

The volume discusses the geographical distribution of alkali soils of the world and the causes leading to the formation or accumulation of alkali. The discussion of alkali soils leads into many of the sciences related to agriculture. Not only are geographical and geological features discussed, but the range covers biology as related to plant and seed injury, native vegetation as indicative of alkali, and the biological conditions of the soil; chemistry, as in the methods employed in determining alkali and the theory of antagonism; physics, as affecting the physical condition of the soil, and the movement of water in the soil; engineering as related to drainage and irrigation of the soil; and crop adaptation for lands containing alkali.

The book seems to have been painstakingly and carefully prepared, and the author has included the fundamental facts concerning soil alkali as published in many places throughout the world, as well as drawing largely from his own experience in dealing with the problem. The bibliography, while not exhaustive, is comprehensive, and no important work seems to have been overlooked. The book fills a long-felt want by workers in this field, and should find wide use, as the author believes, by both students and agriculturalists dealing with alkali soils.

R. O. E. DAVIS

The Modern Electroplater. By KENNETH M. COGGESHALL. 300 pp. Norman W. Henley Publishing Co., New York, 1920. Price, $3.00.

There is to-day in the electroplating industry a great need for a modern American text which will explain clearly the chemical and physical principles of electrodeposition, and their application to commercial processes. Such a book would be of great value not alone to progressive electroplaters, but also to those chemists who are now being brought into contact with the electroplating departments of large factories.

It is with a distinct sense of disappointment that one realizes that the author of this new book has not even attempted to meet that need. In his own words, "The aim of this book is not scientific, but practical." Indeed the author has followed so literally this policy that even in the statement of practical methods he has often failed to be accurate, much less scientific. How can we expect a practical plater to gain any correct conception of an ampere when he is told that "the gallon and the ampere, then, are both units of quantity measurement" (p. 30), although subsequently (p. 37) the author correctly defines a coulomb as the quantity of electricity? Even if the plater is willing to continue the use of the Baumé hydrometer, he should not be encouraged to believe that the reading of this or of any hydrometer is an indication of the metal content of a nickel plating solution containing various compounds other than nickel salts (p. 183). In spite of the fact that all progressive platers have learned to estimate at least roughly the current density employed in their plating operations, the author is content to define the desired rate of deposition by the voltage, giving always a wide latitude, as, for example, "from two to six" volts (p. 188). Although practically all nickel anodes now used commercially contain not more than 95 to 97 per cent nickel, and frequently less, the author refers to 99 per cent nickel anodes as if they were a regular article of commerce.

The above examples suffice to show that the book cannot be of real service to either the plater or the chemist. Its chief value or interest lies in the description of the mechanical equipment used in plating, with modern illustrations derived from numerous catalogs. WILLIAM BLUM

Technical Gas and Fuel Analysis. By ALFRED H. WHITE. Second Edition, Revised and Enlarged. 319 pages, 59 figures, and 13 tables. McGraw-Hill Book Co., Inc., New York, 1920. Price $3.00.

The second edition of this excellent textbook has been revised and enlarged to include the progress made in technical gas and fuel analysis in the seven years intervening since the publication of the first edition.

The greater part of the book, Chapters I to XII, inclusive, deals with the analysis and testing of gases, fuel and illuminating gases primarily. The difficulties involved in collecting and storing a representative gas sample are discussed in detail, special emphasis being laid on changes in composition produced by the solubility of gases in the confining fluid and in rubber connecting tubes. Methods for continuous and intermittent sampling are described, although no mention is made of constant flow mercury sampling tubes which can be used to good advantage where average samples of gases of greatly varying composition must be sampled.

The Hempel method of gas analysis is carefully described, with many valuable details of manipulation that are too often omitted from the average textbook. The excellent discussion on absorption methods for various constituents contains much new material available only within the last two years.

Explosion, fractional, and complete slow combustion methods for determining combustible constituents are described, with especial attention to the more generally used explosion method. A little more attention should have been given to the slow combustion method of Dennis and Hopkins, which is extensively used in miscellaneous gas analyses where the proportion of combustible constituents varies widely. In the opinion of the reviewer this method when carried out properly gives more accurate results than the explosion method.

On page 61 it is stated that as little as 0.005 per cent of carbon monoxide can be detected by the green color produced in a mixture of iodic anhydride with fuming sulfuric acid on pumice. This statement should read 0.05 to 0.1 per cent carbon monoxide.

Methods of exact gas analysis are discussed in connection with the author's bulbed and compensated gas buret. Attention is called to errors from oxidation of nitrogen in both slow combustion and explosion methods, the author giving data from his own experiments.

Other forms of gas analysis apparatus than the Hempel are briefly described, especially those which first embodied valuable principles, such as Schlösing and Rolland's apparatus, Orsat's apparatus, Bunte's buret, and Chollar tubes. With the exception of the portable Orsat apparatus for chimney gas analysis, no attempt is made to discuss the modern forms of these apparatus, such as the Burrell-Orsat for complete gas analysis, and the water-jacketed forms of the Bunte buret, as used in the Elliott and the Morehead apparatus.

Heating value and candle power determinations are treated in two comprehensive chapters, replete with important details on apparatus and accuracy of methods.

Chapter IX is devoted to the difficult problem of estimating suspended particles in gases. Methods of sampling are critically analyzed, and the available methods for collecting these particles are briefly described, perhaps a little too briefly for the unsuspecting technical chemist who has never tried to determine a mixture of tar, soot, and ash in chimney gases.

The chapters on chimney gases and producer gas will be appreciated by both student and technical chemist. The application and interpretation of such analyses are clearly explained.

Sampling, analysis, and special tests for illuminating gas are fully described. Natural gas is treated more briefly, yet with references to recent work on separation of the hydrocarbons and the determination of gasoline in natural gas.

Chapter XIII on liquid fuels describes briefly the principal tests for evaluating liquid fuels, such as heating value, specific gravity, moisture, suspended solids, flash point, and distillation tests. No mention is made of calculating the heating value of petroleum products to within 1 or 2 per cent from constants more easily determinable than the calorific value, or the determination of sulfur in the bomb calorimeter. The need of standardization and development of methods for testing and analyzing liquid fuels is apparent from the limited scope of this chapter.

The chapters on sampling and analysis of coal and coke are quite complete, giving in detail the standard methods of the American Society for Testing Materials, with numerous comments from the authors and references to recent work on the subject appearing in the literature. The importance of proper sampling is especially emphasized.

Chapters XVI and XVII contain an unusually complete discussion of calorimetric determination of heating value. Procedures and descriptions of various forms of calorimeters are given in detail, including a special monel metal bomb used in the calorimeter laboratory of the University of Michigan.

Thirteen tables, very useful in gas calculations, are included in the appendix.

The second edition of Professor White's excellent book should continue to find favor as a text on technical gas and fuel analysis, on account of the concise presentation of the essential principals of fuel analysis together with the necessary details of manipulation and the precautions required to obtain reliable results.

The technical chemist will appreciate the up-to-date references and new material in the revised edition.

A. C. FIELDNER

The Nature of Animal Light. By E. NEWTON HARVEY. Monographs on Experimental Biology edited by Jacques Loeb, T. H. Morgan and W. J. V. Osterhout. viii + 178 pp. J. B. Lippincott Co., Philadelphia and London, 1920. Price, $2.50.

This fascinating topic has been admirably treated by the author in a clear, concise, and very readable manner. The book is so planned, by devoting two of the seven chapters to a summary of the general physics of light production, that even the layman can appreciate the relative significance of this particular branch of the science.

Two chapters describe the various forms of light-giving organisms and the structure of their luminous organs, and the remaining three are devoted to the chemistry of light production and the dynamics of luminescence.

A comprehensive bibliography is appended.

The subject is considered from the experimental standpoint, and a large number of facts and observations are made available for those who wish either to pursue the investigation further, or to correlate the phenomena with the general theory of radiation and molecular structure.

The conclusion is reached that luminescence, in at least three groups of luminous animals, is due to the interaction of two substances, luciferin and luciferase, in the presence of water and oxygen, as suggested by Dubois (1887). Luciferase is unquestionably a protein, heat-sensitive and nondialyzable. Though used up in causing the oxidation of large quantities of luciferin, it behaves in many ways like an enzyme. Luciferin has many properties in common with the proteoses and peptones, is heat-resistant and dialyzable, and oxidizes with production of light in the presence of luciferase.

Unfortunately there appears to be some confusion in the discussion of luminous efficiencies in Chapter III. The definitions on page 48 should be more precisely stated, and one for "total luminous efficiency" included. The data in Table 6, on page 60, giving the comparative efficiencies of different illuminants, are those computed by Ives for total luminous efficiency, while the text indicates them as "visible radiation × visual sensibility ÷ total radiation." The divisor should be "total energy input." The efficiency of the firefly as given, 0.96, refers to radiant luminous efficiency since the total energy input is unknown, and hence it should not be included in this table. Though the radiant luminous efficiency may be very nearly the same as the total luminous efficiency in the case of an incandescent filament, when a source such as the incandescent gas burner is considered, there is a great difference. Here while the radiant luminous efficiency is 0.012, the total luminous efficiency is only 0.0019. From the approximate calculation of McDermott and Ives (*Lighting Journal*, 2 (1914), 61) and Karrer (*J. Frank. Inst.*, 185 (1918), 775) the total luminous efficiency of the firefly would appear to be only about 25 per cent. Even this figure, however, is sufficiently above our best attainments in practice to warrant a search for the mechanism of the reaction which the firefly has evolved.

The book, as a whole, is a very interesting summary of the work which has been done in this field. It will be useful both to the general reader and the specialist.

G. M. J. MACKAY

Margarine. By WILLIAM CLAYTON, M.Sc., Member British Assoc. Com. on "Colloid Chemistry and Its General and Industrial Applications." xi + 186 pp., 12 halftone plates and 12 illustrations. Longmans, Green and Co., London, New York, Bombay, Calcutta, and Madras, 1920. Price, $4.75.

Another of the excellent monographs on industrial chemistry edited by Sir Edward Thorpe makes its appearance. "A succinct account of the modern processes of manufacture of margarine" is the first of its kind in any language. The text, incomplete to be sure, but rich with references to the literature and patents (foreign, as well as British), though compact, yet with a very full bibliography on all phases of margarine technology, deals not alone with the constituents, the finished product, keeping qualities, the methods of their analysis, and their compounding. Butter, renovated butter, lard compounds, and the "denaturing" of margarine are separately treated in a pleasing way.

Margarine is one of the worth-while things that have quickly developed out of the exigencies of war. In 1870 Mége-Mouries, the French chemist, working on the problem of the production of synthetic butter, prior to the Franco-Prussian War, converted his researches into the invention of oleomargarine. The margarine industry acquired preëminence during the World War, and its importance has been established for all time, manipulated fats constituting an essential in the regimen of thickly populated communities.

The author deals with the prejudices, abuses, correctives, advances, etc., of what has developed into a large, decent industry. He cleverly classifies the progress made under two heads, the advances being indicated by four steps in each. From a purely scientific point of view the noteworthy advances were (1) the use of commercial lactic acid cultures to impart a butter flavor; (2) the introduction of vegetable oils and fats to produce "Nuts and Milk Margarine;" (3) introduction of hydrogenated oils; and (4) the use of artificial milk, which is pasteurized, soured, and emulsified.

From a practical standpoint the striking improvements have been: (1) the use of a spray of ice-cold water to solidify the margarine emulsion; (2) the introduction of the brine-cooled rolling drum; (3) employment of a continuous churning apparatus; and (4) the use of butter-working tables, blenders, and other devices for kneading the margarines.

Each of these forward steps receives due attention, but all of them were involved in the production of a material of proper physical texture, which was attained by rapidly cooling a perfect emulsion. An altogether delightful chapter on the "Theory of Emulsification" directs attention to an ample field for research and ends as follows: "So far, practically no work has been done on *solid* emulsions, of which butter and margarines are interesting, if complex, cases."

The nutritional value of margarines receives judicial treatment. The importance of vitamines, or advitants, as Forster insists they should be called, is fully set forth, and their absence from certain margarines noted. While butter is urged for children, adults, "with their stronger digestive powers, may with absolute impunity replace butter by either oleo- or vegetable-margarine; provided they consume sufficient amounts of the vegetative green parts of plants, since these furnish an ample supply of all three vitamines."

CHARLES BASKERVILLE

Industrial Gases. By HAROLD CECIL GREENWOOD. xvii + 371 pp. D. Van Nostrand Co., New York, 1920. Price, $5.00, net.

The author has admirably attained his purpose in giving a comprehensive review of most of the industrial gases, their properties, and manufacture. The viewpoint is chemical rather than engineering, and the theory underlying each process is treated in a clear, readable manner. Particular attention is paid to the historical development of the various methods, and the description of important patents is included. The processes of manufacture are tabulated so that one may easily compare efficiency, cost (on a pre-war basis), and convenience in storage and transportation.

The introduction, besides treating well-known gas laws and their applicability, includes thermodynamical principles, factors influencing catalytic reactions, theory and general methods of testing gases for density, viscosity, and purity. Emphasis is laid on safety precautions in compressing gases for storage and transportation. Deviations from the theoretical volumes under various pressures are tabulated, as are also the relations between degree of filling and pressure developed in cylinders containing liquefied gases. A table of physical constants of the gases and a comprehensive bibliography are valuable additions.

The specific gases dealt with are air, oxygen, nitrogen, rare gases and ozone, hydrogen, carbon monoxide, carbon dioxide, sulfur dioxide, and nitrous oxide. Three sections of interest are on asphyxiating gases, hydrogen for military purposes, and gaseous fuels. The treatment of each gas includes its occurrence, physical and chemical properties, manufacture, and applications. Methods of preparation for laboratory use as well as production on a commercial scale are included. Such gases as ammonia and hydrogen chloride which are omitted are to be treated in another volume of the same series of texts on industrial chemistry. One omission which is noticeable is the class of dissolved gases, a very prominent example of which is acetylene in acetone.

The book recommends itself by its unusually clear correlation of theory and practice. It is of value to both the student seeking general information and the chemical engineer interested in concrete application.

HELEN C. GILLETTE

NEW PUBLICATIONS

Carbohydrates and Alcohol. Samuel Rideal. Price, 12s. 6d. net. Baillière Tindall & Cox, London.

Cement: Fabrication du Ciment. J. Fritsch. 2d edition, revised. 559 pp. 186 figures, 180 illustrations. Price, $6.00. D. Van Nostrand Co., New York.

Chemical Engineering: A Textbook of Chemical Engineering. Edward Hart. 211 pp. 200 illustrations. Price, $4.00. Chemical Publishing Co., Easton, Pa.

Chemistry: Introduction to General Chemistry. H. Copaux. Translated by Henry Leffmann. 195 pp. 30 illustrations. Price, $2.00. P. Blakiston's Son & Co., Philadelphia.

Drugs: Analysis of Drugs and Medicines. Henry C. Fuller. 1072 pp. Illustrated. Price, $10.00, net. John Wiley & Sons, Inc., New York.

Enzymes: The Chemistry of Enzyme Actions. K. George Falk. (American Chemical Society Monographs.) 140 pp. Price, $2.50. The Chemical Catalog Co., Inc., New York.

Fuel Production and Utilization. Hugh S. Taylor. 296 pp. Price, $4.00. D. Van Nostrand Co., New York.

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Fuel: Powdered Coal as a Fuel. C. F. Herington. 2d edition, revised and enlarged. 338 pp. 124 illustrations. Price, $4.50. D. Van Nostrand Co., New York.

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Water Softening and Treatment, Condensing Plant, Feed Pumps and Heaters for Steam Users and Manufacturers. William H. Booth. 2d edition. 324 pp. 92 illustrations. Price, $3.50. D. Van Nostrand Co., New York.

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MARKET REPORT—JANUARY, 1921

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.	.15	.15
Hydrochloric, com'l, 20°	lb.	.01$\frac{7}{8}$	.01$\frac{7}{8}$
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07$\frac{3}{4}$	.07$\frac{3}{4}$
Phosphoric, 50% tech	lb.	.20	.20
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	20.00	20.00
Oleum 20%	ton	23.00	23.00
Alum, ammonia, lump	lb.	.04$\frac{3}{4}$	.04$\frac{3}{4}$
Aluminium Sulfate (iron-free)	lb.	.03$\frac{1}{2}$	.03$\frac{1}{2}$
Ammonium Carbonate, pwd	lb.	.16	.16
Ammonium Chloride, gran	lb.	.10$\frac{1}{2}$	.09$\frac{3}{4}$
Ammonia Water, carboys, 26°	lb.	.11	.11
Arsenic, white	lb.	.12	.12
Barium Chloride	ton	75.00	75.00
Nitrate	lb.	.14	.14
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	3.50	3.50
Borax, cryst., bbls	lb.	.07$\frac{1}{2}$	.07$\frac{1}{2}$
Bromine, tech.	lb.	.53	.53
Calcium Chloride, fused	ton	28.75	28.75
Chalk, precipitated, light	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	6.50	6.50
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.00	4.00
Lead Acetate, white crystals	lb.	.16	.15
Nitrate	lb.	.15	.15
Red American	100 lbs.	.12$\frac{1}{4}$	.11$\frac{1}{4}$
White American	100 lbs.	.10$\frac{1}{2}$	.09$\frac{1}{2}$
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate. Tech	lb.	.12	.12
Magnesite	ton	72.00	72.00
Mercury flask American	75 lbs.	45.00	50.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.17	.17
Bromide, Cryst	lb.	.25	.25
Carbonate, calc., 80–85%	lb.	.14$\frac{1}{2}$	.14$\frac{1}{2}$
Chlorate, cryst	lb.	.10	.09
Hydroxide, 88–92%	lb.	.14	.14
Iodide, bulk	lb.	3.00	3.00
Nitrate	lb.	.12	.12
Permanganate, U. S. P.	lb.	.55	.55
Salt Cake, Bulk	ton	30.00	30.00
Silver Nitrate	oz.	.43	.45
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	1.80	2.05
Caustic, 76%	100 lbs.	3.80	3.80
Sodium Acetate	lb.	.08$\frac{1}{2}$	.08$\frac{1}{2}$
Bicarbonate	100 lbs.	2.00	2.00
Bichromate	lb.	.10	.10
Chlorate	lb.	.10	.10
Cyanide	lb.	.24	.24
Fluoride, technical	lb.	.16	.16
Hyposulfite, bbls	100 lbs.	4.00	4.00
Nitrate, 95%	100 lbs.	2.85	2.75
Silicate, 40°	lb.	.01$\frac{1}{2}$	.01$\frac{1}{2}$
Sulfide	lb.	.08	.08
Bisulfite, powdered	lb.	.07	.07
Strontium Nitrate	lb.	.15	.15
Sulfur, flowers	100 lbs.	4.00	4.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.19$\frac{1}{2}$	.19$\frac{1}{2}$
Oxide	lb.	.50	.50
Zinc Chloride, U. S. P.	lb.	.40	.40
Oxide, bbls	lb.	.10	.10

ORGANIC CHEMICALS

		Jan. 1	Jan. 15
Acetanilide	lb.	.25	.25
Acid, Acetic, 28 p. c.	100 lbs.	3.25	3.25
Glacial	lb.	.10$\frac{1}{2}$	.10$\frac{1}{2}$
Acetylsalicylic	lb.	.70	.70
Benzoic, U. S. P., ex-toluene	lb.	.70	.70
Carbolic, cryst., U. S. P., drs.	lb.	.11	.11
50- to 110-lb. tins	lb.	.23	.21
Citric, crystals, bbls	lb.	.50	.48
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.18	.19
Pyrogallic, resublimed	lb.	2.35	2.35
Salicylic, bulk, U. S. P.	lb.	.35	.28
Tartaric, crystals, U. S. P.	lb.	.40	.37
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.13$\frac{1}{2}$	.13$\frac{1}{2}$
Alcohol, denatured, 190 proof	gal.	.75	.67
Ethyl, 190 proof	gal.	5.25	5.25
Wood, Pure	gal.	1.95	1.65
Amyl Acetate	gal.	3.75	3.75
Camphor, Jap. refined	lb.	.90	.87
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.11	.11
Chloroform, U. S. P.	lb.	.40	.40
Creosote, U. S. P.	lb.	.60	.60
Cresol, U. S. P.	lb.	.18	.18
Dextrin, corn	lb.	.04$\frac{1}{4}$	.04$\frac{1}{4}$
Imported Potato	lb.	.08	.08
Ether, U. S. P., conc., 100 lbs	lb.	.23	.23
Formaldehyde	lb.	.18	.18
Glycerol, dynamite, drums	lb.	.17	.16
Pyridine	gal.	2.75	2.75
Starch, corn	100 lbs.	2.93	2.93
Potato, Jap	lb.	.06$\frac{1}{2}$	.06$\frac{1}{2}$
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Jan. 1	Jan. 15
Beeswax, pure, white	lb.	.55	.55
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10$\frac{1}{2}$	.10$\frac{1}{2}$
Ceresin, yellow	lb.	.13	.13
Corn Oil, crude	lb.	.09$\frac{1}{2}$	.09$\frac{1}{2}$
Cottonseed Oil, crude, f. o. b. mill	lb.	.06	.06$\frac{1}{2}$
Menhaden Oil, crude (southern)	gal.	.30	.30
Neat's-foot Oil, 20°	gal.	1.65	1.65
Paraffin, 128–130 m. p., ref	lb.	.08	.08
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	8.50	8.50
Rosin Oil, first run	gal.	.61	.60
Shellac, T. N.	lb.	.70	.65
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.80	1.80
Stearic Acid, double-pressed	lb.	.13$\frac{1}{2}$	.13$\frac{1}{2}$
Tallow Oil, acidless	gal.	1.25	1.25
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.76	.75

METALS

		Jan. 1	Jan. 15
Aluminium, No. 1, ingots	lb.	.24$\frac{1}{2}$	.21
Antimony, ordinary	100 lbs.	5.25	5.25
Bismuth	lb.	2.72	2.72
Copper, electrolytic	lb.	.13	.13
Lake	lb.	.13$\frac{3}{4}$	.13$\frac{1}{2}$
Lead, N. Y.	lb.	.04$\frac{1}{2}$	.04$\frac{3}{4}$
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	70.00	60.00
Quicksilver, flask Amer.	75 lbs ea.	45.00	50.00
Silver	oz.	.64	.65
Tin	lb.	.32$\frac{1}{2}$	.38$\frac{1}{2}$
Tungsten Wolframite	per unit	6.50	6.50
Zinc, N. Y.	100 lbs.	6.00	5.90

FERTILIZER MATERIALS

		Jan. 1	Jan. 15
Ammonium Sulfate export	100 lbs.	3.35	3.35
Blood, dried, f. o. b. N. Y.	unit	5.10	5.10
Bone, 3 and 50, ground, raw	ton	45.00	45.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	5.00	5.00
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium Muriate, 80%	unit	1.85	1.70
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	4.00	4.00

COAL-TAR CHEMICALS

		Jan. 1	Jan. 15
Crudes			
Anthracene, 80–85%	lb.	.75	.75
Benzene, Pure	gal.	.30	.30
Cresol, U. S. P.	lb.	.18	.18
Cresylic Acid, 97–99%	gal.	.90	.90
Naphthalene, flake	lb.	.08	.08
Phenol, drums	lb.	.10	.09½
Toluene, Pure	gal.	.30	.30
Xylene, 2 deg. dist. range	gal.	.60	.60
Intermediates			
Acids:			
Anthranilic	lb.	2.20	2.20
B	lb.	2.25	2.25
Benzoic	lb.	.70	.70
Broenner's	lb.	1.75	1.75
Cleve's	lb.	2.00	2.00
Gamma	lb.	3.75	3.75
H	lb.	1.35	1.35
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.25	3.25
Napthionic, crude	lb.	.85	.85
Nevile & Winther's	lb.	1.75	1.75
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.33	.33
Tobias	lb.	2.25	2.25
Aminoazobenzene	lb.	1.25	1.25
Aniline Oil	lb.	.20½	.20½
For Red	lb.	.42	.42
Aniline Salt	lb.	.33	.33
Anthraquinone	lb.	2.50	2.50
Benzaldehyde, tech	lb.	.45	.45
U. S. P	lb.	1.00	1.00
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.80	.80
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	8.00	8.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.60	.60
Dinitrobenzene	lb.	.25	.25
Dinitrotoluene	lb.	.28	.28
Diphenylamine	lb.	.70	.70
G Salt	lb.	.80	.80
Hydroquinol	lb.	1.90	1.80
Metol (Rhodol)	lb.	6.75	6.75
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.45	.45
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.36	.36
m-Nitroaniline	lb.	.90	.90
p-Nitroaniline	lb.	1.00	1.00
Nitrobenzene, crude	lb.	.14	.14
Rectified (Oil Mirbane)	lb.	.16	.16
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.25	.25
p-Nitrotoluene	lb.	1.25	1.25
m-Phenylenediamine	lb.	1.30	1.30
p-Phenylenediamine	lb.	2.30	2.30
Phthalic Anhydride	lb.	.65	.65
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.85	.85
Resorcinol, tech	lb.	2.00	2.00
U. S. P.	lb.	2.50	2.50
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilide	lb.	.60	.60
Tolidine (Base)	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.33	.33
m-Toluylenediamine	lb.	1.50	1.50
p-Toluidine	lb.	1.75	1.75
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

		Jan. 1	Jan. 15
Acid Colors			
Black	lb.	1.00	1.00
Blue	lb.	1.50	1.50
Acid Colors (*Concluded*)			
Fuchsin	lb.	2.50	2.50
Orange III	lb.	.60	.60
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.85	.85
Direct Colors			
Black	lb.	.90	.90
Blue 2B	lb.	.70	.70
Brown R	lb.	1.65	1.65
Fast Red	lb.	2.35	2.35
Yellow	lb.	2.00	2.00
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90
Sulfur Colors			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	1.00	1.00
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	2.80	2.80
Basic Colors			
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.90	.90
Bismarck Brown G	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	4.50	4.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	3.25	3.25
Methylene Blue, tech	lb	2.75	2.75
Methyl Violet 3 B	lb.	2.75	2.75
Nigrosine, spts. sol	lb.	.85	.85
Water sol., blue	lb.	.70	.70
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	17.00	17.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00